

# **Sequence Selective Terpolymerisation from Sulfur Containing Monomers**

Dissertation

submitted to obtain the degree of Doctor of Natural Sciences

(Dr. rer. nat.)

at the Faculty of Biology, Chemistry and Earth Sciences

of the University of Bayreuth

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Bayreuth, 2026





The experimental part of this thesis was conducted between July 2022 and June 2025 at Freie Universität Berlin and Universität Bayreuth at the Chair of Macromolecular Chemistry I under the supervision of Junior Professor Dr. Alex J. Plajer.

This is a full reprint of the thesis submitted to obtain the academic degree of Doctor of Natural Sciences (Dr. rer. Nat.) and approved by the Faculty of Biology, Chemistry and Geosciences of the University of Bayreuth.

Form of the thesis: cumulative thesis

Date of submission: 19.01.2026

Admission by the doctoral committee: 28.01.2026

Date of defence: 02.07.2026

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## List of Publications

The most important results of this project are summarized and presented in the form of three manuscripts, two of which have been published in peer-reviewed journals.

The following papers are the subject of this thesis:

- I. **Cesare Gallizioli**, Marina Sebastian, Malte Cornelsen, Christian Rossner, Alex J. Plajer, *Sulphur-Containing Polyesters from Thioanhydride/CS<sub>2</sub>/Epoxide Ring-Opening Terpolymerisation: Monomer Scope and Gold-Nanoparticle Functionalisation*.  
Eur. Polym. J. **2025**, 241, 114373.
- II. **Cesare Gallizioli**, Peter Deglmann, Alex J. Plajer, *Kinetically Enhanced Access to a Dynamic Polyester Platform via Sequence Selective Terpolymerisation of Elemental Sulphur*.  
Angew. Chem. Int. Ed. **2025**, 64 (30), e202501337.
- III. **Cesare Gallizioli**, David Battke, Helmut Schlaad, Peter Deglmann, Alex J. Plajer, *Ring-Opening Terpolymerisation of Elemental Sulphur Waste with Propylene Oxide and Carbon Disulfide via Lithium Catalysis*.  
Angew. Chem. Int. Ed. **2024**, 63 (17), e202319810.

During my PhD, I participated in further collaborations and co-authored the following peer-reviewed publications. As these publications are not in the focus of this thesis, they will not be discussed further:

- IV. Merlin R. Stühler, **Cesare Gallizioli**, Susanne M. Rupf and Alex J. Plajer, *Ring-opening terpolymerisation of phthalic thioanhydride with carbon dioxide and epoxides*, Polym. Chem., **2023**, 14 (42), 4848–4855.
- V. Christoph Fornacon-Wood, Merlin R. Stühler, **Cesare Gallizioli**, Bhargav R. Manjunatha, Volker Wachtendorf, Bernhard Schartel, Alex J. Plajer, *Precise construction of weather-sensitive poly(ester-alt-thioesters) from phthalic thioanhydride and oxetane*, Chem. Commun., **2023**, 59 (76), 11353-11356.
- VI. Peter Deglmann, Sara Machleit, **Cesare Gallizioli**, Susanne M. Rupf and Alex J. Plajer, *Lithium catalysed sequence selective ring-opening terpolymerisation: a mechanistic study*, Catal. Sci. Technol., **2023**, 13 (10), 2937-2945.
- VII. Christoph Fornacon-Wood, Bhargav R. Manjunatha, Merlin R. Stühler, **Cesare Gallizioli**, Carsten Müller, Patrick Pröhm, Alex J. Plajer, *Precise cooperative sulphur placement leads to semi-crystallinity and selective depolymerisability in CS<sub>2</sub>/oxetane copolymers*, Nat. Commun., **2023**, 14 (1), 4525.
- VIII. Bhargav R. Manjunatha, **Cesare Gallizioli**, Christoph Fornacon-Wood, Jenny Stephan, Merlin R. Stühler, Alex J. Plajer, *Sequence Control in Sulphur-Containing Ring-Opening Co- and Terpolymerisations*, Angew. Chem. Int. Ed. **2025**, 64 (26), e202507243

## Summary

Each year, global refining of petroleum and natural gas generates more than 60 million tonnes<sup>[1]</sup> of elemental sulphur as a byproduct. During combustion, sulphur impurities in crude fuels oxidise to sulphur dioxide, which dissolves in rainwater to produce sulphuric acid, a major contributor to acid rain. To avoid this, industrial processes such as hydrodesulphurization and the Claus process<sup>[2,3]</sup> are employed to strip sulphur-containing molecules from fuels, converting them into elemental sulphur instead. Although this recovered sulphur is used in established applications, including fertilisers and sulphuric acid production, the volume produced vastly exceeds demand. As a result, millions of tonnes are stockpiled in large outdoor deposits, raising concerns over their long-term environmental consequences.

Beyond its classical roles, sulphur can be integrated into polymers through vulcanization and inverse vulcanization. Both techniques generate cross-linked sulphur-rich networks, differing in the ratio of sulphur to alkene used. Despite their importance, these methods have drawbacks, including high-temperature requirements (160–200 °C), limited compatibility with solvents and monomers, and the production of insoluble, highly cross-linked materials with limited reprocessability. Although catalytic approaches have been proposed to reduce operating temperatures, they remain constrained in both cost and environmental sustainability.

Efforts to prepare linear polymers with elemental sulphur as a building block have led to scarce results, typically yielding materials with only modest sulphur content. In such systems, sulphur is usually incorporated as a side-group rather than forming part of the polymer backbone. The work presented in this thesis examines alternative routes for creating linear sulphur-based polymers with sequence control, relying on ring-opening polymerisation (ROP) strategies catalysed by lithium alkoxides. The objectives are twofold: first, to deepen the fundamental understanding of sulphur chemistry in polymeric frameworks, with particular attention to polymer growth mechanisms, chain architecture, and sequence definition; and second, to evaluate practical applications of sulphur-rich polymers obtained directly from elemental sulphur.

## IV

By bridging historical developments with modern synthetic tools, this research highlights the potential of sulphur-containing polymers to contribute to sustainable materials science and advanced technologies.

The first section describes the synthesis of novel poly(monothiocarbonate-alt- $S_x$ ) copolymers derived from elemental sulphur, carbon disulfide ( $CS_2$ ), and epoxides. Careful stoichiometric adjustment enabled partial control over polysulfide chain lengths. Mechanistic insights into sulphur incorporation during ROP were obtained through kinetic analysis and density functional theory (DFT) studies. Characterization employed NMR spectroscopy, gel permeation chromatography (GPC), Raman spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). A broad monomer scope enabled structural and thermal tunability. Cross-linking of the propylene oxide-derived polymer yielded reprocessible gel-like materials, but the inherent thermal instability of monothiocarbonate linkages limited long-term performance.

To address these stability issues, the second part of the thesis investigates replacing  $CS_2$  with phthalic thioanhydride (PTA), enabling the creation of poly(ester-alt- $S_x$ ) terpolymers with enhanced resistance to thermal degradation. This chemistry supports a wide range of epoxides, including functionalised, fluorescent, multifunctional, and renewable feedstocks. The resulting materials exhibit glass transition temperatures from  $-40\text{ }^{\circ}\text{C}$  to  $127\text{ }^{\circ}\text{C}$ . Incorporating vanillin-derived epoxides allowed for aldehyde-based cross-linking with diamines, producing dynamic imine networks. Their mechanical properties were assessed through tensile and lap shear tests.

Replacing monothiocarbonates with ester linkages improved thermal stability (up to  $270\text{ }^{\circ}\text{C}$ ), enabling post-synthesis functionalisation of the polysulfide segments. This approach allowed for the incorporation of additional sulphur or reactive groups that are typically incompatible with the polymerisation process, such as carboxylic acids. For example, modification with lipoic acid, a cyclic disulfide with a carboxyl group, greatly enhanced adhesion to aluminium substrates by increasing surface polarity. The method was effective in both linear and cross-linked systems.

The final part of this work investigates the synthesis of  $CS_2$ -derived linear poly(ester-alt-trithiocarbonate)s from PTA and epoxides. The monomer scope was expanded to include fluorinated epoxides and a trimethylsilyl-functionalised epoxide. Post-

polymerisation hydrolysis of the silyl groups produced rubber-like materials. Importantly, trithiocarbonate linkages preserved desirable thermal properties while enabling coordination with metal centres. In collaboration with the Leibniz Institute of Polymer Research Dresden, the potential for hybrid nanomaterial formation was demonstrated through gold nanoparticle grafting, exploiting the strong affinity between sulphur and metal surfaces.

## Zusammenfassung

Die weltweite Raffination von Erdöl und Erdgas erzeugt jedes Jahr mehr als 60 Millionen Tonnen elementaren Schwefel als Nebenprodukt.<sup>[1]</sup> Schwefelhaltige Verunreinigungen in Rohöl würden bei der Verbrennung zu Schwefeldioxid oxidieren, das sich im Regenwasser zu Schwefelsäure löst und so maßgeblich zur Bildung von saurem Regen beiträgt. Um dies zu verhindern, werden Verfahren wie die Hydroentschwefelung und der Claus-Prozess eingesetzt,<sup>[2,3]</sup> bei denen schwefelhaltige Moleküle aus den Brennstoffen entfernt und in elementaren Schwefel umgewandelt werden. Obwohl dieser Schwefel in etablierten Bereichen – etwa bei der Herstellung von Düngemitteln oder Schwefelsäure – Verwendung findet, übersteigt das Angebot den Bedarf bei Weitem. Millionen Tonnen werden daher in großen Freilagerstätten deponiert, was langfristig ökologische Fragen aufwirft.

Neben diesen klassischen Anwendungen lässt sich Schwefel auch in Polymere einbauen, insbesondere durch Vulkanisation und inverse Vulkanisation. Beide Methoden erzeugen schwefelreiche, stark vernetzte Netzwerke und unterscheiden sich hauptsächlich im Verhältnis von Schwefel zu Alkenen. Trotz ihrer Bedeutung weisen diese Verfahren deutliche Einschränkungen auf: Sie erfordern hohe Temperaturen (160–200 °C), sind nur mit einer begrenzten Auswahl an Lösungsmitteln und Monomeren kompatibel und führen meist zu unlöslichen, irreversibel vernetzten Materialien, die kaum wiederaufbereitet werden können. Katalytische Systeme konnten die Reaktionstemperaturen zwar senken, ihre wirtschaftliche und ökologische Tragfähigkeit ist jedoch weiterhin begrenzt.

Versuche, lineare Polymere mit elementarem Schwefel als Baustein herzustellen, waren bislang nur wenig erfolgreich. Meist gelingt lediglich ein geringer Schwefelgehalt, der zudem oft nur als funktionelle Gruppe an der Seitenkette eingebaut wird, nicht aber im Polymerhauptgerüst. Diese Arbeit untersucht daher alternative Strategien zur Synthese linearer Schwefelpolymere mit kontrollierter Sequenz, basierend auf Ringöffnungs-Polymerisation (ROP) unter Einsatz von Lithiumalkoxiden als Katalysatoren. Ziel ist es einerseits, die Grundlagen der Schwefelchemie in Polymeren besser zu verstehen – insbesondere Mechanismen des Kettenwachstums, die Architektur der Ketten und die



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Sequenzsteuerung. Andererseits sollen mögliche Anwendungen und Eigenschaften von schwefelreichen Polymeren aus elementarem Schwefel ausgelotet werden. Durch die Verknüpfung historischer Ansätze mit modernen Methoden zeigt die Arbeit, wie schwefelhaltige Polymere zu nachhaltigen Materialien und neuen Technologien beitragen können.

Im ersten Teil werden neuartige Poly(monothiocarbonat-alt- $S_x$ )-Copolymere vorgestellt, die aus elementarem Schwefel, Kohlenstoffdisulfid ( $CS_2$ ) und Epoxiden entstehen. Eine gezielte Variation der Stöchiometrie ermöglichte die teilweise Kontrolle über die Länge der Oligosulfidsegmente. Mechanistische Einblicke in den Schwefeleinbau während der ROP lieferten kinetische Studien sowie DFT-Berechnungen. Die Polymere wurden mittels NMR-Spektroskopie, Gelpermeationschromatographie (GPC), Raman-Spektroskopie, Differenzialscanningkalorimetrie (DSC) und Thermogravimetrie (TGA) umfassend charakterisiert. Die breite Monomer-Vielfalt erlaubte eine gezielte Anpassung der Struktur und thermischen Eigenschaften. Durch nachträgliche Vernetzung des aus Propylenoxid gewonnenen Polymers entstanden wiederverwertbare gelartige Materialien, deren Langzeitstabilität jedoch durch die thermische Empfindlichkeit der Monothiocarbonatbindungen begrenzt war.

Um diese Einschränkung zu überwinden, wurde im zweiten Teil  $CS_2$  durch Phthalsäurethioanhydrid (PTA) ersetzt. Auf diese Weise konnten Poly(ester-alt- $S_x$ )-Terpolymere mit deutlich verbesserter thermischer Stabilität hergestellt werden. Dieses System ist mit einer Vielzahl von Epoxiden kompatibel, darunter funktionalisierte, fluoreszierende, multifunktionale und biobasierte Monomere. Die resultierenden Materialien zeigten Glasübergangstemperaturen zwischen  $-40\text{ °C}$  und  $127\text{ °C}$ . Vanillinbasierte Epoxide ermöglichten eine Aldehyd-vermittelte Vernetzung mit Diaminen, wodurch dynamische Imin-Netzwerke gebildet wurden. Ihre mechanischen Eigenschaften wurden mittels Zug- und Scherversuchen untersucht.

Der Ersatz der Monothiocarbonate durch Esterbindungen erhöhte die thermische Stabilität auf bis zu  $270\text{ °C}$  und eröffnete die Möglichkeit einer nachträglichen Funktionalisierung der Polysulfideinheiten. So konnten zusätzliche Schwefelatome oder reaktive Gruppen eingeführt werden, die während der Polymerisation nicht kompatibel sind, etwa Carbonsäuren. Ein Beispiel ist die Modifizierung mit Liponsäure – einem cyclischen Disulfid mit Carboxylgruppe –, die die Haftung auf Aluminiumoberflächen

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durch erhöhte Oberflächenpolarität deutlich verbesserte. Diese Strategie erwies sich sowohl bei linearen als auch bei vernetzten Systemen als wirksam.

Im letzten Teil der Arbeit wird die Synthese linearer Poly(ester-alt-trithiocarbonat)e aus PTA,  $\text{CS}_2$  und Epoxiden beschrieben. Das Monomerspektrum wurde auf fluoridierte Epoxide und ein trimethylsilylsubstituiertes Epoxid ausgeweitet. Nach Hydrolyse der Silylgruppen entstanden gummiartige Materialien. Die Trithiocarbonatbindungen erhielten nicht nur die thermischen Eigenschaften, sondern ermöglichten auch die Koordination mit Metallen. In Zusammenarbeit mit dem Leibniz-Institut für Polymerforschung Dresden konnte zudem gezeigt werden, dass durch Anbindung von Goldnanopartikeln Hybridmaterialien entstehen, die die starke Affinität von Schwefel zu Metalloberflächen nutzen.

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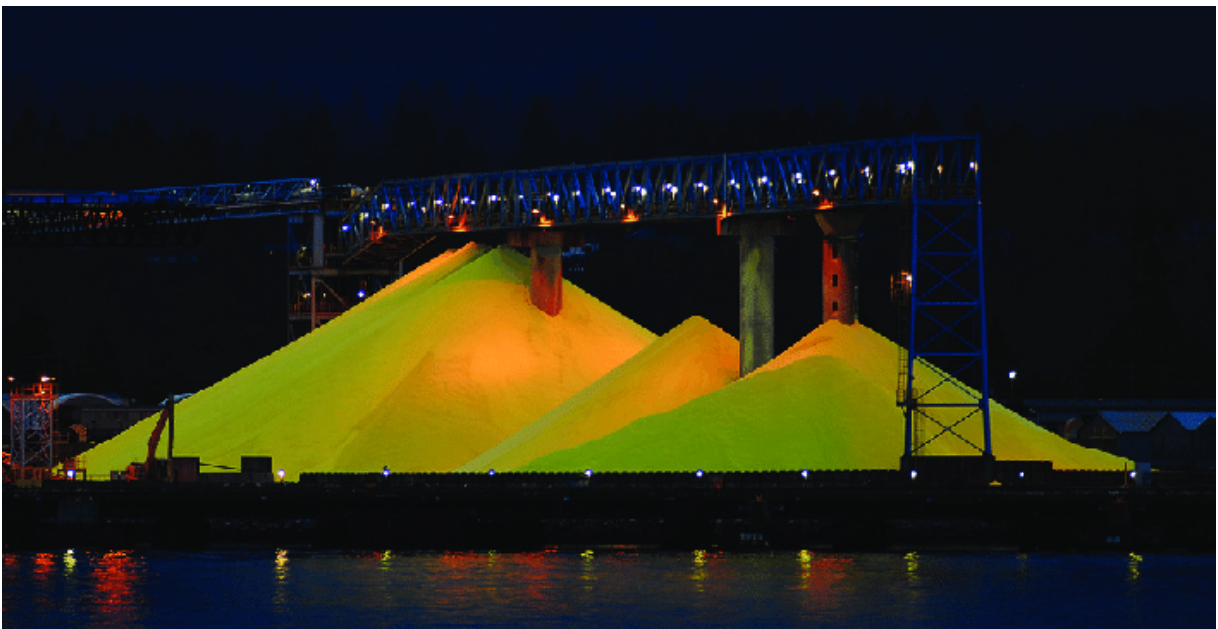
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## Introduction

### 1. Motivation and Scope

Polymers have become an integral part of modern life, shaping the development of countless technologies, consumer goods, and industrial processes. From everyday packaging materials and textiles to high-performance engineering plastics and biomedical devices, polymers are indispensable in providing solutions that balance functionality, durability, and cost. Over the past century, the field of polymer science has witnessed remarkable innovation, driven by the search for materials with tailored properties such as enhanced thermal stability, mechanical resilience, chemical resistance, and optical or electronic functionalities. Despite these advances, challenges remain in developing polymers that are not only high performing but also sustainable, environmentally friendly, and derived from abundant or underutilized resources [1,2].



*Figure 1: Industrial deposit of sulphur extracted during petroleum refinement through the hydrodesulphurisation process.  
Image credit: Gord McKenna, made available through a Creative Commons license: <https://www.flickr.com/photos/gord99/5170487123/>.*

One of the elements attracting increasing attention in polymer research is sulphur, a non-metal with unique chemical properties. Sulphur is an abundant byproduct of petroleum refining and natural gas processing, often produced in quantities exceeding tens of millions of tonnes annually worldwide [3,4]. Most of it ends up in open-air deposits, where it contributes to environmental pollution through water contamination (Figure 1). Historically, large fractions of this sulphur have

been stockpiled or disposed of due to limited industrial applications, resulting in a significant underutilization of a potentially valuable resource. Beyond its abundance, sulphur offers unique chemical versatility: It can form single and multiple bonds with carbon, participate in radical and nucleophilic reactions, and provide unusual electronic and physical properties to polymeric systems <sup>[5,6]</sup>. These characteristics make sulphur an attractive candidate for creating new materials with properties that cannot be easily achieved using traditional carbon- or oxygen-based monomers.

This thesis focuses primarily on linear polymers derived from elemental sulphur, a class of materials that remains relatively underexplored compared to crosslinked sulphur networks such as vulcanized rubber. Linear sulphur polymers are of particular interest because they offer processability, the potential for precise molecular weight control, and opportunities for sequence-specific functionalisation, which are essential for advanced applications in electronics, optics, and energy storage (Figure 2). Achieving controlled synthesis of these polymers, however, requires overcoming challenges related to sulphur's high reactivity, propensity to cyclize, and sensitivity to polymerisation conditions <sup>[7,8]</sup>.

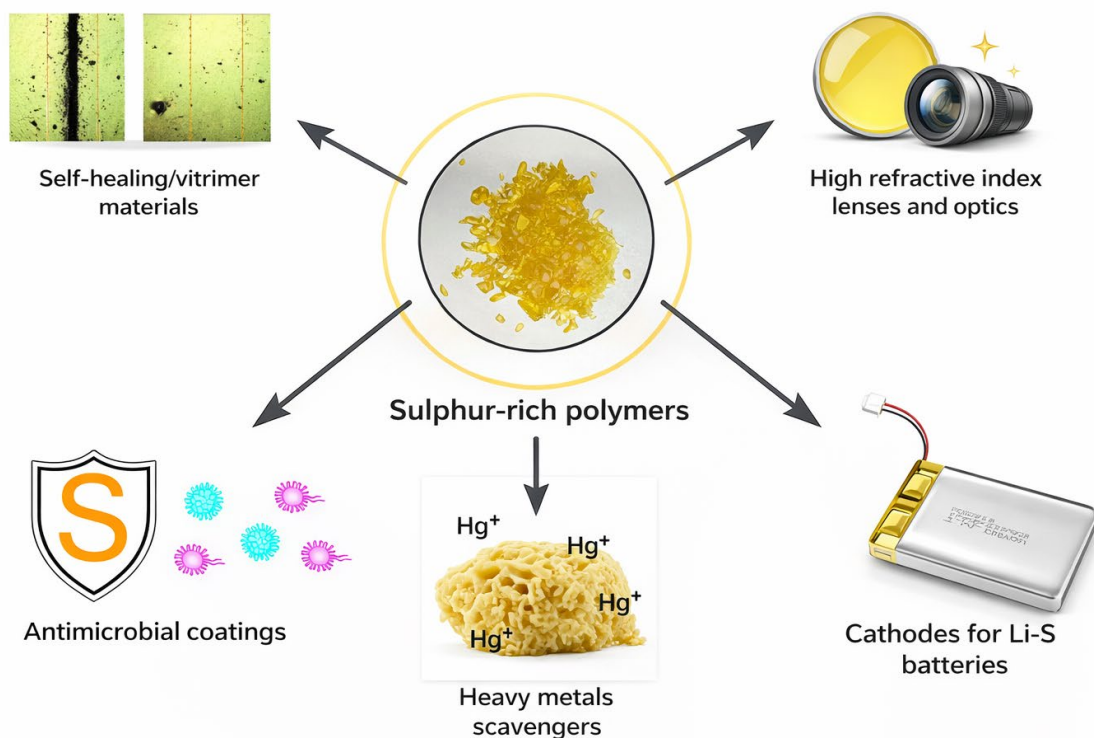


Figure 2: Possible applications for sulphur-rich polymers.

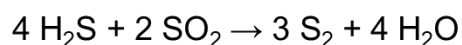
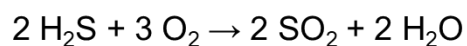
In addition to experimental investigations, this work emphasizes a theoretical understanding of polymerisation processes, including kinetic and thermodynamic considerations. A comprehensive knowledge of these factors is critical for predicting polymer behaviour, optimizing synthesis protocols, and designing materials with tailored properties. By combining mechanistic insights with practical polymerisation strategies, this thesis seeks to contribute both to the fundamental knowledge of sulphur polymer chemistry and to its application in advanced materials development.<sup>[9]</sup>

The scope of this work encompasses several interconnected themes. First, it reviews the historical and modern roles of sulphur in polymer science, including classical vulcanization and emerging methods such as inverse vulcanization. Second, it examines the challenges associated with synthesizing linear sulphur polymers, with emphasis on kinetic and thermodynamic control. Third, it explores modern polymerisation strategies, including ring-opening polymerisation (ROP) and multicomponent polymerisation, highlighting the potential for sequence control and advanced material design.

## 2. Sulphur in Polymer Science

Elemental sulphur is produced on a massive scale as a byproduct of petroleum and gas desulphurization, making it an inexpensive and widely available feedstock. The procedure to do so consists of a hydrodesulphurization (HDS) step and, subsequently, the Claus process.

HDS is a process that treats petroleum fractions with H<sub>2</sub> gas at 400°C in the presence of catalytic amounts of tungsten supported on Al<sub>2</sub>O<sub>3</sub> to break the C-S bonds, generating cleaned hydrocarbons and H<sub>2</sub>S as a gas. After that, the Claus process allows sulphur recovery in a two-step procedure: initially, part of the H<sub>2</sub>S is burned to generate SO<sub>2</sub>, which then reacts with the remaining hydrogen sulfide to form water and S<sub>8</sub> (Scheme 1).



*Scheme 1: Reaction scheme for the Claus process.*

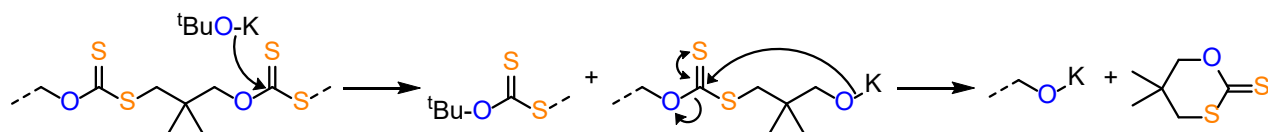
Considering the high energy consumption required for the HDS process, research has been conducted on newer and more cost-effective methods to remove organic sulphur under ambient



conditions.<sup>[10,11,12]</sup> Among them, adsorptive desulphurization<sup>[13]</sup> (ADS) with zeolites and MOFs<sup>[14]</sup> appears to provide a suitable alternative to HDS.

The electronic configuration of sulphur and its ability to adopt a range of oxidation states enable the formation of diverse linkages with carbon and heteroatoms, providing opportunities for the design of linear, branched, or cross-linked polymeric architectures. Sulphur-containing polymers are distinguished by high polarizability, redox activity, and unusual thermal<sup>[15]</sup> and mechanical<sup>[16]</sup> properties, which can be harnessed in areas spanning from optics<sup>[17,18]</sup> and electronics<sup>[19]</sup> to environmental remediation.

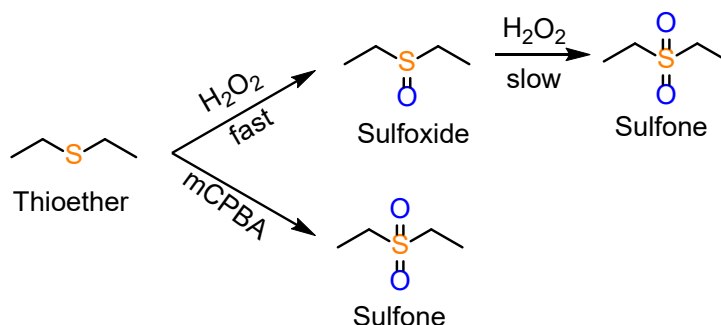
Using sulphur as a monomer in polymerisation reactions offers two main benefits for sustainability. First, it helps utilize a waste product that cannot be fully employed by existing industrial processes, such as the production of carbon disulfide (CS<sub>2</sub>), sulphuric acid, and the manufacturing of cross-linked materials through vulcanization and inverse vulcanization; therefore, expanding the industrial uses of this abundant compound is crucial. The second sustainability benefit arises from the fact that, besides imparting different thermal, optical, and mechanical properties to materials, having sulphur atoms inside a polymer chain can significantly enhance their degradability<sup>[20,21,22]</sup> compared to their oxygenated analogues<sup>[23,24]</sup>. This is because C-S bonds are relatively weaker than C-O and C-C bonds, making them easier to break through various chemical pathways, including redox reactions, hydrolysis, or radical cleavage, depending on the functional groups involved. The presence of labile sulphur bonds can provide convenient breaking points within the polymer chain; sulphur's larger atomic radius and angular flexibility reduce ring strain in heterocycles, lowering their ceiling temperatures and facilitating depolymerisation. Then again, depolymerisation itself can't grant a circular economy, and the ideal solution would be to have materials that, once depolymerised, would yield compounds that can act as monomers for a subsequent repolymerisation to obtain the same polymer sequence or even a new one. To achieve this, a possible solution is to induce a backbiting cascade process along the chain. This way, it's possible to generate smaller cyclic molecules that can then be purified and employed in a new polymerization pathway (Scheme 2).



*Scheme 2: Proposed depolymerisation pathway for a CS<sub>2</sub>/oxetane copolymer. Modified with permission from Springer Nature.<sup>[23]</sup>*

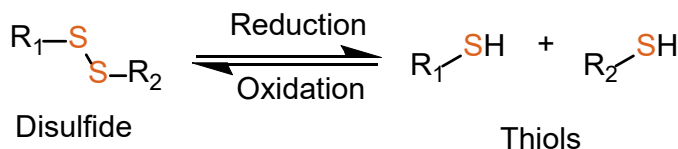
At room temperature, elemental sulphur is most stable as octasulphur ( $S_8$ ), a crown-shaped molecule stabilized by S–S bonds. Upon heating or catalytic activation, these rings can undergo homolytic cleavage, giving reactive polysulfane chains. Compared with oxygen or nitrogen, sulphur forms weaker covalent bonds; this intrinsic lability underpins the ability of many sulphur-rich materials to form covalent adaptable networks that can be thermally reshaped without the need for additional catalysts. Such reversible exchange reactions also provide the basis for self-healing<sup>[25,26]</sup> and recyclable polymer systems. Furthermore, many sulphur-containing polymers exhibit enhanced semi-crystallinity<sup>[27,28]</sup> relative to oxygen analogues, resulting in improved mechanical performance that translates into materials with broader applications.

The redox chemistry of sulphur adds another dimension to its utility. Thioethers, for instance, can be oxidised stepwise to sulfoxides or sulfones (Scheme 3), providing a convenient handle to tune polymer polarity, solubility, and degradation profiles.



*Scheme 3: Oxidation of thioether linkage to sulfoxide/sulfone via  $H_2O_2$  and  $mCPBA$  (3-chloroperbenzoic acid). Modified with permission from Royal Society of Chemistry.<sup>[143]</sup>*

Disulfide linkages, though relatively weak, impart dynamic character to polymer networks. Through reduction and oxidation cycles, they can undergo reversible cleavage and re-formation, conferring self-healing and stimuli-responsive behaviour<sup>[29]</sup> (Scheme 4).



*Scheme 4: Disulfide/thiol exchange through redox cycle.*

Their reactivity is particularly pronounced when embedded in strained cyclic structures, such as lipoic or asparagusic acid derivatives (Figure 3). Work by Bowman and co-workers has demonstrated the photo-polymerisation of dithiolanes to yield multiresponsive dynamic

hydrogels<sup>[30]</sup>, as well as their copolymerisation with alkynes to generate polymers with high refractive indices.<sup>[31]</sup>

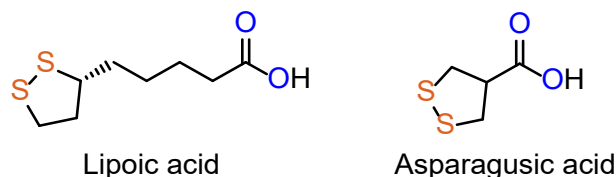
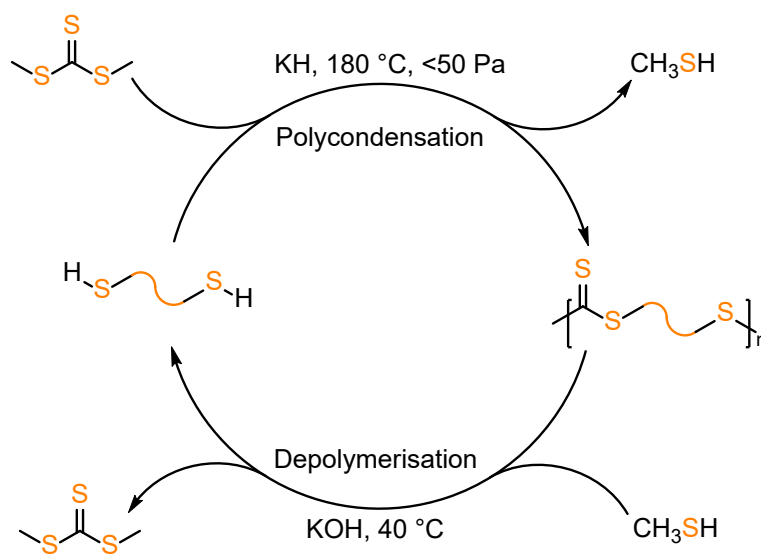


Figure 3: Chemical structure of lipoic and asparagusic acids.

Thiocarbonates (mono-, di-, and trithiocarbonates) are another important sulphur motif. These groups are more polarizable than oxygen-based carbonates, which increases refractive index and introduces sites of controlled lability. Their relative instability can be exploited to create more degradable materials, while the sulphur lone pairs improve the coordination with soft metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , or  $\text{Au}^{3+}$ . This makes thiocarbonate-containing polymers useful for metal capture, catalysis, and nanocomposite manufacturing. Di- and trithiocarbonates are key in reversible addition–fragmentation chain transfer (RAFT) polymerisation, acting as dynamic chain transfer agents. A recent work from Wei-Min Ren et al.<sup>[32]</sup> shows a polycondensation reaction between dithiols and dimethyl trithiocarbonates to synthesize polytrithiocarbonate chains that can be easily depolymerised with KOH at 40 °C (Scheme 5). Ideally, through further investigation in the field, these thiocarbonate motifs might enable post-functionalisation and chain reshuffling.



Scheme 5: Polymerisation and depolymerisation process proposed by W.M. Ren et al. Modified with permission from Springer Nature.<sup>[32]</sup>

Given all these properties and advantages that sulphur can provide to polymer materials, it is of great importance to find new pathways to exploit and include elemental sulfur, as it represents a great resource that must be considered to improve our technology and the transitions towards a more environmentally conscious manufacturing, this is of particular importance when considering that the vast majority of the industrial polymerisation process that involve elemental sulfur are based on vulcanisation which yields heavily cross-linked structures that cannot be reprocessed or degraded. For this reason, the scientific community must focus on the development of linear, reprocessable polymers from sulfur. This thesis is a summary of my progress on the topic.

## **2.1 Cross-Linked Polymers from Elemental Sulphur: Vulcanization and Inverse Vulcanization**

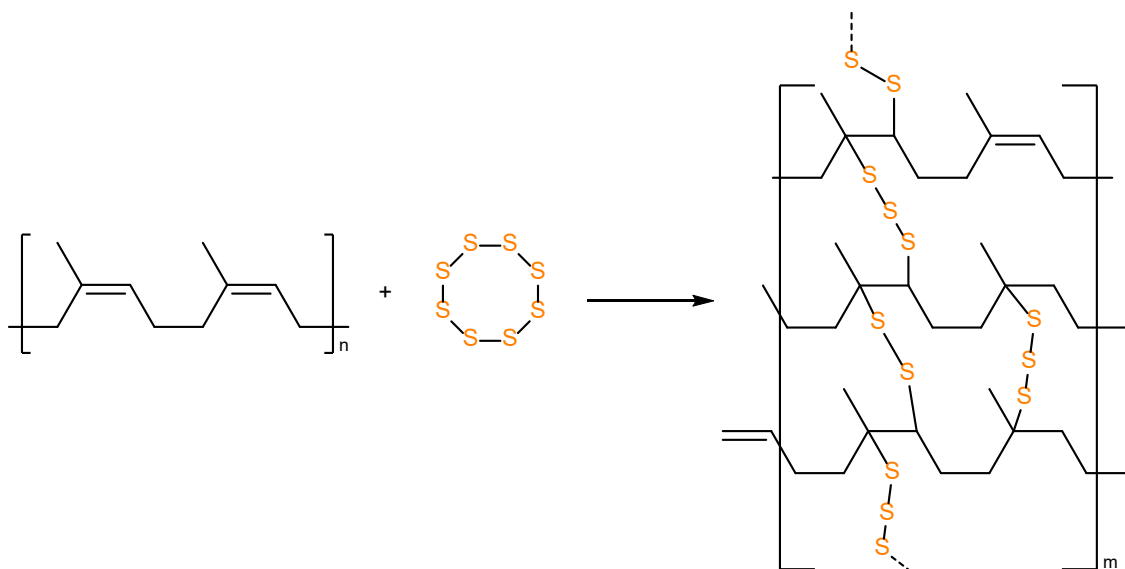
The industrial relevance of sulphur in polymer chemistry dates to the 19th century with Charles Goodyear's discovery of rubber vulcanization. In this process, sulphur forms cross-links between polyolefin chains, dramatically improving the elasticity, durability, and thermal resistance of rubbers. This breakthrough revolutionized the performance of elastomers, enabling the production of resilient tires, seals, and countless industrial components. Beyond rubber, sulphur found early use in resins, adhesives, and coatings, where its ability to form thioether and disulfide bonds contributed to enhanced stability<sup>[33,34]</sup> and chemical resistance.<sup>[35,36]</sup>

A further improvement from vulcanisation, where sulphur constitutes a small percentage of the whole reaction mixture, is inverse vulcanisation, which deploys elemental sulphur as a primary structural component of polymers rather than as a minor additive.<sup>[37]</sup>

Although these two methods don't produce linear materials that are easily depolymerized, they still represent the most efficient current method for using elemental sulfur to create polymers with strong and useful properties. Understanding these principles and what can be obtained from them helps us establish a baseline for developing future polymers with improved characteristics.

### **2.1.1 Vulcanization**

Upon heating, cyclo-octasulphur ( $S_8$ ) undergoes ring-opening to generate reactive sulphur species capable of adding across the  $C=C$  bonds of olefin-rich polymers such as polyisoprene or polybutadiene (Scheme 6).



*Scheme 6: Polyisoprene crosslinking through vulcanisation.*

These reactions proceed through radical and polar pathways <sup>[38]</sup>, producing sulphur bridges that connect polymer chains and markedly enhance mechanical and thermal stability.

Crosslink density determines the elasticity and stiffness of the resulting material: low densities give flexible elastomers, while highly dense networks produce more rigid structures. Because vulcanized rubber forms a permanent covalent network, it swells in solvents but does not dissolve. Variants such as efficient vulcanization (EV) <sup>[39,40]</sup> rely on optimized mixtures of accelerators and activators to improve homogeneity and mechanical performance, although the underlying chemistry remains that of network formation.

### 2.1.2 Inverse Vulcanization

Inverse vulcanization, introduced in 2013<sup>[41]</sup>, fundamentally differs from classical vulcanization by reversing the monomer ratio: elemental sulphur becomes the continuous matrix, and a small fraction of unsaturated organic comonomer stabilizes the network.<sup>[41,42]</sup> In their absence, sulphur rapidly reverts to crystalline S<sub>8</sub> upon cooling. Inverse vulcanized polymers typically contain 50–90 wt% sulphur,<sup>[37,43]</sup> providing an even stronger method to consume elemental sulfur waste when compared with regular vulcanisation. The method thus highlights sulphur's potential as a structural building block in functional materials, transforming abundant, low-value sulphur into high-performance polymers.

Despite its appeal, inverse vulcanization faces important limitations. The products are crosslinked networks, restricting both structural tunability and recyclability; although some progress has been reported <sup>[44,45]</sup>, reprocessing remains difficult. The reaction also requires elevated temperatures (160–200 °C), which limits monomer scope and may cause degradation. Additional challenges include thermal runaway driven by the Trommsdorff–Norrish effect: a phenomenon in which increased viscosity during polymerization suppresses termination reactions, leading to auto-acceleration. This can produce inconsistent materials due to runaway processes<sup>[46]</sup> or pose safety concerns. These constraints restrict the versatility of inverse vulcanization and motivate alternative strategies for producing sulphur-containing polymers with improved control.

### **2.1.3 Catalysis and Photochemical Approaches**

To overcome the limitations of thermal activation, industrial vulcanization and inverse vulcanization frequently employ accelerators and activators (thiazoles, dithiocarbamates, metal salts, fatty acids) that lower the effective activation energy and improve crosslinking control.<sup>[47]</sup>

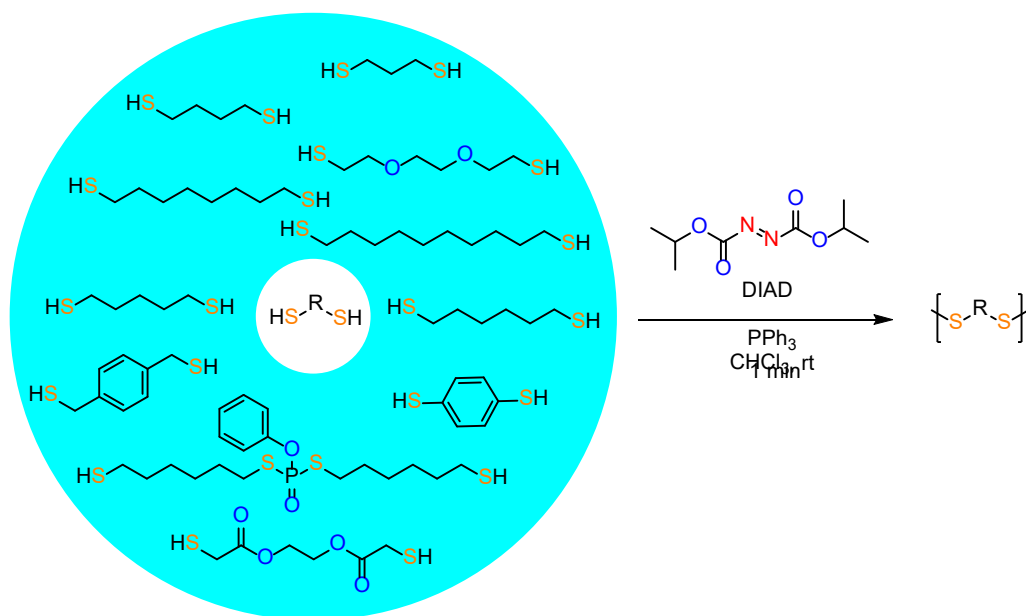
A significant advancement is photoinduced inverse vulcanization (PIV),<sup>[48]</sup> which operates at room temperature and avoids metal co-catalysts, long curing times, and H<sub>2</sub>S formation. PIV greatly expands the range of accessible comonomers, enabling the use of volatile or thermally sensitive alkenes and alkynes not tolerated in standard thermal methods. The resulting sulphur-rich polymers can achieve high molecular weights and offer a more sustainable route to functional materials.

## **2.2: Linear Sulphur Polymers: Fundamentals and Challenges**

While crosslinked sulphur networks have traditionally dominated sulphur polymer research, linear sulphur-containing polymers are gaining increasing attention because of their improved processability, tuneable properties, and suitability for advanced applications. Their linear architecture enables precise control over molecular weight, chain length, and sequence, features that are essential for functional materials in electronics,<sup>[49,50,51]</sup> coatings,<sup>[52,53]</sup> and biomedical devices.<sup>[54,55,56]</sup> In contrast, traditional approaches such as vulcanization and inverse vulcanization rely on networked structures, high synthesis temperatures, thus making them poorly suited for applications requiring architectural precision. Moreover, they are burdened by an inherently limited recyclability, also due to their lack of reprocessability, either thermal or through solvents. These

limitations further reinforce the need for linear, sequence-controlled sulphur-containing polymers, which can be accessed through the ring-opening polymerisation strategies introduced in the following chapters.

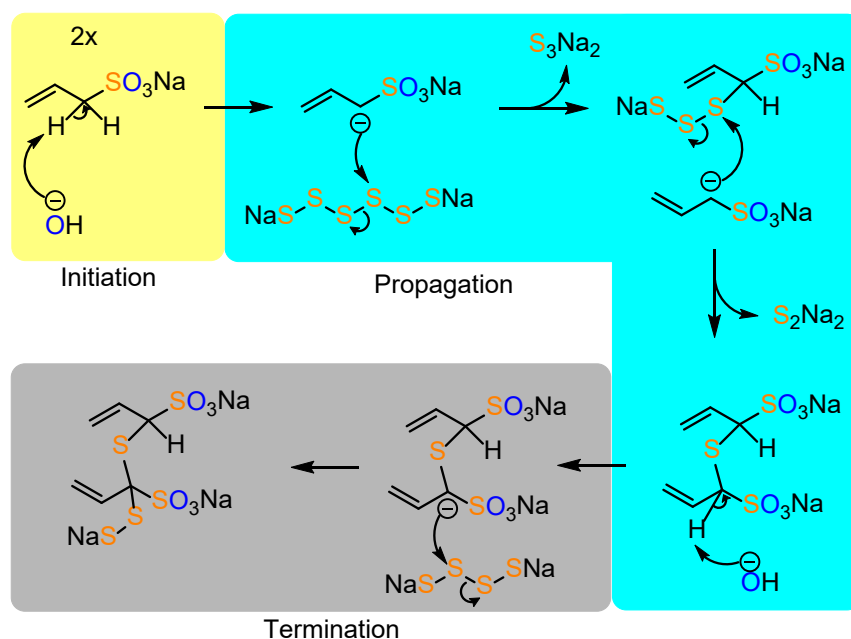
Literature shows numerous examples of linear polymers that contain sulphur atoms. For instance, linear polymers made from monomers with di-mercaptan groups were first synthesized in 1968 by E. Goethals and C. Sillis,<sup>[57]</sup> who created poly(disulfides) by thermally oxidizing di-mercaptan monomers at 160 °C in DMSO. These materials were mostly insoluble in organic solvents due to their high molecular weights. Later methods improved the control over poly(disulfide) synthesis, such as using reactive pyridyl disulfides<sup>[58]</sup> to include dithiol monomers, producing polymers up to 10 kDa. More recent catalytic techniques enable rapid synthesis of poly(disulfides) with molecular weights reaching 50 kDa (Scheme 7).<sup>[59]</sup>



Scheme 7: General representation for rapid poly(disulfide) synthesis. Modified with permission from ACS Publications.<sup>[59]</sup>

Recent developments have expanded the synthetic toolkit through multicomponent polymerisation.<sup>[60]</sup> One example involves alternating dithiol and dibromo short chains in carbon disulfide ( $\text{CS}_2$ ) to create linear trithiocarbonate-bearing polymers, which show unusual luminescent properties, crystallinity, and adjustable mechanical strength. Another approach uses elemental sulphur combined with diamines and dicarboxylic acids to produce poly(thioureas).<sup>[61]</sup> Although sulphur is incorporated in this process, the amount used is low and does not fully address the large surplus of elemental sulphur.

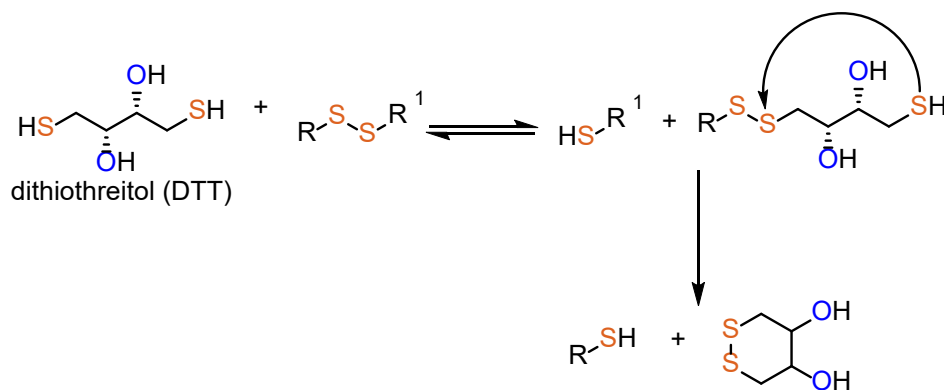
Linear sulphur-containing polymers have also been synthesized through Michael-type additions of acrylates, yielding both linear and crosslinked materials. These polymers are promising as adhesives and structural materials due to their strength, self-healing properties, and ability to be photocured.<sup>[62,63]</sup> A related method involves Sodium allyl sulfonate<sup>[64]</sup> and elemental sulphur (activated by NaOH), producing polymers around 10 kDa (Scheme 8). These materials have dehydrating properties and can be used as flocculants for the capture of metals such as  $V^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $As^{3+}$ ,  $Cd^{2+}$ ,  $Au^{3+}$ , and  $Hg^+$  due to their sulfonate groups, and importantly, this process uses elemental sulphur in a 1:1 ratio with the monomer, making it attractive for industry.



*Scheme 8: Proposed mechanism for the polymerisation between sodium allyl sulfonate and NaOH-activated elemental sulphur. The process involves deprotonation by  $OH^-$  followed by reaction with  $S_6^{2-}$  polysulfide in propagation, and  $S_4^{2-}$  polysulfides in termination. Modified with permission from Wiley.<sup>[64]</sup>*

Ring-opening, a polymerisation strategy that will be further discussed in Chapter 3 of this introduction, has also been explored. Cyclic disulfide precursors derived from short-chain dithiols<sup>[65]</sup> or monomers like 1,4,5-oxadithiepan-2-one (OTP)<sup>[66]</sup> were deployed as building blocks for the synthesis of sulphur-containing polymers. However, these monomers often require expensive or complex precursors. A greener option uses naturally derived cyclic disulfide,<sup>[30,31,67]</sup> for example, lipoic acid, which is easily functionalised because of its reactive carboxylic group. While disulfides are appealing due to their dynamic exchange and ease of breaking under reducing conditions, e.g., with dithiothreitol (DTT) (Scheme 9),<sup>[68]</sup> their functional use in advanced applications remains somewhat limited.





*Scheme 9: Mechanism of disulfide reduction by DTT oxidation. This principle can be used to have a controlled depolymerisation of polymers containing disulfide moieties in the repeating unit.*

Professor Hadjichristidis' group recently developed a step-growth polymerisation involving elemental sulphur and aziridines, with DBU as the catalyst.<sup>[69]</sup> In this process, sulphur anions open the aziridine rings, forming linear polymers with strong adhesive properties on various surfaces. However, this method still only uses limited sulphur amounts and requires the complex synthesis of bis-aziridines, including chromatography steps, which limits scalability.

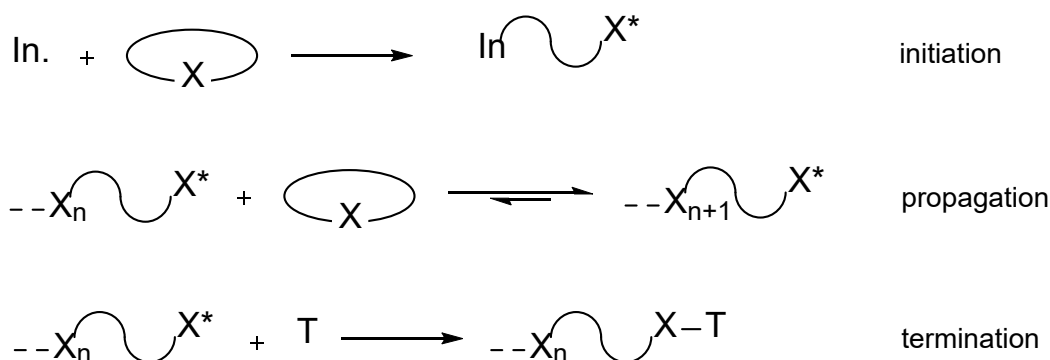
### 2.2.1 Challenges and Theoretical Basis

The synthesis of linear sulphur polymers presents significant challenges due to the intrinsic reactivity of elemental sulphur. The conversion of S<sub>8</sub> rings into linear chains involves ring-opening reactions. These can compete with side reactions such as cyclization, which can be thermodynamically favoured due to the entropic gain. This happens naturally with the homopolymerisation of elemental sulfur, which, after a short time, reverts to the more stable octasulfur configuration, chain transfer, or uncontrolled crosslinking. Crosslinking side reactions are of relevance when considering monomers bearing olefins, which can be attacked by activated sulfur, thus generating networks and errors in the polymer sequence; the same goes for functional groups that can undergo a substitution-like reaction. A clear example is epichlorohydrin, in which the chlorine group can exchange itself with a nucleophile group such as S<sup>-</sup>. This intrinsic reactivity makes achieving controlled polymerisation difficult as it requires careful consideration of reaction kinetics, thermodynamics, and experimental conditions. Defining methods to control the amount and the position of sulfur atoms throughout the polymer sequence enables the tuning of material properties. For example, incorporating thioether or trithiocarbonate units at defined positions along the chain can enhance flexibility, introduce redox-active sites, or provide anchor points for post-

polymerisation modification.<sup>[70]</sup> Such control is challenging in crosslinked systems, making linear polymers an attractive platform for advanced material design.

### 3. Ring-Opening Polymerisations

Ring-opening polymerisation (ROP) is a well-established polymerisation mechanism that enables the formation of linear or branched polymer chains from industrially relevant monomers, playing a critical role in the development of advanced materials. ROP involves the conversion of cyclic monomers into linear polymers through ring bond cleavage. The cyclic monomers typically possess inherent ring strain, which drives the polymerisation reaction toward the formation of linear chains. A key feature of ROP, especially when compared to polymerisations involving vinyl monomers, is its often-reversible nature. At equilibrium, a substantial portion of monomers may remain unreacted, particularly in systems where the energy barrier for ring-closing is similar to the one for ring-opening. This type of polymerisation requires three main steps to happen in a synergic way: initiation, propagation, and termination (Scheme 10).



*Scheme 10: General steps for successful ring-opening polymerisation. The propagation step must be faster and more favourable than ring closing. For a living polymerisation situation, the termination step must happen in a controlled manner, and the chain transfer reaction must be suppressed.*

This approach accommodates a broad array of monomer structures, including purely hydrocarbon-based rings as well as heterocycles incorporating oxygen,<sup>[71,72,73]</sup> nitrogen,<sup>[74,75]</sup> sulphur,<sup>[76,77]</sup> phosphorus,<sup>[78,79]</sup> or silicon.<sup>[80,81]</sup> Examples include epoxides, lactones, lactams, aziridines, cyclosiloxanes, thioanhydrides, cyclic thioesters and disulfides.

Historically, ROP has been applied primarily to oxygen-containing monomers such as lactones and epoxides. However, the expansion of ROP to sulphur-containing systems has opened new

possibilities for creating high sulphur-containing polymers with unique properties. The controlled introduction of sulphur along a linear chain also allows for an exploration of dynamic chemical behaviour, such as reversible disulfide linkages, which can impart self-healing or stimuli-responsive capabilities. Thanks to decades of research, robust polymerisation conditions have been developed for many of these systems, allowing for the synthesis of polymers with controlled architectures, molecular weights, and functionalities.

The success of ROP depends on meeting two central criteria: thermodynamic favourability and kinetic feasibility. From a thermodynamic standpoint, polymerisation must lead to a net decrease in Gibbs free energy. In practice, this requires the ring strain or enthalpic driving force of the monomer to outweigh the entropic penalty of converting many monomers into a single macromolecule (Figure 4). Commonly, strained cyclic structures such as small lactones or epoxides fulfil this criterion, shifting the equilibrium toward polymer formation.

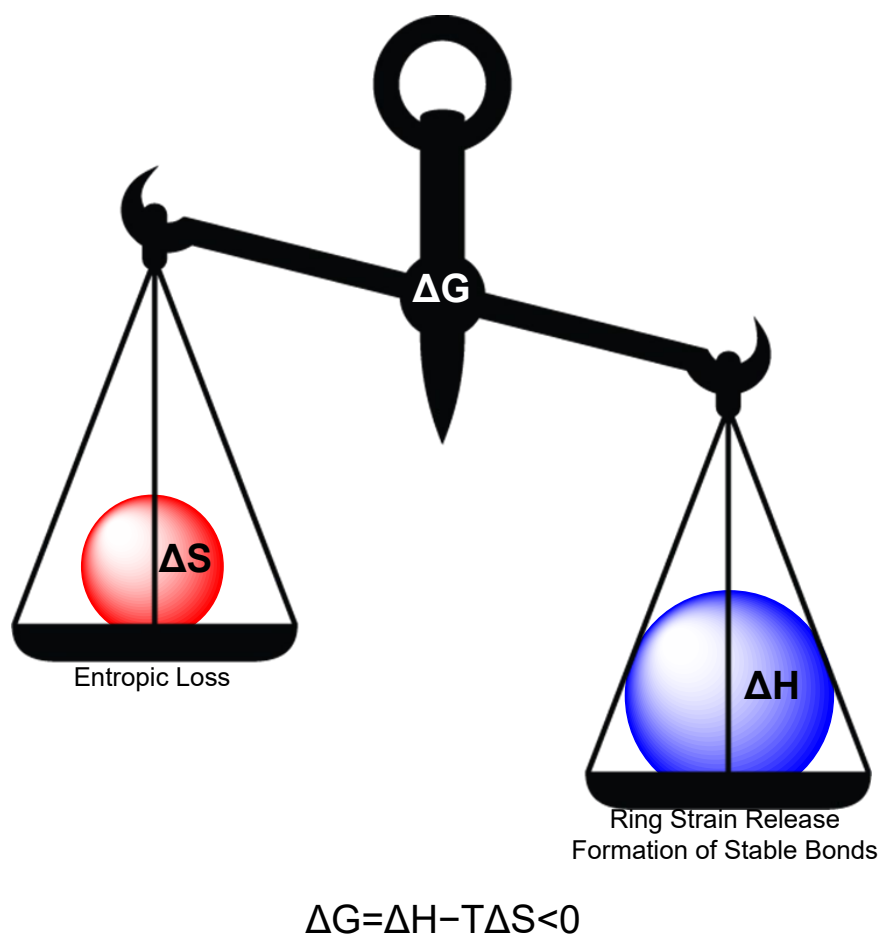


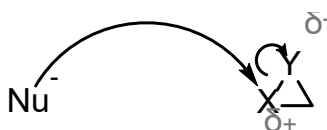
Figure 4: For the ROP to take place, the enthalpic effect must outweigh the entropic penalty.

However, thermodynamic favourability alone is insufficient: kinetically accessible mechanisms are also essential. Polymerisation must proceed at a practical rate under the reaction conditions, with sufficient selectivity and minimal side reactions. Depending on the system, a variety of mechanisms can be employed to achieve this goal, including ionic (both anionic and cationic),<sup>[82,83,84]</sup> coordination-insertion,<sup>[79]</sup> radical,<sup>[85]</sup> metathesis,<sup>[86,87]</sup> covalent, and even enzymatic processes.<sup>[88,89]</sup> Additionally, solvent, temperature, and monomer concentration can significantly impact reaction outcomes, particularly regarding the polymer length and its sequence control, highlighting the importance of precise experimental control.

Considering an anionic ROP, initiation is typically achieved using nucleophilic reagents such as organometallic compounds (e.g., alkyl lithium, alkyl magnesium bromide, alkyl aluminium), metal amides, alkoxides, phosphines, amines, alcohols, or even water. Monomers that participate in this process generally contain polarized bonds, including ester, carbonate, amide, urethane, and phosphate groups, which generate the corresponding polyester, polycarbonate, polyamide, polyurethane, and polyphosphate polymers.

When the monomer structure contains a three-membered ring, the inherent ring strain facilitates polymerisation even in the presence of less electrophilic functionalities such as ether, amine, or thioether groups. Examples of such strained cyclic monomers include epoxides, thiiranes, and aziridines, of considerable technological relevance. This is particularly true for epoxides since ethylene oxide and propylene oxide constitute major industrial products with around 11 million tons of propylene oxide produced yearly.<sup>[90]</sup> The reactive site of the cyclic monomer can be represented by atoms X and Y, where X is most often a carbon atom rendered electron-deficient due to the strong electron-withdrawing influence of Y (typically oxygen, nitrogen, or sulphur).

The nucleophilic initiator attacks X, cleaving the bond and releasing Y<sup>-</sup>. The resulting anionic species then propagates by successively attacking additional monomer units, thereby generating the polymer chain (Scheme 11).

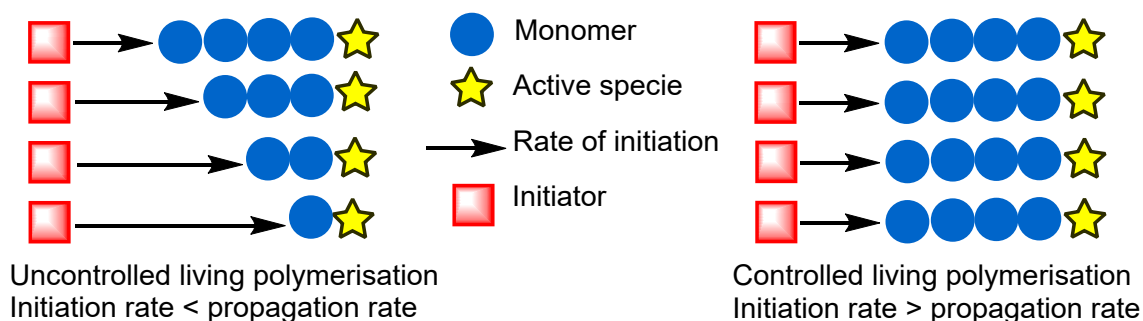


*Scheme 11: Anionic ring-opening of a three membered ring*

For sulphur-containing monomers, the polarizability and nucleophilicity of sulphur atoms influence both the reactivity of the monomer and the stability of the propagating species. Ring-opening reactions of sulphur-containing cycles, just like the others, must be carefully controlled. Consequently, the selection of catalysts, initiators, and reaction conditions is crucial for achieving high-fidelity linear polymers.

The advantages of ROP extend beyond molecular weight control. This approach enables tailored end-group functionality,<sup>[91]</sup> allowing for further chemical modification,<sup>[92]</sup> chain extension, or grafting<sup>[93,94,95]</sup> of functional moieties.

ROP can be adapted to living or controlled polymerisations, where termination and chain transfer reactions are suppressed. In such systems, careful tuning of the initiation rate, which must be equal to or faster than the propagation rate, enables precise control over the molecular weight distribution and chain-end fidelity (Figure 5).



*Figure 5: When the rate of initiation is slower than the propagation rate, polymerisation is not controlled, and the result is a polymer with a high molecular weight dispersity. A faster initiation rate causes all the reactive species to form simultaneously, allowing the chain growth to occur at the same rate.*

These features are essential for the synthesis of block copolymers, sequence-defined polymers, and other advanced macromolecular architectures. The concept of living polymerisation, first demonstrated in the anionic polymerisation of vinyl monomers by Szwarc et al.,<sup>[96,97]</sup> has since been extended to numerous ROP systems.

Modern polymer chemistry increasingly depends on ring-opening polymerisation as a flexible method for creating well-defined polymers. ROP allows for accurate control over molecular weight, dispersity, and the placement of functional groups. In the realm of sulphur polymers, ROP and its advanced variations offer a way to produce linear polymers with customized sequences, functionalities, and performance.

### 3.1 ROCOP and ROTERP Principles

Ring-opening copolymerisation (ROCOP) and ring-opening terpolymerisation (ROTERP) represent advanced strategies for achieving sequence control in polymer synthesis. ROCOP involves the alternating polymerisation of two different monomers, where at least one of them has a cyclic structure, enabling the construction of regular, predictable sequences with specific functional groups. ROTERP extends this concept to three monomers, allowing the formation of more complex structures with higher variation, composition, and functionality, while aiming for the same sequence control typically achieved in successful ROPs.

For sulphur-containing polymers, ROCOP and ROTERP are particularly valuable because, unlike vulcanization and inverse vulcanization, they allow the introduction of sulphur units at defined intervals along the polymer backbone. This precise placement<sup>[98]</sup> is critical for tuning physical properties such as thermal stability, mechanical strength, and solubility, as well as for incorporating redox-active or chemically reactive sites. By combining sulphur monomers with oxygen- or carbon-based monomers, chemists can create hybrid materials that leverage the advantages of both types of building blocks.

The practical implementation of ROCOP and ROTERP relies on careful catalyst design and reaction engineering: the ideal catalyst must selectively activate one monomer over another, control chain propagation rates, and minimize side reactions. Recent advances in homogeneous and heterogeneous catalysis have expanded the scope of ROCOP and ROTERP for sulphur polymers, enabling the synthesis of well-defined block copolymers, gradient copolymers, and sequence-controlled architectures (Figure 6).<sup>[99,100]</sup>

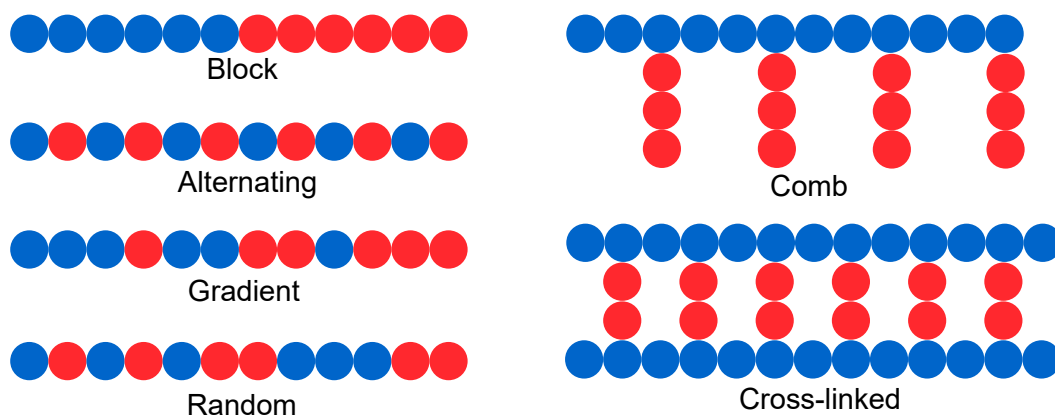


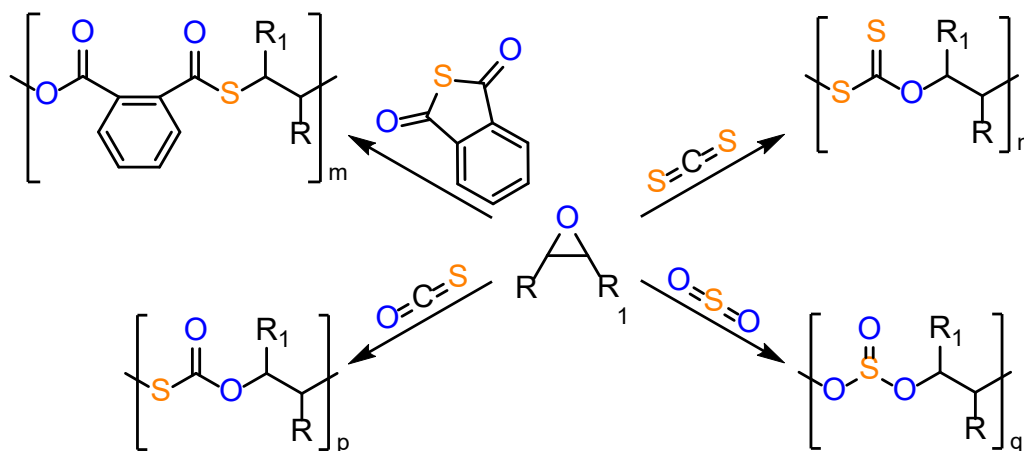
Figure 6: Typical examples of copolymers.

## 4. Ring-Opening Polymerisation as a Strategy to Obtain Linear Sulphur-Containing Polymers.

### 4.1 Copolymers of Epoxides with Sulphur-Containing Monomers

Epoxides are fundamental intermediates in polymer synthesis and, through ring-opening copolymerisations with sulphur-containing monomers, provide access to structurally diverse poly(monothiocarbonates), poly(trithiocarbonates), polysulfides, and polythioesters (scheme 12).

[101,102,103,104,105]

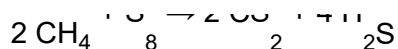


*Scheme 12: Typical copolymerisations with epoxide and sulphur-containing monomers, accurate catalyst choice leads to unscrambled polymers with controlled sequence. Modified with permission from ACS Publications <sup>[144]</sup>.*

Despite this versatility, achieving structural precision remains difficult. The high nucleophilicity of sulphur and the strong coordinating ability of thiolate intermediates frequently trigger competing pathways such as transesterification, O/S exchange, and catalyst deactivation. These complications make stereochemical and sequence control significantly more demanding than in oxygen-based systems.

#### 4.1.1 Copolymerisation of Epoxides with Carbon Disulfide

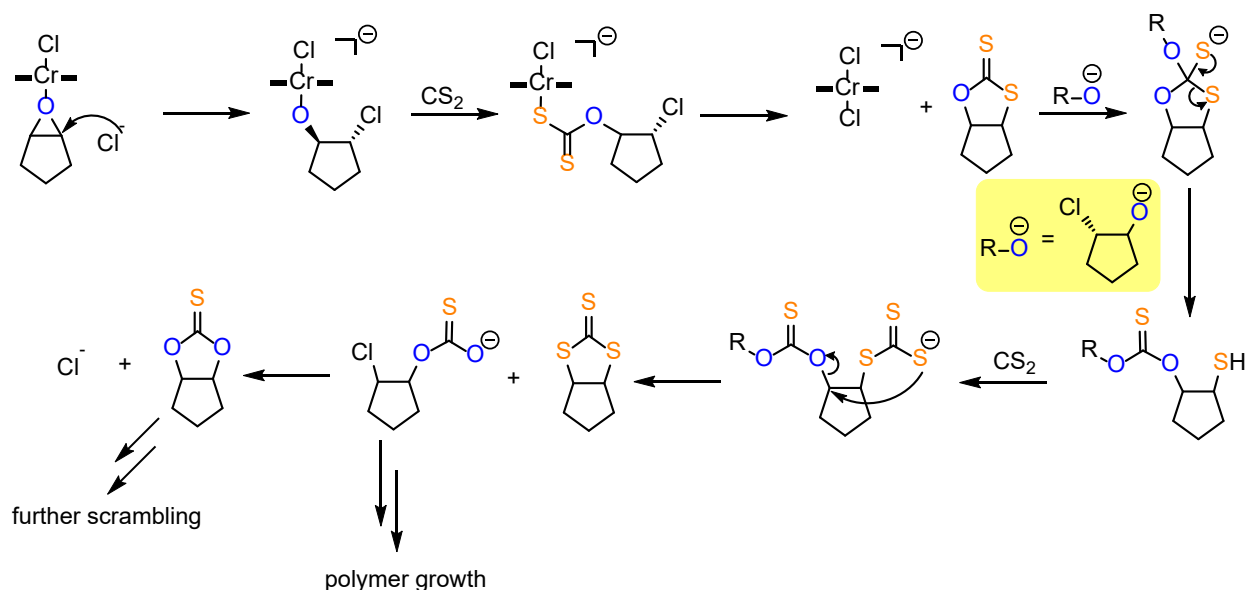
Among sulphur derivatives, carbon disulfide (CS<sub>2</sub>) stands out because it is produced commercially by reacting methane with sulphur at elevated temperatures (Scheme 13) and is one of the main large-scale uses of elemental sulphur.



Scheme 13: Industrial synthesis of CS<sub>2</sub>. Requires 600 °C, and the natural gas acts as a carbon source in the presence of silica gel or alumina catalysts.

Copolymerisation of CS<sub>2</sub> with epoxides was first reported by Inoue et al. using ZnEt<sub>2</sub> combined with electron donors. These initial systems displayed low efficiency and sequence control, yielding mixtures of dithiocarbonate and trithiocarbonate linkages generated through extensive O/S exchange during propagation.<sup>[106,107]</sup> Subsequent studies improved catalytic performance using double-metal cyanide complexes such as Zn–Co(III), which increased activity and enabled the formation of polymers with moderate molecular weights, although detailed analyses still revealed the coexistence of carbonate and thiocarbonate linkages due to persistent O/S scrambling.<sup>[108]</sup>

Further exploration with meso-epoxides afforded polymers with molecular weights up to 34 kg mol<sup>-1</sup> and narrow dispersity. Structural analysis indicated that the polymeric fraction was oxygen-enriched, while the cyclic byproducts were sulphur-enriched thiocarbonates, a distribution consistent with the higher thermodynamic stability of sulphur-rich cyclic species and the proposed mechanism for transesterification and thiocarbonate rearrangement<sup>[109,110]</sup> (Scheme 14).



Scheme 14: Proposed mechanism for the O/S exchange reaction in the presence of a chromium catalyst. Modified with permission from ACS Publications<sup>[144]</sup>.

Anionic pathways initiated with lithium tert-butoxide enabled access to higher molecular weights (up to 109 kg mol<sup>-1</sup>), yet O/S exchange remained unavoidable. The predominant linkages were



monothiocarbonates and trithiocarbonates, formed with high regioselectivity, leading, respectively, to tail-to-tail (TT) and head-to-head (HH) configurations of the carbon–sulphur fragments. <sup>[111]</sup>

The terms “head” and “tail” refer to the two non-equivalent ends of an unsymmetrical monomer, typically arising from differences in substitution or electronic environment. During chain-growth processes, monomers can connect in different orientations depending on which end of one monomer reacts with which end of the next. The most common arrangement is head-to-tail (HT), where the “head” of one monomer links to the “tail” of the next. Less common but still significant are head-to-head (HH) and tail-to-tail (TT) linkages (Figure 7). The presence and proportion of HH or TT linkages can significantly influence polymer properties, affecting crystallinity, tacticity, thermal transitions, and mechanical behaviour.

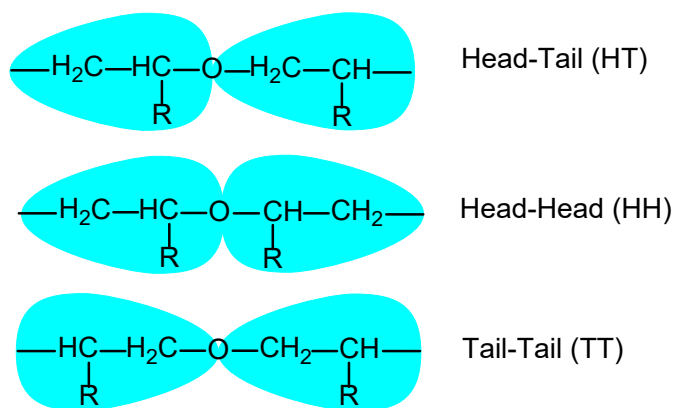


Figure 7: Different configurations for polymer chains.

#### 4.1.2 Copolymerisation of Epoxides with Carbonyl Sulfide

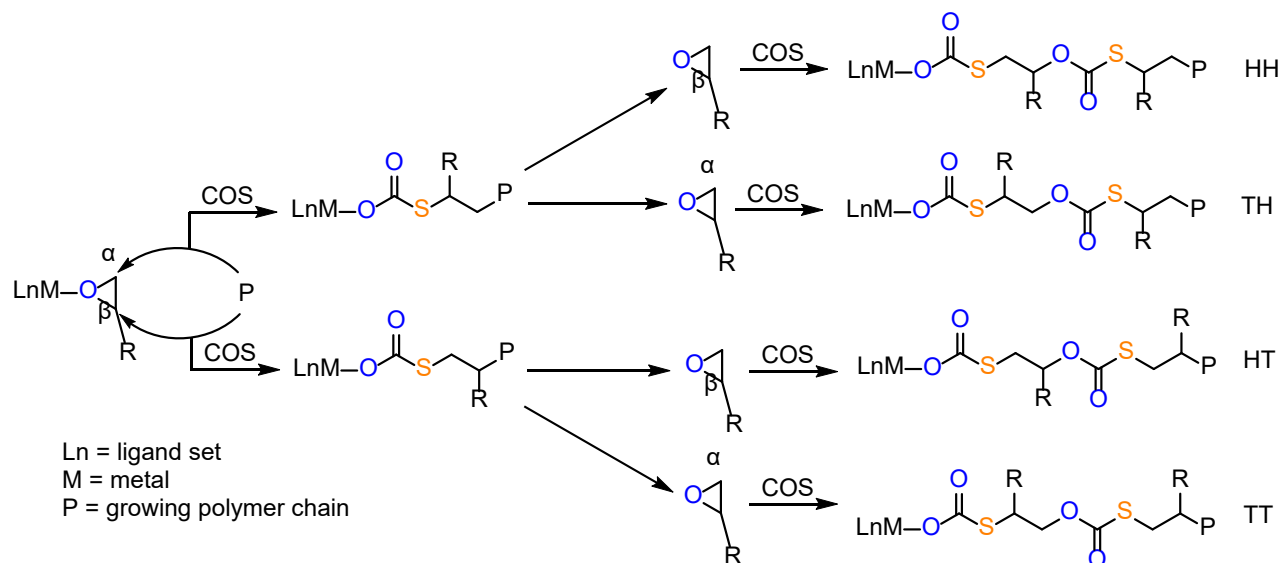
Carbonyl sulfide (COS), structurally analogous to CO<sub>2</sub> but more reactive, can undergo uncatalysed copolymerisation with epoxides. <sup>[112,113,114,115]</sup> However, uncontrolled O/S exchange and cyclic monothiocarbonate formation often occur, motivating the development of catalysts capable of suppressing such side reactions.

A key advance was the introduction of the SalenCrCl/PPNCl system, which enabled alternating copolymerisation at room temperature with high turnover frequencies and high polymer selectivity. At higher temperatures, O/S exchange reappeared, and mechanistic studies identified water-mediated formation of Cr–OH and Cr–SH species as the initiators of undesired pathways. <sup>[101]</sup>

To overcome these issues, bifunctional catalysts combining a Lewis acidic metal centre with a proximal organic base were developed. Chromium and iron complexes of this type produced highly regular poly(monothiocarbonate)s with no detectable O/S exchange even at elevated temperatures and with activities significantly higher than earlier systems. These catalysts demonstrate how spatially adjacent acidic and basic sites can cooperatively activate both epoxide and COS, enhancing monomer insertion while suppressing transesterification.<sup>[116,117]</sup>

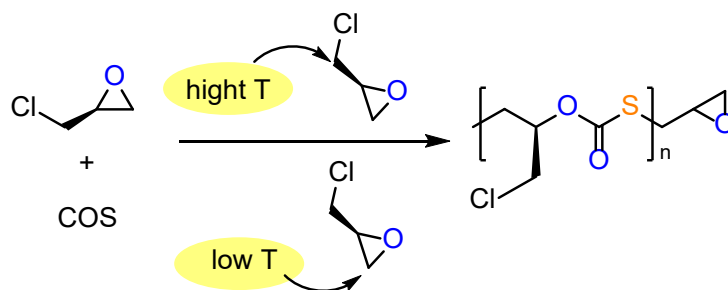
Metal-free systems have also proven effective. Combinations of weak Lewis's acids such as trialkylboranes with suitable bases yield colourless, high-molecular-weight polymers at elevated temperatures without cyclic byproducts.<sup>[118]</sup>

Regioselectivity is strongly influenced by catalyst steric hindrance. SalenCrCl, for example, directs nucleophilic attack toward the benzylic carbon of styrene oxide, while less hindered catalysts favour the alternative site. Even small percentages of regioerrors affect tacticity and crystallinity and have been traced to water-mediated chain-transfer events<sup>[119]</sup> (Scheme 15).



*Scheme 15: Regioselectivity during the copolymerisation of COS and terminal epoxides. Modified with permission from the Royal Society of Chemistry. <sup>[119]</sup>*

Stereochemical control is equally crucial. Enantiopure epichlorohydrin yields crystalline poly(monothiocarbonate)s with melting points near 97 °C, whereas racemic mixtures lead to amorphous materials. Dinuclear SalenCo(III) complexes have demonstrated remarkable stereo control in the polymerisation of meso-epoxides, producing isotactic polymers with melting points between 141 and 232 °C, highlighting the importance of precise catalyst geometry<sup>[120]</sup> (Scheme 16).



Scheme 16: Stereo-controlled copolymerisation of COS and epichlorohydrin. Modified with permission from ACS Publications.<sup>[120]</sup>

#### 4.1.3 Epoxides with Cyclic Thioanhydrides

Cyclic thioanhydrides such as phthalic thioanhydride (PTA) form alternating ester–thioester copolymers with epoxides. Early systems using SalenCrCl/PPNCl suffered from side reactions that produced mixtures of ester–thioester, thioester–thioester, ester–ester units, and ether byproducts. These irregularities arise from transesterification caused by a nucleophilic attack of the propagating alkoxide on thioester moieties unless monomer insertion occurs rapidly.<sup>[104]</sup>

Intramolecularly cooperative chromium catalysts bearing tethered Lewis basic sites were later developed to accelerate thioanhydride insertion relative to transesterification, yielding perfectly alternating copolymers through simultaneous activation of epoxide and thioanhydride.<sup>[121]</sup> Chiral SalenCr complexes further enabled stereoselective copolymerisations, affording isotactic polythioesters with regioselectivities above 92%. Blends of opposite isotactic configurations formed stereo complexes with melting points near 127 °C, significantly higher than the amorphous homochiral materials.<sup>[122]</sup>

Multicomponent polymerisations involving epoxides, thioanhydrides, and anhydrides have been used to form block copolymers through chemoselective monomer insertion. Lithium tert-butoxide enables sequence-controlled terpolymerisation of epoxides/PTA/CS<sub>2</sub>, achieving high molecular weights and controlled alternation patterns. This approach, pioneered by Plajer and co-workers, established the (ABA'C)<sub>n</sub> enchainment motif characteristic of Li-mediated selective ring-opening terpolymerisation.<sup>[123,124]</sup>

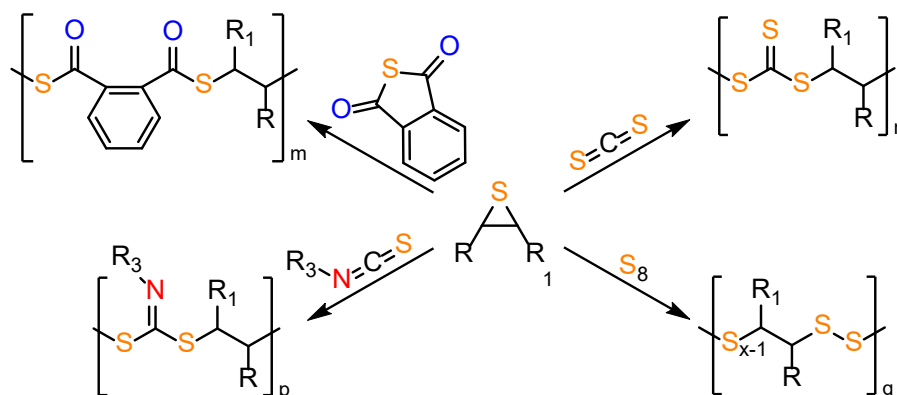
#### 4.1.4 Epoxides with Sulphur Dioxide

SO<sub>2</sub> behaves as a strong sulphur electrophile capable of alternately inserting into epoxide ring-opening sequences to form polysulphides. Early systems displayed low molecular weights and extensive epoxide homopolymerisation. Lewis acids such as SnCl<sub>4</sub>, SbCl<sub>5</sub>, FeCl<sub>3</sub>, or TiCl<sub>4</sub>

promoted cationic pathways that produced long polyether segments interrupted by occasional sulphite units.<sup>[125]</sup> Lewis' base catalysis provided an alternative mechanistic pathway: Amines such as pyridine or quinoline form zwitterionic adducts with SO<sub>2</sub> and epoxides that propagate in an anionic, alternating fashion. Solvents like dimethoxyethane are essential to suppress epoxide homopolymerisation and obtain perfectly alternating structures.<sup>[126,127]</sup>

## 4.2 Copolymers from Thiiranes

Thiiranes (Episulphides), the sulphur analogues of epoxides, exhibit substantially higher reactivity due to increased ring strain and weaker C–S bonds. Their polymerisation typically proceeds without Lewis' acid activation, although uncontrolled homopolymerisation often results in broad dispersity. For this reason, copolymerisation is frequently employed to channel thiirane reactivity into more selective ring-opening pathways<sup>[128,129]</sup> (Scheme 17).

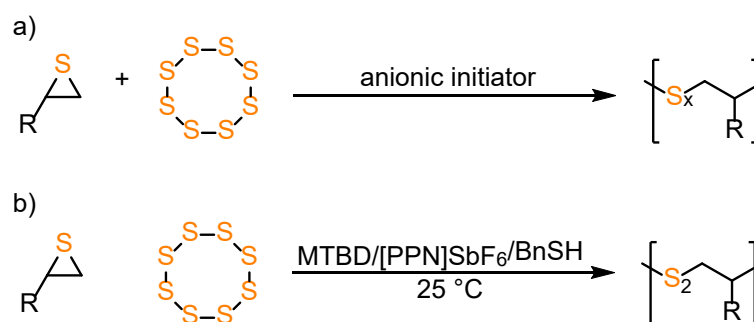


*Scheme 17: Typical copolymerisations with thiiranes and sulphur-rich monomers, accurate catalyst choice leads to unscrambled polymers with controlled sequence. Modified with permission from ACS Publications<sup>[144]</sup>.*

Early thiirane copolymerisations with CS<sub>2</sub>, initiated by organometallic reagents such as CdEt<sub>2</sub>, ZnEt<sub>2</sub>, or Hg(SBu)<sub>2</sub>, produced mixtures of poly(trithiocarbonate)s and unreacted cyclic trithiocarbonates, illustrating the limited stereoelectronic control achievable in early systems.<sup>[102]</sup> Improved sequence control was later obtained using SalphenCrCl/PPNCl, which enabled fully alternating CS<sub>2</sub>/propylene sulfide copolymers with molecular weights up to 42.6 kg mol<sup>-1</sup> and refractive indices close to 1.78.<sup>[130]</sup> Metal-free approaches, including phosphazene benzoxides or PPNCl alone, also demonstrated that thiiranes can be efficiently activated through purely nucleophilic mechanisms.<sup>[131]</sup>

Within the broader context of sulphur chemistry, the most relevant thiirane processes for the present discussion are those involving elemental sulphur (S<sub>8</sub>). Early work by Penczek showed that thiiranes undergo rapid anionic copolymerisation with S<sub>8</sub> at room temperature, forming sulphur-rich

polysulfides containing up to 90% sulphur (Scheme 18a). This behaviour arises because thiolate intermediates preferentially react with  $S_8$  over thiirane, resulting in alternating insertions and characteristic sulphur chain-length distributions.<sup>[132]</sup> A major conceptual advance came with the development of sterically demanding organic cations capable of promoting the controlled disassembly of  $S_8$ . Ren and co-workers showed that combining the strong MTBD base with a weakly coordinating counterion such as  $SbF_6^-$  enables living polymerisation based on the selective formation of linear  $S_2$  units. This method yields exclusively polydisulfides, with predictable molecular weights up to  $371 \text{ kg mol}^{-1}$ , narrow dispersity, and refractive indices around 1.66<sup>[133]</sup> (Scheme 18b).



*Scheme 18: Copolymerisations of thiiranes with elemental sulphur. The length of the polysulfide chain depends on the catalyst. a) An anionic initiator leads to a polymer with uncontrolled polysulfide length. b) A combination of a strong base and a weakly coordinating counterion allows selective formation of polydisulfides. Modified with permission from ACS Publications<sup>[144]</sup>.*

These controlled pathways produce linear, well-defined polysulfides that are markedly different from traditional inverse vulcanization products, which often form cross-linked or statistical networks. As such,  $S_8$ -based thiirane copolymerisation represents a sustainable and versatile platform within modern sulphur polymer chemistry and is particularly relevant in the context of sulphur-rich materials.

Cyclic thioanhydrides can undergo alternating copolymerisation with thiiranes to form sulfur-rich polythioesters, although this strategy has been explored far less extensively than epoxide-based systems. The first successful example was reported in 2019 using quaternary ammonium salts as initiators for the copolymerisation of propylene sulfide (PS) and succinic thioanhydride (STA). When  $[PPN]OAc$  was employed, efficient polymerisation proceeded at ambient temperature, affording high-molar-mass polythioesters ( $M_n$  up to  $43.7 \text{ kg mol}^{-1}$ ) with narrow dispersity and perfectly alternating microstructures, as evidenced by the absence of thioether linkages.<sup>[134]</sup>

The copolymerization of episulphides with isothiocyanates was first reported in 1972,<sup>[135]</sup> yielding low-molar-mass but crystalline materials, after which the field remained unexplored for decades. Recently, Wu et al. revived this chemistry using organic ammonium salts to efficiently initiate the alternating copolymerization of episulphides and isothiocyanates under mild conditions, obtaining perfectly alternating sulfur-rich copolymers.<sup>[136]</sup> Polymerisation efficiency was strongly influenced by both the steric bulk of the ammonium cation and the nucleophilicity of the counterion. The system further enabled a self-switchable, one-pot process combining alternating copolymerisation and episulphide homopolymerisation to access triblock copolymers with thermoplastic elastomeric behaviour.<sup>[137]</sup>

### 4.3 Copolymers from Aziridines

Aziridines are strained three-membered nitrogen heterocycles whose reactivity depends strongly on the electronic properties of the nitrogen substituent. Electron-withdrawing groups promote anionic ring-opening polymerisation, whereas electron-donating groups favour cationic pathways.<sup>[138]</sup>

A representative example is the copolymerisation of aziridines with carbonyl sulfide (COS). Luo and Darensbourg demonstrated that unsubstituted aziridines undergo catalyst-free, zwitterionic alternating polymerisation with COS to form cyclic polythiourethanes with high efficiency.<sup>[139]</sup>

Beyond COS, aziridines also copolymerise with cyclic thioanhydrides. Under phosphazene catalysis (for example,  $t\text{-BuP}_1$ ), aziridines undergo selective ring-opening to form well-defined, alternating poly(thioester sulphonamide)s. These materials exhibit controlled molecular weights and can serve as building blocks for more complex block copolymer architectures.<sup>[140]</sup>

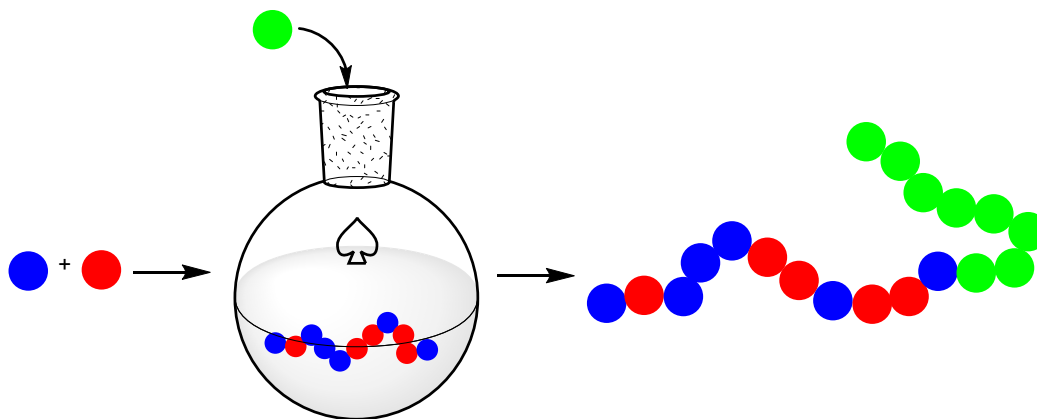
## 5. Sequence Control and Advanced Strategies

Control over monomer sequence is a central parameter in synthetic polymer design, as it directly determines microstructure and, consequently, macroscopic material properties. In sulphur-containing polymers, sequence effects are especially pronounced because the incorporation of C–S, C–O, and S–S linkages introduces large contrasts in bond strength, polarity, and chemical reactivity. These differences enable access to properties such as dynamic behaviour, redox activity, and degradability, but simultaneously impose stringent demands on polymerisation selectivity.

In practice, sequence control in sulphur polymers is most effectively achieved through chemoselective ring-opening polymerisation processes, in which the identity of the propagating chain end and the relative reactivity of heteroallenes dictate monomer enchainment. Alternating copolymerisations between sulphur-containing monomers (e.g., CS<sub>2</sub>, COS, cyclic thioanhydrides, episulphides) and oxygen-based comonomers provide a direct route to periodic sequences while suppressing uncontrolled homopolymerisation pathways.<sup>[99]</sup> However, the high nucleophilicity of alkoxide and thiolate propagating species often promotes side reactions such as transesterification, O/S exchange, or chain transfer, which can rapidly degrade sequence fidelity if monomer insertion is not kinetically favoured.<sup>[124]</sup>

Catalyst and initiator design, therefore, play a decisive role in enforcing sequence selectivity in sulphur-rich systems. Cooperative metal catalysts and alkali-metal initiators have been shown to regulate propagation kinetics, selectively activate specific monomers, and stabilise reactive chain ends, thereby suppressing scrambling pathways. In particular, lithium-mediated selective ring-opening terpolymerisation (ROTERP) enables controlled enchainment from ternary monomer mixtures by exploiting the differential reactivity of heteroallenes toward lithium alkoxide and thiolate species, resulting in predictable and reproducible sequence motifs.<sup>[123]</sup> This approach has demonstrated that high levels of sequence control are achievable even in systems containing highly reactive sulphur monomers.

Beyond intrinsic chemoselectivity, temporal control over monomer availability provides an additional lever to regulate sequence evolution along the polymer chain. Temporal monomer addition allows deliberate switching between distinct propagation regimes, such as alternating copolymerisation and homopolymerisation, enabling the formation of block or gradient architectures within a single reaction vessel<sup>[141,142]</sup> (Figure 8).



*Figure 8: Temporal addition polymerisation, a copolymer chain is formed at first, and then a third monomer is added to the reaction mixture to generate a terpolymer in a controlled manner.*

In sulphur-containing ring-opening systems, such strategies are particularly effective because changes in the monomer feed directly alter the dominant chain-end chemistry and thus the active propagation pathway.<sup>[100]</sup>

Post-polymerisation modification further expands the design space of sequence-controlled sulphur polymers. Functional motifs such as disulfides, thioethers, and trithiocarbonates can be selectively transformed after polymer formation, allowing the introduction of dynamic, degradable, or stimuli-responsive elements without disrupting the underlying backbone sequence.<sup>[41]</sup>

These transformations exploit the inherent chemical versatility of sulphur and provide access to self-healing materials, redox-active polymers, and adaptive networks with spatially defined functionality.

As a consequence of these combined strategies, sequence-controlled sulphur polymers frequently exhibit properties that are inaccessible to statistical analogues. Precise control over sulphur placement also enables systematic investigation of structure–property relationships, providing insight into how local monomer environments influence bulk behaviour.<sup>[133]</sup> Despite these advances, achieving high-fidelity sequence control over long chain lengths remains challenging due to competing side reactions and the intrinsic reactivity of sulphur-based monomers. Therefore, continued further development of selective catalysts, reaction engineering strategies, and advanced microstructural characterisation methods remain necessary.



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## Synopsis

### 1. Research Context and Conceptual Motivation

Elemental sulphur ( $S_8$ ) is one of the most abundant byproducts of the petrochemical industry, generated on a multimegaton scale each year due to desulphurization processes in fossil fuel refinement. Its accumulation has led to massive stockpiles of a chemically rich but industrially underutilized element. Transforming this low-value byproduct into functional, processable materials has therefore become a key goal in sustainable polymer chemistry. In recent decades, sulphur has transcended its classical association with vulcanized rubbers, gaining prominence in new forms of sulphur polymerisation, from inverse vulcanization to step-growth and ring-opening strategies.

While traditional approaches, such as vulcanization and inverse vulcanization, have successfully integrated sulphur into crosslinked polymeric networks, these materials are often thermosets, insoluble, and thermally unstable at processing temperatures above 160 °C. Moreover, inverse vulcanization typically yields amorphous networks with limited processability and little molecular control. In contrast, linear sulphur-containing polymers offer a platform for molecular precision, allowing tuning of chain length, sulphur content, and sequence: parameters that directly govern physical properties such as flexibility, semi-crystallinity, and mechanical strength.

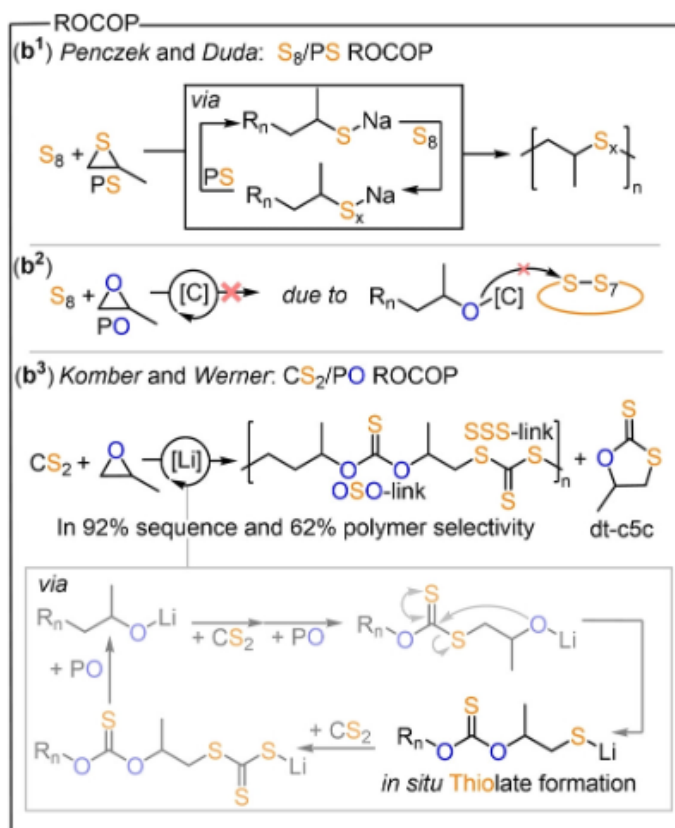
The goal of this research was to establish a controlled and scalable method for incorporating elemental sulphur into linear polymer chains, using ring-opening terpolymerisation (ROTERP) as a guiding strategy. Across three interconnected studies, this work demonstrates how kinetic control, mechanistic insight, and modular design can be leveraged to direct S-incorporation and tune material performance, progressing from fundamental chemistry to stable functional materials and, ultimately, hybrid interfaces.

### 2. Theoretical Framework: O/S Scrambling and Mechanistic Foundations

The ring-opening of elemental sulphur to achieve linear polymers was first clarified through the pioneering studies of Penczek and Duda on the nucleophilic activation of elemental sulphur via thiiranes.<sup>[1]</sup> They showed that thiolate species could open  $S_8$  rings to form polysulfides, which challenged the perception of sulphur's inertness in polymer chemistry (Scheme 19 b<sup>1</sup>).

The traditional approach relies on the use of costly thiiranes, many of which are not commercially available. A more appealing alternative would be to copolymerise elemental sulphur ( $S_8$ ) with the

oxygen analogues of thiiranes: epoxides, since several, such as propylene oxide (PO), are produced on an industrial scale. However, direct copolymerisation of  $S_8$  with epoxides is not feasible because the metal-alkoxide intermediates generated upon epoxide ring-opening fail to form stable linkages or intermediates with sulphur (Scheme 19 b<sup>2</sup>).<sup>[2,3,4]</sup> A potential solution lies in generating thiolate intermediates during epoxide polymerisations, which could in turn react productively with  $S_8$ .



Scheme 19: b<sup>1</sup>) Representation of PS- $S_8$  copolymerisation proposed by Penczek and Duda, b<sup>2</sup>) impossibility to achieve octasulphur ring-opening with an alkoxide, b<sup>3</sup>)  $CS_2$ /PO copolymerisation proposed by Komber and Werner, the two monomers yield a polymer bearing an unexpected monothiocarbonate-alt-trithiocarbonate structure—explanation of the mechanism behind the formation of such a sequence. Reproduced with permission from Wiley.<sup>[6]</sup>

In this context, Komber and Werner and co-workers demonstrated that the lithium-alkoxide-catalysed ring-opening copolymerisation (ROCOP) of  $CS_2$  and PO produces poly(monothiocarbonate-alt-trithiocarbonate)s comprising alternating  $-O-C(=S)-O-$  ("OSO") and  $-S-C(=S)-S-$  ("SSS") linkages (Scheme 19 b<sup>3</sup>) instead of poly(dithiocarbonate)s bearing  $-O-C(=S)-S-$  ("OSS") units.<sup>[5]</sup> These polymers display an atypical head-to-head-alt-tail-to-tail microstructure, in which tertiary CH groups (from PO ring-opening) are adjacent to OSO units, while secondary  $CH_2$  groups are positioned next to SSS linkages. This specific sequence has been

attributed to an O/S exchange process occurring at the propagating chain end, which converts lithium alkoxide species into thiolate intermediates. Such O/S scrambling phenomena are frequently observed, though seldom precisely controlled, in ROCOP reactions involving epoxides or oxetanes with sulphur-containing comonomers.

Suddenly, this O/S scrambling allowed the formation of a thiolate chain end, able to open octasulphur. From a cheap and industrially relevant epoxide such as PO, it was then possible to include elemental sulphur as a monomer in a terpolymerisation involving epoxides and another sulphur-bearing compound such as CS<sub>2</sub> or phthalic thioanhydride (PTA).

Across all three studies, the reactions rely on nucleophilic ring-opening catalysis—typically lithium alkoxide-mediated—to initiate polymer growth from small, strained monomers such as epoxides. The catalysis follows a cascade sequence: (1) nucleophilic opening of the epoxide ring to form an alkoxide chain end, (2) capture of an electrophilic sulphur species (either CS<sub>2</sub>, PTA), (3) intramolecular backbiting leading to the O/S scrambling that generates a thiolate chain end, and (4) the nucleophilic attack on S<sub>8</sub> or CS<sub>2</sub>. Characterization across the project relies on complementary techniques: multinuclear NMR spectroscopy, Raman spectroscopy (to probe S–S and C–S bonds), GPC (for molecular weights), DSC/TGA (for thermal transitions), and application-specific tests (lap-shear tests, DLS, Rheology).

### 3. Conceptual Progression Across the Three Publications

#### 3.1 Overview

The three publications forming this thesis are designed as a progressive narrative, each addressing a limitation or open question left by the previous one:

- Publication I: *Ring-Opening Terpolymerisation of Elemental Sulphur Waste with Propylene Oxide and Carbon Disulfide via Lithium Catalysis.*

Establishes the mechanistic feasibility of incorporating S<sub>8</sub> directly into polymer chains, defining control over the polysulfide sequence and its length along the polymer's repeating unit. Cross-linking is briefly investigated, but the low thermal resistance of the material poses an issue for its applications.

- Publication II: *Kinetically Enhanced Access to a Dynamic Polyester Platform via Sequence Selective Terpolymerisation of Elemental Sulphur.*

Introduces aromatic esters into the polymer backbone, which enhances the mechanistic stability, allowing for a wider range of epoxides to be used, while boosting the thermal stability of the material. This enables post-polymerisation chain modification through molecule insertion into the polysulfide groups. Finally, the material is reversibly cross-linked and evaluated as a reprocessable adhesive on different substrates. The reversible character of the adhesive allows simple substrate detaching with acid hydrolysis.

- Publication III: *Sulphur-containing polyesters from thioanhydride/CS<sub>2</sub>/epoxide ring-opening terpolymerisation: monomer scope and gold-nanoparticle functionalisation.*

Switches from elemental sulphur to CS<sub>2</sub>, an industrially relevant derivative of S<sub>8</sub>. This allows the introduction of trithiocarbonate linkages, achieving functional interaction with gold nanoparticles to obtain a pH-responsive nanoprobe, and demonstrating practical hybrid applications.

Together, these works represent a coherent evolution from conceptual feasibility to functional materials development, to investigate the applications of elemental sulphur waste products as a monomer for relevant and controlled polymerisations, guided by mechanistic insight into O/S exchange chemistry and kinetic control.

## 4. Mechanistic Control and Proof of Concept (Publication I)

### 4.1 Objective and Chemical Strategy

The first study establishes the chemical basis by addressing a straightforward question: Can elemental sulphur itself engage in a controlled ring-opening terpolymerisation with affordable and industrially available epoxides, to produce linear polymers with specific sequences and sulphur content?

Using different epoxides and CS<sub>2</sub> as co-monomers, the research shows that S<sub>8</sub> function as a direct sulphur source under lithium alkoxide catalysis, forming poly(monothiocarbonate-alt-S<sub>x</sub>) structures presenting a variety of lateral chains depending on the employed epoxide.

### 4.2 Kinetic and Stoichiometric Control

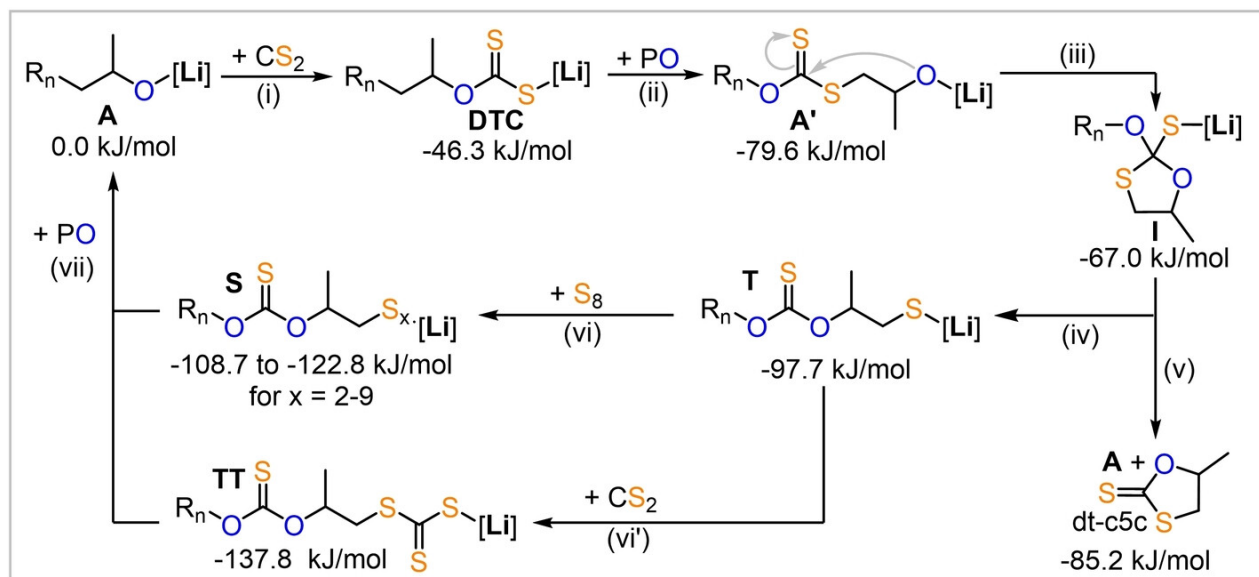
The central achievement of Publication I lies in the kinetic tunability of the resulting polymers. By varying the S<sub>8</sub> ratio, it was possible to define the average length of polysulfide (S<sub>x</sub>) segments and the ratio of oligo- versus disulfide linkages in a reproducible manner. Kinetic analysis, supported by DFT calculations, revealed distinct activation barriers for CS<sub>2</sub> insertion versus S<sub>8</sub> propagation, allowing the reaction to be tuned toward selective outcomes.

- Increasing CS<sub>2</sub> concentration favoured trithiocarbonate due to competition with elemental sulphur for the nucleophilic attack of the lithium thiolate. While CS<sub>2</sub> is thermodynamically more favoured than S<sub>8</sub>, the nucleophilic attack on CS<sub>2</sub> has a reversible nature, while this is not the case with elemental sulphur. This, united with a higher nucleophilic character of the polysulfide moieties obtained from the nucleophilic attack on octasulphur, acts as a thermodynamic sink that drives the reaction towards the consumption of S<sub>8</sub>.
- Variations of S<sub>8</sub> loadings allowed the tuning of the polysulfide length. A higher amount of elemental sulphur led to a maximum chain length of S<sub>4</sub> and S<sub>5</sub>, as demonstrated through Raman analysis and DFT calculations. Higher loadings of octasulphur led to unreacted leftovers in the reaction vessel.
- Temperature control proved essential: mild conditions minimized unwanted scrambling and favoured monomer alternation at the expense of the reaction speed.

These results provide a resolution of both the O/S scrambling and the scarcity of thiiranes challenges, demonstrating that sulphur can be predictably integrated when the reactive sequence is properly orchestrated.

### 4.3 Mechanistic Elucidation

Spectroscopic and kinetic evidence support a stepwise chain-growth mechanism: epoxide ring-opening forms a lithium alkoxide, which can attack  $\text{CS}_2$  or  $\text{S}_8$  (Scheme 20). The reversibility of these steps allows for partial equilibration of O/S linkages, as shown by time-dependent NMR spectra. Computational modelling further confirms that the lithium cation has a dual role, acting as both a Lewis acid that polarizes the epoxide and a templating ion that organizes sulphur species, thus promoting regioselective propagation (Figure 9).



*Scheme 20: Mechanistic hypothesis for  $\text{S}_8/\text{CS}_2/\text{PO}$  ROTERP. Gibbs free energies associated with the respective intermediates, labelled below, were assessed from a series of structures involving different Li coordination modes. Reproduced with permission from Wiley. [6]*



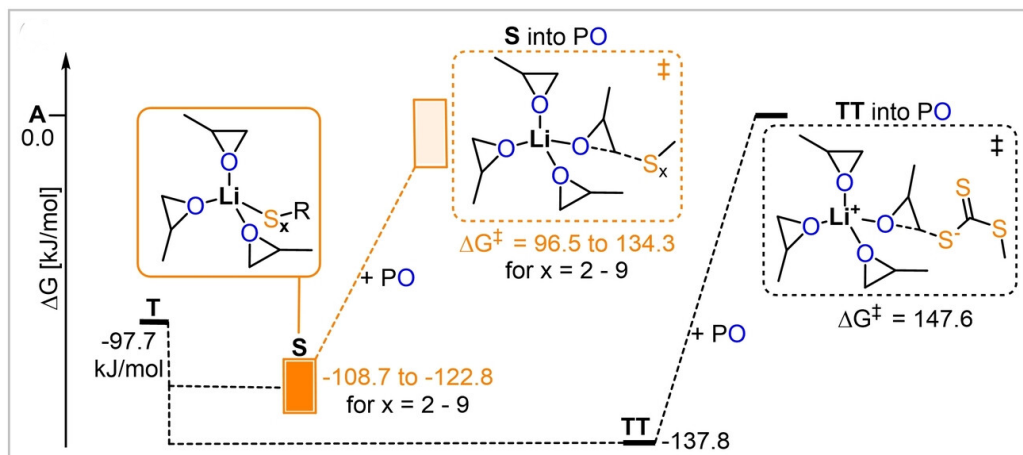


Figure 9: Computed PO ring-opening barriers by **S** and **TT**. lower activation energies for the lithium polysulfide **S** inserting into PO than for the trithiocarbonate **TT**. In other words, lithium polysulfides **S** are better nucleophiles than lithium trithiocarbonates. Reproduced with permission from Wiley. <sup>[6]</sup>

#### 4.4 Limitations

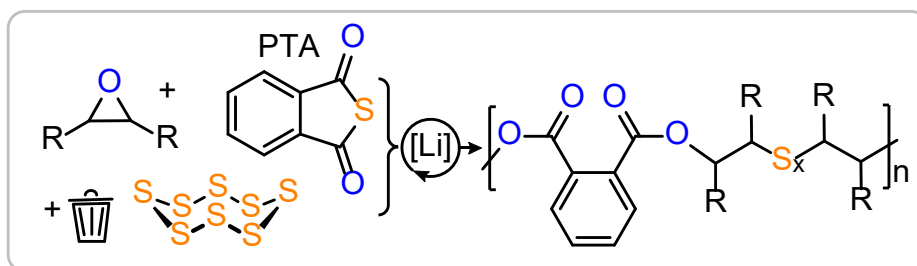
The resulting polymers achieved molecular weights up to  $\approx 30$  kDa with moderate dispersity. Raman and NMR spectra confirmed alternating sequences, while DSC/TGA data revealed limited thermal stability ( $\sim 180$  °C onset). The materials exhibited promising reprocessability but suffered degradation upon extended heating due to cleavage of monothiocarbonate linkages and the subsequent elimination of COS gas.

These shortcomings defined the next research step: enhancing thermal and mechanical stability while retaining control over sulphur insertion.

## 5. Thermal Stabilization, Functionality, and Post-Modification (Publication II)

### 5.1 Objective and Chemical Strategy

Building on the insights from Publication I, the second study aimed to improve material stability and functionality by replacing CS<sub>2</sub> with phthalic thioanhydride (PTA) (Scheme 21). The PTA monomer supplies sulphur atoms while also introducing aromatic ester linkages that enhance mechanical strength and structural resistance. This method not only stabilizes the polymer backbone but also makes it stiffer and increases its thermal stability, enabling new post-functionalisation chemistry through heat-driven processes. Part of the improvement stems from the aromatic ring of PTA, which stabilizes reaction intermediates via resonance, thereby facilitating the incorporation of more challenging monomers that need longer reaction times. For this reason, the study employs a broader range of functional and bio-based epoxides, such as vanillin-derived epoxides.



*Scheme 21: Representation of PTA/PO/S<sub>8</sub> terpolymerisation yielding a poly(ester-alt-polysulfide) material. Reproduced with permission from Wiley. <sup>[7]</sup>*

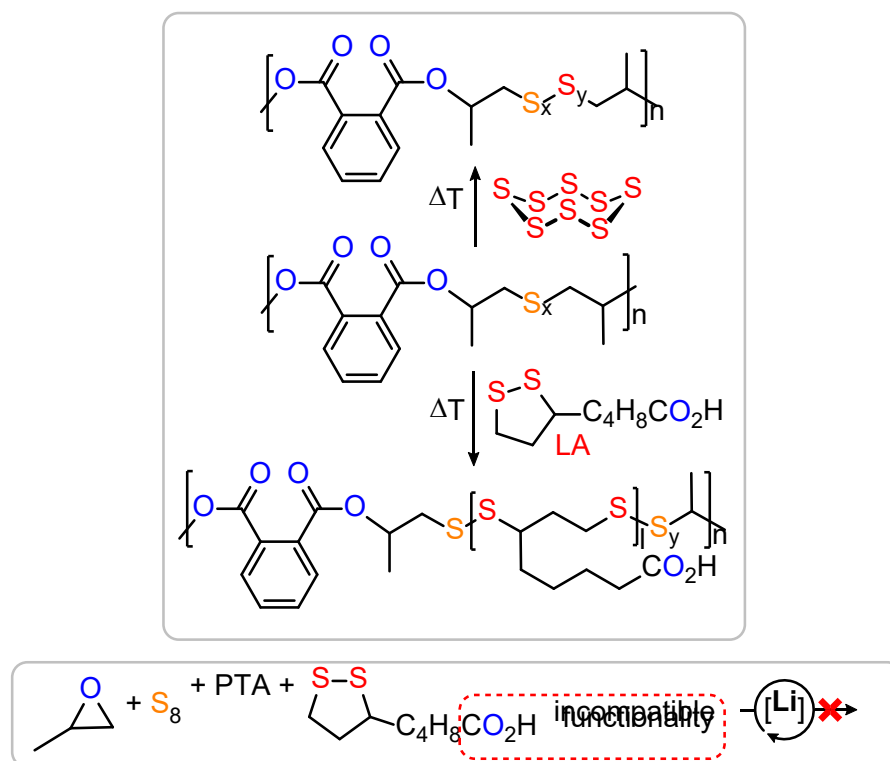
Thermal gravimetric analysis revealed onset degradation temperatures up to 270 °C, a significant improvement over Publication I. Glass transition temperatures ( $T_g$ ) spanned from -40 °C to +127 °C depending on the monomer's structure and sulphur loading, confirming the system's adaptability from viscous liquids to rigid plastics.

Moreover, vanillin-derived epoxide bearing free aldehyde groups allowed the reversible cross-linking reaction with diamines via imine bond formation, generating a reprocessable network that could be easily degraded under acid hydrolysis conditions. These networks were then evaluated as reprocessable adhesives on different substrates.

### 5.2 Post-Functionalisation Enabled by Thermal Stability

One of the key achievements of Publication II is demonstrating that enhanced stability allows chemical modification of the polymer after synthesis (Scheme 22).

- Additional sulphur loadings: Thermal activation of elemental sulphur in the presence of the polymer material enabled further sulphur incorporation, increasing the oligosulphide chains' length, without running into material decomposition.
- Lipoic acid incorporation: Cyclic disulfide-containing lipoic acid was successfully inserted into the polymer backbone through the thermal activation of its polysulfide moieties. This allowed the inclusion of a monomer that is not compatible with the polymerisation mechanism due to the presence of carboxylic acids that would interact with the lithium catalyst. This procedure worked not only on the linear polymer but also on the imine network, where the obtained material proved to possess an improved surface adhesion towards aluminium due to its increased polarity derived from the inclusion of carboxylic acid moieties.



Scheme 22: Polymer post-functionalisation with elemental sulphur and lipoic acid. The carboxylic acid groups on lipoic acid make them unsuitable for direct polymerisation with lithium catalysts. Reproduced with permission from Wiley. <sup>[7]</sup>

The improved materials opened the door for targeted applications but remained limited in terms of interface specificity or advanced function. This prompted the third and final phase: directing sulphur chemistry toward coordination and interfacial applications.

## **6. Trithiocarbonate Chemistry and Hybrid Interfaces (Publication III)**

### **6.1 Conceptual Expansion**

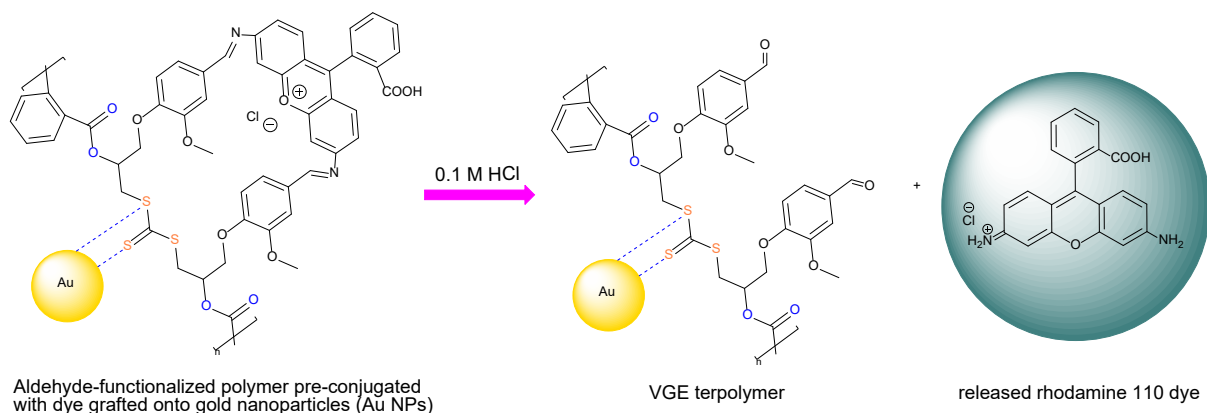
The final study extends the sulphur-polymer platform from bulk materials to hybrid systems capable of interfacing with metal nanoparticles. The key design element is the trithiocarbonate unit, a motif that combines sulphur-rich bonding with coordinative potential toward metals. The goal was to demonstrate how sulphur-rich linear polymers can bridge molecular design and interfacial function, transforming reactive chains into tuneable coatings or nanoparticle stabilizers.

### **6.2 Synthetic Design**

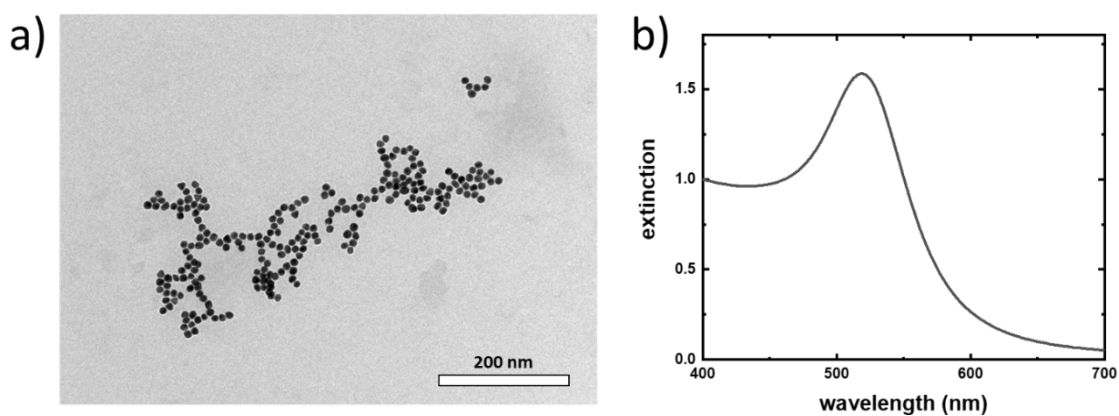
Monomers such as fluorinated and trimethylsilyl-functionalised epoxides endowed the polymers with tailored surface energies and post-functional handles. Hydrolysis of silyl groups afforded rubber-like materials. Thermal and spectroscopic analyses confirmed the retention of high stability and controlled sequence formation.

### **6.3 Gold Nanoparticle Grafting and Hybrid Properties**

Collaboration with the Leibniz Institute of Polymer Research demonstrated the polymers' ability to graft onto gold nanoparticles (AuNPs) through sulphur–metal coordination. Exploiting sulphur–metal affinity to generate stable nanocomposites that were then conjugated with a rhodamine 110 dye, and the system was used as a pH-responsive nanoprobe (Scheme 23). The resulting hybrids retained plasmonic characteristics and displayed tuneable interparticle spacing depending on polymer grafting density. UV–vis spectroscopy and TEM imaging (Figure 10) confirmed homogeneous coating and strong metal–sulphur binding. This confirmed that trithiocarbonate linkages provide strong, selective anchoring to metal surfaces, paving the way for sulphur-based hybrid nanomaterials.



*Scheme 23: Schematic illustration of the dye release process, showing the aldehyde functionalised polymer pre-conjugated with the dye, grafted onto the gold nanoparticles, and subsequent dye release upon acid treatment. Reproduced with permission from Elsevier. <sup>[8]</sup>*



*Figure 10: a). TEM image of Au nanoparticles deposited from an aqueous dispersion onto a carbon-coated copper grid by drop-casting. b) Visible extinction spectrum of Au nanospheres dispersed in water, showing the characteristic localized surface plasmon resonance. Reproduced with permission from Elsevier <sup>[8]</sup>*

## 7. Conclusions and Outlook

Across the three studies presented in this thesis, O/S scrambling emerges not as a mechanistic complication but as a central design principle. What initially appears to be an uncontrolled side reaction becomes a tuneable feature once its kinetic and thermodynamic foundations are understood. By learning how to direct, suppress, or exploit O/S exchange, the work reshapes a mechanistic obstacle into an enabling tool for constructing sulphur-rich linear polymers with sequence control.

From a sustainability perspective, the research contributes to the broader effort of valorising elemental sulphur, a waste product increasingly abundant due to modern desulphurisation technologies. Transforming this low-value byproduct into tuneable, high-performance polymers demonstrates a feasible route from waste feedstock to functional materials. The trajectory of the three publications illustrates this progression clearly. Conceptual proof-of-principle polymers in Publication I evolve into more thermally robust and post-functionalisable materials in Publication II, and ultimately into hybrid nanomaterials with metal-coordination capabilities in Publication III. Together, these studies show how fundamental mechanistic understanding can enable new applications and unlock the potential of industrial sulphur derivatives.

Although these works establish a methodology for generating linear polymers from elemental sulphur and its derivatives, several aspects require refinement before the technology can reach its full potential. Improving sequence control and increasing achievable molecular weights remain important objectives. In addition, closing the loop through controlled depolymerisation and repolymerisation strategies is essential for developing materials that can meaningfully contribute to circular-materials initiatives and environmental sustainability.

Stoichiometric investigations performed during this research clarified optimal monomer ratios, yet catalyst development remains comparatively underexplored. Empirical findings, supported by DFT analysis, consistently indicate that  $\text{Li}^+$  plays a pivotal role in enabling selective polymerisation, whereas other alkali-metal counterions such as  $\text{Na}^+$  or  $\text{K}^+$  fail to support productive catalysis. Expanding the catalyst scope, for example, by exploring alternative bases or more sterically demanding alkoxides, may enhance sequence control or allow more precise regulation of polysulfide segment length. The use of chiral catalysts also represents an intriguing opportunity for stereo control in epoxide insertion, with the potential to produce tactic polymers whose semicrystalline behaviour could provide enhanced mechanical properties.

Recyclability represents another critical direction for future development. The relative weakness of C–S bonds enables depolymerisation through hydrolysis, reduction, or thermal pathways. However, the challenge lies in achieving controlled depolymerisation rather than indiscriminate chain cleavage. An ideal scenario would involve backbiting processes that generate well-defined cyclic species capable of undergoing clean ring-opening polymerisation. Achieving this type of closed loop would enable a true chemical recycling strategy. Designing systems that consistently favour such cyclic depolymerisation pathways remains an open but promising research avenue.

Finally, the long-term impact of this chemistry depends on its scalability. Developing dependable, safe, and economically viable procedures capable of producing kilogram-scale batches is essential if sulphur-rich polymers are to make a substantive contribution to mitigating global sulphur waste accumulation.

Sulphur has proven to be a highly versatile element in polymer chemistry. It imparts dynamic behaviour, enables post-synthetic modification, and adopts multiple oxidation states that provide diverse reactivity beyond that of oxygen. These features present significant opportunities for designing next-generation materials that address both technological needs and environmental challenges. Continued exploration of sulphur-based polymer architectures, including their synthesis, reactivity, and recyclability, will be crucial in transforming this abundant waste element into a cornerstone of sustainable materials science.

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## Publications

### 1. Individual Contributions to Joint Publications

All publications included in this thesis are the result of close collaborative work of several researchers across multiple disciplines. The individual contributions of each author and coauthor are given in this section.

#### **Publication I: *Ring-Opening Terpolymerisation of Elemental Sulphur Waste with Propylene Oxide and Carbon Disulfide via Lithium Catalysis.***

*Angewandte Chemie International Edition* **2024**, 63, e202319810

Cesare Gallizioli, David Battke, Helmut Schlaad, Peter Deglmann, and Alex J. Plajer.

The first publication investigates a mechanistic phenomenon initially observed during the copolymerisation of carbon disulfide (CS<sub>2</sub>) and propylene oxide (PO), where an intramolecular backbiting reaction converts an alkoxide chain end into a thiolate, a process known as O/S scrambling. This distinctive pathway enables the selective incorporation of elemental sulphur, which can be attacked and opened by negatively charged sulphur species.

I performed most of the synthetic work for this study, including the optimization of reaction conditions presented in Table 1, the monomer scope detailed in Table 2, and the cross-linking experiments employing pentaerythritol tetrakis(3-mercaptopropionate). David Battke, a master's student from Freie Universität Berlin, assisted by reproducing polymerisations to verify data reproducibility and to generate material for subsequent experiments, such as cross-linking studies. He also conducted kinetic investigations that elucidated the polysulfide–disulfide rearrangement and established kinetic relationships for both the terpolymerisation and copolymerisation processes occurring after complete consumption of elemental sulphur.

Peter Deglmann conducted the DFT calculations that defined the underlying reaction mechanism and the maximum length of the polysulfide segments within the repeating units. Helmut Schlaad provided valuable insights during polymer characterization and proposed end-capping the polymers with Ellman's reagent to enhance their stability during GPC analysis. Alex J. Plajer conceived the initial research idea, contributed to ongoing scientific discussions, and assisted in interpreting the results. Both Alex J. Plajer and Peter Deglmann participated in finalizing the manuscript.

**Publication II: *Kinetically Enhanced Access to a Dynamic Polyester Platform via Sequence Selective Terpolymerisation of Elemental Sulphur*:**

*Angewandte Chemie International Edition* **2025**, 64, e202501337

Cesare Gallizioli, Peter Deglmann, and Alex J. Plajer

This publication describes the development of a more thermally and mechanically robust material synthesized from elemental sulphur, phthalic thioanhydride (PTA), and various epoxides. Among the resulting polymers, one derived from a vanillin-based epoxide was subsequently cross-linked through the formation of reversible imine bonds, yielding a dynamic network that was applied as an adhesive for diverse substrates. Post-synthetic modifications of the polymer chains enabled fine-tuning of the adhesive performance.

I conducted all the synthetic aspects of this project, including the initial condition screening reported in Table 1, the monomer scope summarized in Table 2, the cross-linking experiments, and the subsequent post-synthesis modifications. I also performed the kinetic investigations using in situ IR spectroscopy and conducted lap-shear tests to evaluate the adhesion strength of the material. Peter Deglmann provided the DFT analysis for this study, offering mechanistic insight into the different kinetic behaviours observed between terpolymerisation and copolymerisation. Alex J. Plajer contributed to the interpretation of the results and the overall narrative development of the publication.

All three authors contributed to the finalization of the manuscript.

**Publication III: Sulphur-containing polyesters from thioanhydride/CS<sub>2</sub>/epoxide ring-opening terpolymerisation: monomer scope and gold-nanoparticle functionalisation.**

Cesare Gallizioli, Marina Sebastian, Malte Cornelsen, Christian Rossner, Alex J. Plajer

*European Polymer Journal* **2025**, 188, 122345.

In this publication, a terpolymer containing trithiocarbonate moieties was synthesized. To achieve this, elemental sulphur was replaced with carbon disulfide (CS<sub>2</sub>), an industrially relevant sulphur derivative. The resulting polymers were then evaluated as functionalizing agents for gold nanoparticles, as the trithiocarbonate groups readily interact with metal surfaces. A polymer chain bearing free aldehyde groups, derived from a vanillin-based epoxide, was employed as a grafting agent for the nanoparticles. The presence of aldehyde functionalities enabled post-functionalisation of the polymer with rhodamine dye through imine bond formation. Rhodamine fluorescence was quenched by its interaction with the gold nanoparticles; however, upon acidification of the solution, hydrolysis of the imine bonds released the rhodamine dye and restored fluorescence, thereby demonstrating the potential of this system as a pH-responsive nanoprobe.

I conducted the monomer screening with various epoxides, characterized each polymer, and elucidated the polymerisation mechanism. Marina Sebastian, from the Leibniz-Institut für Polymerforschung in Dresden, synthesized the gold nanoparticles, grafted the polymer chains onto their surface, and performed dynamic light scattering (DLS) measurements to determine their hydrodynamic diameters. She also conducted visible extinction spectroscopy to observe the red shift of the plasmon resonance and conducted the acid-triggered dye release experiments. Malte Cornelsen assisted during the polymer synthesis and the purification of the monomers. He also conducted the stoichiometric investigations and synthesized the polymer derived from enantiopure R-propylene oxide (R-PO). Christian Rossner provided crucial expertise on nanoparticle deployment within hybrid systems, guiding the optimal integration of our polymers for this application. He also contributed to the finalization of the manuscript. Alex J. Plajer contributed to the interpretation of the scientific data and the conceptual development of the work toward hybrid materials. Marina Sebastian and I jointly prepared the initial draft of the manuscript, which was subsequently refined by Alex J. Plajer. All authors contributed to the final version of the manuscript.





# Ring-Opening Terpolymerisation of Elemental Sulfur Waste with Propylene Oxide and Carbon Disulfide via Lithium Catalysis

Cesare Gallizioli, David Battke, Helmut Schlaad, Peter Deglmann, and Alex J. Plajer\*

**Abstract:** Elemental sulfur, a waste product of the oil refinement process, represents a promising raw material for the synthesis of degradable polymers. We show that simple lithium alkoxides facilitate the polymerisation of elemental sulfur  $S_8$  with industrially relevant propylene oxide (PO) and  $CS_2$  (a base chemical sourced from waste  $S_8$  itself) to give poly(monothiocarbonate-alt- $S_x$ ) in which  $x$  can be controlled by the amount of supplied sulfur. The in situ generation of thiolate intermediates obtained by a rearrangement, which follows  $CS_2$  and PO incorporation, allows to combine  $S_8$  and epoxides into one polymer sequence that would otherwise not be possible. Mechanistic investigations reveal that alkyl oligosulfide intermediates from  $S_8$  ring opening and sulfur chain length equilibration represent the better nucleophiles for inserting the next PO if compared to the trithiocarbonates obtained from the competing  $CS_2$  addition, which causes the sequence selectivity. The polymers can be crosslinked in situ with multifunctional thiols to yield reprocessable and degradable networks. Our report demonstrates how mechanistic understanding allows to combine intrinsically incompatible building blocks for sulfur waste utilisation.

## Introduction

Sulfur-containing polymers have shown promise as redox and light responsive, sensorics as well as chemically recyc-

ble materials with improved thermal and optical properties as compared to their non-sulfurated counterparts.<sup>[1–11]</sup> In the societal context, it is beneficial to access these directly from  $S_8$ , which is a megaton scale waste product of the petrochemical industry from oil refining (Figure 1 (a)), or from high sulfur-wt % base chemicals sourced from  $S_8$  such as carbon disulfide  $CS_2$ .<sup>[12,13]</sup> Consequently, a great deal of effort is currently concerned with the synthesis of useful polymeric materials from  $S_8$  itself or chemicals directly sourced from  $S_8$ .<sup>[14–17]</sup> For example, many crosslinked polymers have been synthesised in recent years through *inverse vulcanisation* which have found numerous applications as lenses, electrodes, elastomers, heavy metal scavengers and reprocessable thermosets.<sup>[18–22,22–26]</sup> Although linear thermoplastics can be prepared via different (typically polycondensation) methods, these often require expensive or highly reactive reagents, only incorporate low amounts of sulfur or yield oligomers.<sup>[27]</sup> Given the cyclic structure of  $S_8$ , one might imagine that ring-opening polymerisation would be suitable to produce polysulfur  $S_n$ , however this process is thermodynamically unfavourable at ambient condition (floor temperature 159 °C) and requires copolymerisation techniques to obtain stable polymers.<sup>[28]</sup>

In this regard, Penczek and Duda (Figure 1 (b<sup>1</sup>)) reported in the late 1970s that  $S_8$  undergoes ring-opening copolymerisation (ROCOP) with thiiranes under  $CdCO_3$  or  $NaSPh@18\text{-crown-6}$  catalysis to form polysulfide of the type  $[-CR_2-CH_2-S_x-]_n$  ( $R=H, Me; x=1-9$ ).<sup>[23–25]</sup> Ren et al. very recently expanded this approach to  $PPNSbF_6/MTBD$  catalysis to selectively yield polydisulfides.<sup>[26]</sup> In both cases the key to  $S_8$  activation was that thiirane ring opening leads to a thiolate intermediate, which can open the  $S_8$  ring under formation of an anionic oligosulfide and then propagates. Again, these methodologies depend on the use of expensive or even non-commercial thiiranes. It would be much more attractive to be able to copolymerise  $S_8$  with the lighter homologous of thiiranes, namely epoxides, as some of these, e.g. propylene oxide PO, are large scale industrial chemicals.<sup>[32,33]</sup> Unfortunately, epoxides do not copolymerise with  $S_8$  as the metal-alkoxide intermediates formed from epoxide ring opening does not form stable intermediate or links with  $S_8$  (Figure 1(b<sup>2</sup>)).<sup>[34]</sup> However if one could generate thiolate intermediates in epoxide polymerisations their copolymerisation with  $S_8$  could be achieved. In this regard, Komber and Werner et al. reported that the lithium alkoxide-catalysed ROCOP of  $CS_2/PO$  yields poly(monothio-alt-trithiocarbonate)s (i.e.  $-O-C(=S)-O-$  or “OSO” groups in alternation with  $-S-C(=S)-S-$  or “SSS” groups, Figure 1 (b<sup>3</sup>)) rather than poly(dithiocarbonate)s

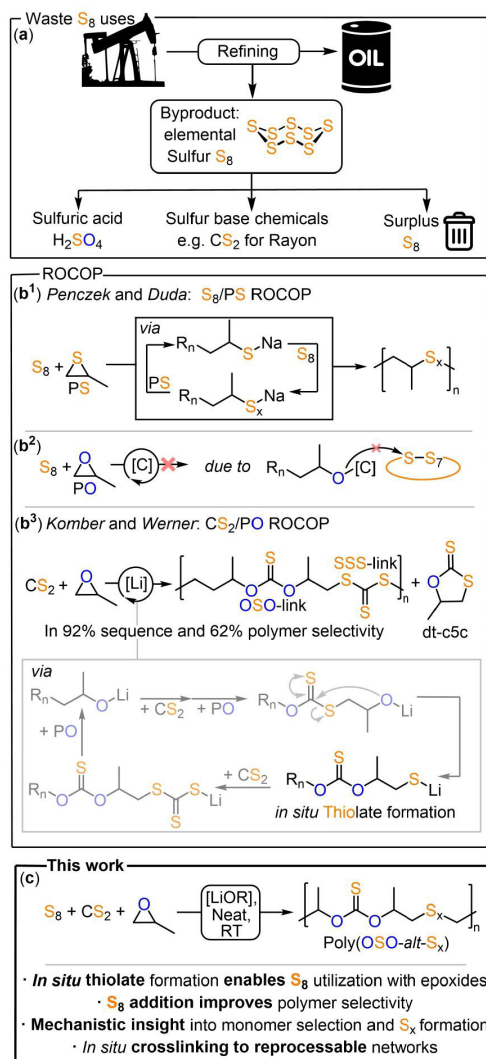
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**Figure 1.** (a) Conceptual Scheme concerning the production and use of  $S_8$ . (b) Ring-opening copolymerisation (ROCOP) of  $S_8$  with propylene sulfide (PS) via thiolate intermediates. (b<sup>2</sup>) Alkoxide intermediates from propylene oxide (PO) ring-opening prevent  $S_8$ /PO ROCOP; [C] denotes catalyst,  $R_n$  denotes polymer chain. (b<sup>3</sup>) In situ thiolate formation during  $CS_2$ /PO ROCOP. (c) Key finding of the presented work.

with  $-O-C(=S)-S-$  or “OSS” links.<sup>[35]</sup> The polymers show an unusual head-to-head-*alt*-tail-to-tail sequence in that the tertiary “head” CH groups from PO ring opening sits next to OSO links and secondary “tail”  $CH_2$  groups sits next to SSS links. The sequence can be rationalised by an O/S exchange process at the chain end transforming lithium alkoxides into lithium thiolate intermediates and it is commonplace, albeit rarely controlled in the ROCOP of epoxides and oxetanes with sulfurated comonomers.<sup>[36–43]</sup> Accordingly, we hypothesised that these thiolates might be

capable of activating  $S_8$  to allow polymer formation from epoxides,  $S_8$  and  $CS_2$  which we report in this contribution.

## Results and discussion

In an initial attempt to achieve  $S_8$ / $CS_2$ /PO ring-opening terpolymerisation (ROTERP) at room temperature, we tested the polymerisation with 1 eq. lithium benzyl oxide (LiOBn, generated from  $Li[N(SiMe_3)_2]$  and BnOH, see ESI Section S2), 250 eq. PO, 500 eq.  $CS_2$  and 125 eq. S (i.e. 1/8  $S_8$ ) (Table 1 run #1). Aliquot analysis of the product mixture after 3 h by  $^1H$  NMR spectroscopy revealed the emergence of indicative broad resonances at 5.80–5.40 ppm, corresponding to CH protons from ring-opened PO adjacent to OSO groups, and 3.50–2.80 ppm, corresponding to  $CH_2$  adjacent to  $S_x$  groups (verified by Raman spectroscopy, see below) (Figure 2(a)); these resonances can be tentatively assigned in reference to the copolymers produced by ROCOP of  $CS_2$ /PO and  $S_8$ /PS.<sup>[31,44]</sup> In addition to formation of 84 % polymer (i.e., polymer selectivity is 84 %), we also obtained approximately 16 % cyclic five-membered propylene dithiocarbonate (dt-c5c) by-product; this can be easily removed from the crude reaction mixture by precipitation from DCM/MeOH. 2D NMR spectroscopy of the isolated polymer showed tertiary carbons ( $\delta(C')=78$  ppm) bound to OSO ( $\delta(C')=193$  ppm) links and secondary carbons ( $\delta(C'')=43$  ppm) adjacent to  $S_x$  links. Hence the copolymer exhibits a poly(OSO-*alt*- $S_x$ ) microstructure in head-to-head-*alt*-tail-to-tail regioselectivity, which is reminiscent of the poly(OSO-*alt*-SSS) structure described by Komber and Werner et al. with  $S_x$  in place of trithiocarbonate links.<sup>[35]</sup> The selectivity of OSO and  $S_x$  versus other links (e.g. dithio- OSS and trithiocarbonate SSS) is 98 %. No (thio)ether links could be observed. Note that during this process  $H_2S$  evolution did not occur, which otherwise is a common problem in other  $S_8$  copolymerisations.<sup>[45]</sup> GPC analysis reveals an apparent weight-average molar mass of the copolymer of  $M_w=20$  kDa ( $D=1.7$ ). The copolymer is obtained as yellow semi-solid, due to the presence of the  $C=S$  chromophore. It is soluble in common organic solvents such as THF, benzene or  $CHCl_3$  and can be hot-pressed into optically clear films (Figure 2(a)). The material features a high refractive index of 1.58 due to the high molar refractivity of the sulfur centres present in the polymer chain.

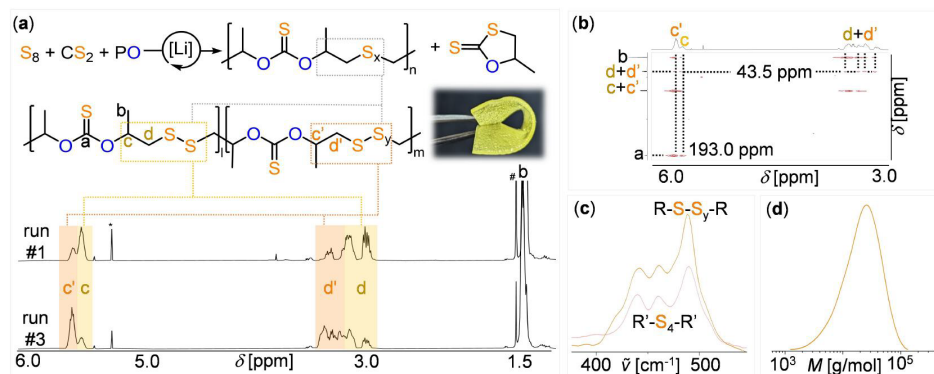
Moving to different sulfur loadings (Table 1, run #2–#5) showed that polymer and sequence selectivity positively correlate with the amount of supplied  $S_8$  in the starting monomer feed. Very high sequence selectivity of > 98 % and polymer selectivity of > 90 % could be achieved. Note that the lithium-alkoxide catalysed ROCOP of  $CS_2$ /PO in the absence of  $S_8$  gave a decreased polymer selectivity of ca. 60 %.<sup>[35]</sup> This is particularly dramatic at a higher reaction temperature of 80 °C, for which ROTERP (run #6) gave 90 % polymer selectivity while ROCOP of  $CS_2$ /PO (run #7) produced no copolymer but only cyclic dithiocarbonate. Near quantitative polymer selectivity is even observed at 120 °C for the ROTERP (run #8) albeit with reduced linkage



**Table 1:** Reaction conditions and molecular characteristics of the polymers obtained by ROTERP of  $S_8/CS_2/PO$ .

| Run              | LiOBn:PO:CS <sub>2</sub> : <sup>1</sup> / <sub>8</sub> S <sub>8</sub> | T [°C] | t [h] | Conv. [%] <sup>a</sup> | Polymer [%] <sup>b</sup> | Disulfide [%] <sup>c</sup> | Linkage [%] <sup>d</sup> | M <sub>w</sub> [kDa] <sup>e</sup> | Đ <sup>e</sup> |
|------------------|-----------------------------------------------------------------------|--------|-------|------------------------|--------------------------|----------------------------|--------------------------|-----------------------------------|----------------|
| #1               | 1:250:250:125                                                         | RT     | 3     | 96                     | 84                       | 70                         | 98                       | 20                                | 1.7            |
| #2               | 1:250:250:250                                                         | RT     | 4     | 99                     | 89                       | 44                         | 97                       | 28                                | 1.7            |
| #3               | 1:250:250:500                                                         | RT     | 4     | 99                     | 91                       | 24                         | 97                       | 27                                | 1.7            |
| #4               | 1:250:250:1000                                                        | RT     | 3     | 94                     | 92                       | 15                         | 93                       | 25                                | 1.5            |
| #5               | 1:250:250:90                                                          | RT     | 4     | 100                    | 72                       | 89                         | 92                       | 17                                | 1.7            |
| #6               | 1:250:250:250                                                         | 80     | 1     | 81                     | 89                       | 46                         | 87                       | 5                                 | 1.5            |
| #7               | 1:250:250:0                                                           | 80     | 1     | 99                     | 0                        | —                          | —                        | —                                 | —              |
| #8               | 1:250:250:250                                                         | 120    | 0.17  | 99                     | 97                       | 18                         | 80                       | 7                                 | 1.5            |
| #9               | 1:250:500:250                                                         | RT     | 16    | 99                     | 90                       | 33                         | 95                       | 28                                | 1.6            |
| #10              | 1:250:750:125                                                         | RT     | 4     | 94                     | 77                       | 73                         | 94                       | 19                                | 1.6            |
| #11              | 1:250:500:500                                                         | RT     | 2     | 73                     | 90                       | 25                         | 96                       | 27                                | 1.8            |
| #12              | 1:250:500:1000                                                        | RT     | 2     | 79                     | 89                       | 20                         | 98                       | 20                                | 1.8            |
| #13              | 1:1000:1000:500                                                       | RT     | 72    | 99                     | 85                       | 69                         | 94                       | 45                                | 1.5            |
| #14              | 1:2000:2000:1000                                                      | RT     | 26    | 98                     | 83                       | 66                         | 97                       | 43                                | 1.5            |
| #15 <sup>f</sup> | 1:400:0:400                                                           | RT     | 24    | 73                     | —                        | —                          | —                        | 24                                | 1.6            |
| #16 <sup>g</sup> | 1:250:500:500                                                         | RT     | 24    | 38                     | 99                       | 19                         | 96                       | n.d.                              | n.d.           |
| #17 <sup>h</sup> | 1:250:500:500                                                         | RT     | 24    | 5                      | 90                       | 18                         | 98                       | n.d.                              | n.d.           |

<sup>a</sup>Relative integral in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tertiary CHMe resonances due to polymer and dt-cSc versus unconsumed PO in the crude polymerisation mixture. <sup>b</sup>Relative integrals in the normalised <sup>1</sup>H NMR spectrum of tertiary CHMe resonances due to polymer versus dt-cSc in the crude polymerisation mixture. <sup>c</sup>Relative integrals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tertiary CHMe resonances part of repeat units comprising R–S–S–R versus R–S–S<sub>y</sub>–R links. <sup>d</sup>Relative integrals in the normalised <sup>1</sup>H NMR spectrum of resonances due to OSO and S<sub>x</sub> versus other links in the precipitated polymer. <sup>e</sup>Determined by GPC (gel permeation chromatography) measurements conducted in THF with polystyrene calibration. <sup>f</sup>1 eq. Ph<sub>3</sub>NPh<sub>3</sub>Cl:400 eq. PS: 400 eq. S with 50vol% toluene in Reference to Ref.<sup>[31]</sup> <sup>g</sup>Na was used as catalyst instead of Li. <sup>h</sup>K was used as catalyst instead of Li.



**Figure 2.** (a) Synthetic scheme, photograph of polymer film and overlaid <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz) of polymers corresponding to Table 1 run #1 and #3. \* Denotes residual DCM from purification. # residual H<sub>2</sub>O. (b) <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectra of polymer corresponding to Table 1 run #1. (c) Zoom into the overlaid Raman spectra of polymer corresponding to Table 1 run #3 and a small molecule R'-S<sub>4</sub>-R' standard. (d) Molar mass distribution of the copolymer corresponding to Table 1 run #1 as obtained by GPC (eluent: THF) with polystyrene calibration.

selectivity. Evidently, supplying additional  $S_8$  is beneficial to improve polymer selectivity. Comparing the <sup>1</sup>H NMR spectra of the obtained copolymers showed that the tertiary CH resonances are always observed as two overlapping resonances centred around 5.64 and 5.72 ppm, and the latter becoming increasingly pronounced in copolymers obtained with higher initial  $S_8$  loading. Employing enantiopure (R)-PO instead of racemic PO allows for deconvolution of the CH<sub>2</sub> <sup>1</sup>H NMR resonances adjacent to the S<sub>x</sub> links in the precipitated polymers for which analogous sets of signals can be observed (ESI Figure S3). Comparing the Raman spectra of the precipitated polymers with small molecule

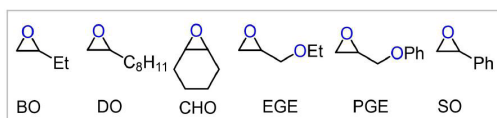
standards for di- (R–S–S–R), tri- (R–S–S–S–R) and tetrasulfide (R–S–S–S–S–R) allowed us to draw some further conclusions about the S<sub>x</sub> links (ESI Figure S12–15). At low sulfur loadings (run #5) disulfide links (sharp signal around  $\tilde{\nu}$ =507 cm<sup>-1</sup>) were mostly formed, while at higher sulfur loadings (run #3) tetrasulfide links (Figure 2(c)) were predominant. As Raman spectroscopy clearly revealed more R–S–S<sub>y</sub>–R ( $y > 1$ ) polysulfide versus R–S–S–R disulfide links at higher sulfur loading, we assigned the <sup>1</sup>H NMR signal centred around 5.64 ppm to CH groups as part of repeat units containing R–S–S–R disulfide and the signal centred around 5.72 ppm to CH groups as part of repeat

units containing R–S–S<sub>y</sub>–R polysulfide links. By peak deconvolution in each case, the R–S–S–R to R–S–S<sub>y</sub>–R ratios were found to change from 89:11 to 15:85 at low to high sulfur loadings. Furthermore, for run #4 we observed unreacted elemental sulfur to be left in the crude reaction mixture indicating that there appears to be an upper limit to how much sulfur can be incorporated into the R–S–S<sub>y</sub>–R links which is reminiscent of Penczek and Duda's original findings.<sup>[29]</sup> Next, we assessed the effects of different S<sub>8</sub> to CS<sub>2</sub> loading ratios (run #9–#12) and found excellent sequence selectivities and similar molar masses in each case. However, polymer selectivity was somewhat decreased to 77 % for lower CS<sub>2</sub> loadings. Decreasing the catalyst loading at a fixed monomer ratio leads to larger obtained molar masses of *M<sub>w</sub>* = 45 kDa (run #13), though the highest achievable molar mass appears to be limited. A decrease of the catalyst loading (run #14) does not lead to further increase of the molar mass beyond 45 kDa. Accordingly, GPC analysis of aliquots removed at regular time intervals revealed increasing molar masses with conversion, reaching a plateau in the high conversion regime (ESI Figure S19). This could be due to the formation of cyclic polymers although the BnO end group could be identified, hence the copolymers are also likely linear chains. Nevertheless, molar masses between 10–50 kDa seems to be typical for S<sub>8</sub> ROCOP (and ROTERP), as reproducing a literature known S<sub>8</sub>/PS ROCOP<sup>[31]</sup> at a comparable loading (run #15, compared to runs #2–4) gave copolymers with similar molar masses. Employing NaOBn or KOBN (run #16–17) instead of the LiOBn catalyst led to significantly slower indicating that Li acts as a true catalyst rather than a mere spectator counteraction to the chain end. Looking at the combined

results from Table 1 no clear conclusion can be drawn how the monomer feed ratio affects the observed linkage selectivity due to the overall high selectivity observed.

We also investigated the suitability of other epoxides than PO to our new methodology (ESI Section S6) and found a range of monosubstituted and alicyclic epoxides (Figure 3) to likewise undergo ROTERP with S<sub>8</sub> and CS<sub>2</sub> (Table 2) which we examined at the monomer feeds and conditions of Table 1 **run #1**.

Moving to monosubstituted epoxides with longer alkyl chains, such as butylene oxide (BO) and 1,2-decylene oxide (DO), gave similar results as the ROTERP of PO under the same conditions, producing a poly(OSO-*alt*-S<sub>x</sub>) with head-to-head-*alt*-tail-to-tail regioselectivity. Compared to the *T<sub>g</sub>* of the PO terpolymer (4 °C), the BO terpolymer shows a slightly higher *T<sub>g</sub>* of 19 °C while the DO terpolymer shows a slightly lower *T<sub>g</sub>* of –12 °C. The ROTERP of cyclohexene oxide (CHO) yielded a material with an increased *T<sub>g</sub>* of 70 °C at a somewhat reduced linkage selectivity compared to the monosubstituted epoxides. This is in line with findings by Werner and Komber et al. who observed reduced linkage selectivity in the parent CS<sub>2</sub>/CHO ROCOP.<sup>[35]</sup> Glycidyl ethers can also be terpolymerised with almost quantitative linkage selectivity and excellent OSO-*alt*-S<sub>x</sub> (head-to-head-*alt*-tail-to-tail) selectivity, yielding materials with a *T<sub>g</sub>* below room temperature (–12 °C) for the ethyl derivative EGE and above room temperature (+30 °C) for the phenyl derivative PGE. Lastly, terpolymerisation of styrene oxide (SO), which is an intrinsically challenging epoxide in ROCOP catalysis, could also be achieved although maximum conversion and molar mass were reduced (Table 2) resulting in a *T<sub>g</sub>* of 12 °C. Multinuclear NMR analysis revealed a regio-random microstructure as opposed to a head-to-head-*alt*-tail-to-tail sequence although OSO links could also be identified.<sup>[46]</sup> It should be noted that the *T<sub>g</sub>*'s should be considered with caution due to the differences in molecular weight, regioselectivity, linkage errors and length of polysulfide chain. In fact, surveying different PO terpolymers from Table 1 by DSC (see ESI Figure S20) shows that the *T<sub>g</sub>* can vary by 20 °C implying that further investigations



**Figure 3.** Epoxides explored for ROTERP with S<sub>8</sub> and CS<sub>2</sub>.

**Table 2:** Reaction conditions and molecular characteristics of the polymers obtained by ROTERP of various epoxides with S<sub>8</sub> and CS<sub>2</sub>.

| Epoxide | t   | Conv. [%] <sup>a</sup> | Polymer [%] <sup>b</sup> | -SS- [%] <sup>c</sup> | Linkage select. [%] <sup>d</sup> | <i>M<sub>w</sub></i> [kDa] <sup>e</sup> | <i>D<sub>p</sub></i> | <i>T<sub>g</sub></i> [°C] <sup>f</sup> | <i>T<sub>g,5%</sub></i> [°C] |
|---------|-----|------------------------|--------------------------|-----------------------|----------------------------------|-----------------------------------------|----------------------|----------------------------------------|------------------------------|
| PO      | 3 h | 96                     | 84                       | 70                    | 98                               | 20                                      | 1.7                  | 4                                      | 160                          |
| BO      | 3 w | 60                     | 90                       | 67                    | 97                               | 16                                      | 1.7                  | 19                                     | 160                          |
| DO      | 2 d | 63                     | 75                       | 70                    | 96                               | 12                                      | 1.4                  | –12                                    | 170                          |
| CHO     | 2 d | 47                     | 66                       | 42                    | 82                               | 15                                      | 1.7                  | 70                                     | 150                          |
| EGE     | 2 d | 95                     | 73                       | 54                    | 99                               | 19                                      | 1.6                  | –13                                    | 175                          |
| PGE     | 2 d | 62                     | 68                       | 50                    | 98                               | 9                                       | 1.4                  | 30                                     | 180                          |
| SO      | 1 w | 14                     | 52                       | n.d.                  | n.d. <sup>f</sup>                | 4                                       | 1.3                  | 13                                     | 150                          |

ROTERP conducted at 30 °C with 1 eq. LiOBn; 250 eq. Epoxide; 250 eq. CS<sub>2</sub>; 125 eq. <sup>1</sup>/<sub>8</sub> S<sub>8</sub>. <sup>a</sup> Relative peak integrals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tertiary CHMe resonances due to polymer and cyclic dithiocarbonate versus unconsumed epoxide. <sup>b</sup> Relative integrals in the normalised <sup>1</sup>H NMR spectrum of tertiary CHMe resonances due to polymer versus cyclic dithiocarbonate. <sup>c</sup> Relative integral in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tertiary CHMe resonances part of repeat units comprising –S–S– versus –S–S<sub>y</sub>– links. <sup>d</sup> Relative integrals in the normalised <sup>1</sup>H NMR spectrum of tertiary CHMe resonances due to OSO and S<sub>x</sub> versus other links. <sup>e</sup> Determined by GPC (gel permeation chromatography) measurements conducted in THF with a narrow polystyrene standard. <sup>f</sup> Linkage selectivity could not be determined due to complexity of the spectrum. <sup>g</sup> Determined by DSC from second heating curve at 10 K/min.



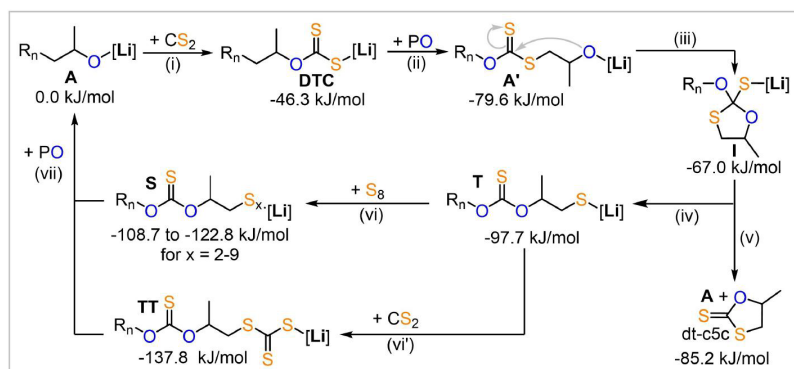
are required to make definite statements on structure–property relationships. In terms of  $T_{d,5\%}$  these range between 150 and 180 °C as presented in Table 2. Again, the  $T_{d,5\%}$  vary by ca. 10 °C for PO terpolymers of different composition from Table 1 (see ESI Figure S21) limiting statements about structure–property relationships at the current stage.

Next, we tried to elucidate the polymerisation mechanism with quantum chemical studies to understand the origin of sequence selectivity as well as how sulfur centres get distributed along the polymer chain. For all DFT-calculations presented in the following it was tried to account for all types of more probable coordination modes around Li (including dinuclear species) and to explore conformational spaces of each species as exhaustive as possible, for details see ESI Section S8. In the following, for each intermediate of the catalytic cycle only the species with the lowest Gibbs free energy is discussed. Figure 4(a) shows a mechanistic hypothesis which makes sense from a thermodynamic point of view as Gibbs free energy decreases along any polymer growth step. Our mechanistic hypothesis starts from a lithium alkoxide **A** that serves as the energetic reference at 0.0 kJ/mol. **A** generates a lithium dithiocarbonate **DTC** by addition to CS<sub>2</sub> in step (i). PO ring opening by **DTC** in step (ii) leads to a lithium alkoxide **A'** that rearranges via an intermediate **I** in step (iii) into a lithium thiolate **T** in step (iv), analogous to reports by Komber and Werner et al.<sup>[35]</sup> Elimination of alkoxide **A** from the intermediate **I** in step (v) instead of O/S exchange yields the cyclic dithiocarbonate dt-c5c by-product. In the next step (vi) or (vi'), S<sub>8</sub> or CS<sub>2</sub> is inserted to form a lithium oligosulfide **S** in (vi) or a lithium trithiocarbonate **TT** in (vi'), whereas the latter case appears to occur substantially less given the observed sequence selectivity. As it is well established that S<sub>8</sub> forms a distribution of anionic oligosulfides upon ring opening, **S** likely corresponds to a distribution of lithium oligosulfides R-S<sub>x</sub>-Li with a maximum clearly below the initial  $x=9$ .<sup>[47]</sup> Formation of longer polysulfides is thermodynamically unfeasible below the floor temperature of elemental sulfur, as previously shown by Penczek and

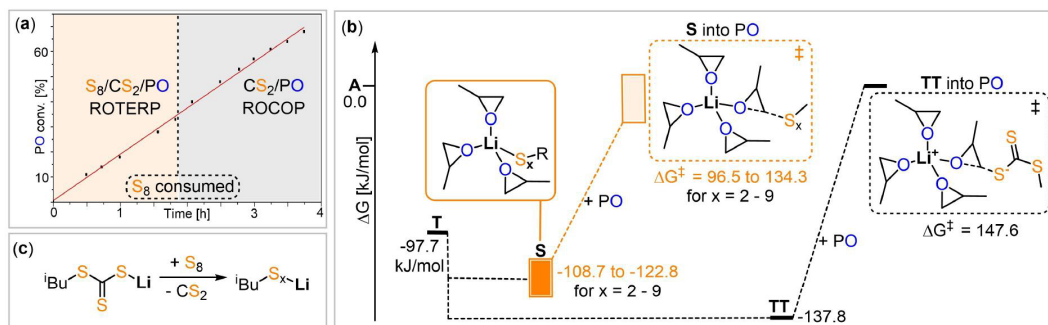
Duda.<sup>[29]</sup> Thereafter PO insertion in (vii) regenerates the alkoxide **A** to close the cycle.

As PO or S<sub>8</sub> are not expected to react with the alkoxides **A** or **A'** for kinetic (PO) or thermodynamic (S<sub>8</sub>) reasons and as PO ring opening by lithium thiolates **T** must be kinetically disfavoured compared to an addition to CS<sub>2</sub> (nucleophilic substitution vs addition to a carbonyl centre), the question remains what causes sequence selectivity towards an S<sub>8</sub> incorporation over trithiocarbonate formation in (vi).<sup>[48]</sup> Elucidating the reaction kinetics, we followed the PO consumption (ESI Figure S22, Figure 5(a)) of a ROTERP by <sup>1</sup>H NMR at an initial loading of LiOBn:PO:CS<sub>2</sub>:S = 1:500:500:70. This revealed a 0<sup>th</sup> order dependence of the ROTERP with respect to S<sub>8</sub>. After the completion of ROTERP the reaction switches to CS<sub>2</sub>/PO ROCOP which is maintaining the rate of PO consumption. This indicates that CS<sub>2</sub>/PO ROCOP and S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP likely have the same rate-determining step which supposedly is (ii) as epoxide ring-opening typically represents the slowest reaction step(s) in such reactions, as mentioned before.<sup>[48]</sup> Furthermore, from these results, one would assume that S<sub>8</sub> insertion by **T** is much faster than the other reaction steps.

Considering the thermodynamics of S<sub>8</sub> versus CS<sub>2</sub> insertion by **T** (Figure 5(b)), DFT calculations show that the latter is more favourable from a thermodynamic point of view. Assuming an also rather high epoxide ring opening barrier for (vi) and (vi'), this would imply that there is an equilibration between **S** and **TT** (with significant amounts of **TT** in the mixture) and the observed sequence selectivity must have kinetic reasons. This is in fact confirmed by computations of the propagation barriers revealing lower activation energies for the lithium oligosulfide **S** inserting into PO ( $\Delta G^\ddagger = 96.5$  to 134.2 kJ/mol depending on the S<sub>x</sub> length) than for the trithiocarbonate **TT** ( $\Delta G^\ddagger = 147.6$  kJ/mol). In other words, lithium oligosulfide **S** are better nucleophiles than lithium trithiocarbonates **TT**. It is worth mentioning that the most preferred transition states for both (vi) and (vi') are zwitterionic in the sense that they occur via chain-end dissociation away from the lithium centre and subsequent attack of the CH<sub>2</sub> group of PO in an almost 180°



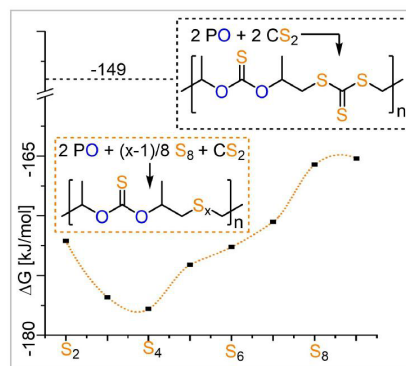
**Figure 4.** (a) Mechanistic hypothesis for S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP. Gibbs free energies associated with the respective intermediates below the labels was assessed from a series of structures involving different Li coordination modi which are outlined in the Supporting Information (ESI Section S8).



**Figure 5.** (a) Kinetic reaction traces of S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP switching into CS<sub>2</sub>/PO ROCOP after S<sub>8</sub> consumption. (b) Computed PO ring opening barriers by **S** and **TT**. (c) Small molecule model reaction substantiating the reversibility of CS<sub>2</sub> insertion.

angle with respect to the broken bond, which is the preferred constellation to the C-atom in S<sub>N</sub>2 reactions. A mechanistic alternative would be a bimetallic transition state; this was also tried and leads to the same trend in Gibbs free activation energies for the reactions of **TT** versus **S** (see ESI Section S8) but is generally disfavoured with respect to the zwitterionic pathways. If propagation from **S** is kinetically favoured but formation of **TT** is thermodynamically favoured, CS<sub>2</sub> insertion must be reversible so that **TT** can transform into **S** and the kinetically more viable pathway can be accessed to form the observed Poly(OSO-*alt*-S<sub>x</sub>) sequence. Seeking to validate this experimentally we undertook a small molecule model reaction (Figure 5(c)) in which we exposed a lithium thiolate, t-BuSLi, first to CS<sub>2</sub> in d<sub>8</sub>-THF to quantitatively form the corresponding lithium trithiocarbonate t-BuS(C=S)SLi and thereafter added elemental sulfur. Indeed, <sup>1</sup>H NMR analysis of the reaction mixture (ESI Figure S27) reveals the partial disappearance of the signals of t-BuS(C=S)SLi and the appearance of new signals which can be assigned to S<sub>8</sub> insertion products by comparison to the stand-alone reaction between t-BuSLi and S<sub>8</sub>. This unambiguously proves that CS<sub>2</sub> insertion is reversible and that **TT** can transform into **S** to access the kinetically favourable propagation pathway. Furthermore we infer that this effective promotion of propagation due to the presence of S<sub>8</sub> in reaction mixtures effectively limits the lifetime of **T** which in principle can also produce dt-c5c by-products by reversion of step (iv) and this helps to explain the improvement in polymer selectivity of S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP compared to CS<sub>2</sub>/PO ROCOP.

In terms of overall polymerisation thermodynamics, computational assessment of the Gibbs free energy of formation of possible repeat units from CS<sub>2</sub>/PO versus S<sub>8</sub>/CS<sub>2</sub>/PO is shown in Figure 6. Here formation of the poly(OSO-*alt*-S<sub>x</sub>) sequence from S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP is more exergonic than the poly(OSO-*alt*-SSS) sequence from CS<sub>2</sub>/PO ROCOP irrespective of the length of S<sub>x</sub>. Interestingly there is a shallow minimum for sequences with tetrasulfide S<sub>4</sub> links which could also be experimentally identified as pronounced links in the polymers by Raman spectroscopy (see above). This shows that S<sub>8</sub>/CS<sub>2</sub>/PO

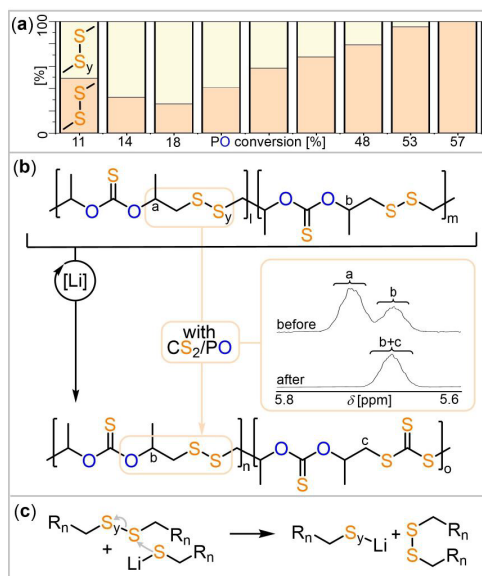


**Figure 6.** Gibbs free energy of formation for links from CS<sub>2</sub>/PO ROCOP versus S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP with different S<sub>x</sub> length.

ROTERP is also thermodynamically favoured to occur over CS<sub>2</sub>/PO ROCOP.

A final open question concerns whether the R-S<sub>x</sub>-R links remain reactive after formation in (vii) which is a likely hypothesis due to the chemical similarity of neutral R-S<sub>x</sub>-R to S<sub>8</sub>. As we can spectroscopically identify the disulfide R-S-S-R and oligosulfide R-S-S<sub>y</sub>-R links, we used these as an experimental handle. <sup>1</sup>H NMR aliquot analysis of a ROTERP at a loading of LiOBn:PO:CS<sub>2</sub>:S = 1:500:500:70 revealed that the proportion of R-S-S-R and R-S-S<sub>y</sub>-R links changes throughout polymerisation. As can be seen in Figure 7(a), R-S-S<sub>y</sub>-R polysulfide links were formed at an early stage of the polymerisation and these slowly declined at above 18 % PO conversion until they could no longer be observed at 57 % PO conversion. This implies that the polysulfide R-S-S<sub>y</sub>-R links remain reactive and undergo sulfur redistribution. Seeking to confirm this hypothesis we added a preformed S<sub>8</sub>/CS<sub>2</sub>/PO terpolymer (Table 1 run #2) containing R-S-S<sub>y</sub>-R links to a ROCOP of CS<sub>2</sub>/PO. As thiolate intermediates are formed in ROCOP, these must react with the R-S-S<sub>y</sub>-R links to eventually reshuffle the sulfur centres into new disulfide R-S-S-R links—which is indeed what we observed, see Figure 6(b). Furthermore, we recognised a slight increase of M<sub>w</sub> from 23 to 35 kDa (ESI





**Figure 7.** (a) Evolution of di and polysulfide link distribution during ROTERP of S<sub>8</sub>/CS<sub>2</sub>/PO at 1 eq. LiOBn : 500 eq. PO: 500 eq. CS<sub>2</sub>: 70 eq S. (b) Transformation of R-S-Sy-R links in a ROTERP polymer into R-S-Sy-R links when CS<sub>2</sub>/PO ROCOP occurs via in situ formed thiolates. (c) Mechanistic hypothesis concerning the reshuffling of sulfur centres exemplified with the intermolecular formation of R-S-Sy-R from R-S-Sy-R links.

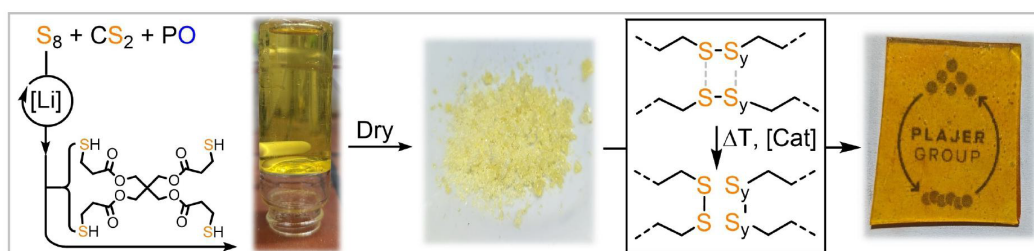
Figure S28), suggesting that the reshuffling process reactivates the ROTERP chains to insert further monomer. We therefore suggest a reshuffling pathway as shown in Figure 7(c). Here R-S-Sy-R links are susceptible to nucleophilic attack by thiolate intermediates, alike reaction step (vi) in Figure 4, in which now R-S-Sy-R links are cleaved in place of S<sub>8</sub>.

Having learned that the polysulfide R-S-Sy-R links remain reactive after formation, we were intrigued to see if these could serve as sites for the crosslinking of multiple chains. Inspired by the precedence concerning base-mediated thiol-disulfide exchange,<sup>[49]</sup> we attempted crosslinking of the copolymers in situ after ROTERP by addition of a tetrafunctional thiol (pentaerythritol tetrakis(3-mercaptopropionate), ca. 25 wt % versus polymer) in air. We assumed

that the anionic lithium chain ends could act as a base to catalyse the thiol-disulfide exchange reaction. Indeed, while the diluted ROTERP reaction mixture (Table 1 run #14) at full PO consumption was freely flowing, it turned into a stable network or gel, which resided at the top of the reaction vial after inversion, upon addition of the crosslinker (Figure 8). Interestingly, during crosslinking, we recognised the evolution of a gas, which could be identified as carbonyl sulfide (IR  $\tilde{\nu}$  (COS)=2060 cm<sup>-1</sup>, ESI Figure S59); a mechanistic hypothesis of the crosslinking process is shown in the Supporting Information (Scheme S6). The Raman spectrum of the crosslinked material clearly shows the presence of polysulfide R-S<sub>x</sub>-R groups ( $\tilde{\nu}$ =350 - 550 cm<sup>-1</sup>) but no SH functionalities ( $\tilde{\nu}$ =2500–2600 cm<sup>-1</sup>) (ESI Figure S66–67). We infer that this is due oxidative coupling of thiols to R-S-S-R disulfides as part of the crosslinking process in air.

Drying of the gel yielded a rubbery material ( $T_g$  = -2 °C) with a degradation profile that shows a similar onset of degradation ( $T_{d,5\%}$  ca. 160 °C) as the linear parent polymer but some higher thermal stability above 200 °C (ESI Figure S63). Comparative rheological analysis of linear and crosslinked polymer shows an increasing gap ( $G' - G''$  with  $G' > G''$ ) between the elastic ( $G'$ ) and viscous ( $G''$ ) component, further substantiating successful crosslinking (ESI Figure S64). Importantly, the rheological profile of the material in the amplitude sweep test was affected by the amount of tetra-thiol crosslinker, which suggests some tunability of the mechanical properties of our materials (ESI Figure S65). The crosslinked material is yellow and optically transparent (see below), shows a good refractive index (RI = 1.63) and an Abbe number of 30, potentially rendering it interesting for optical applications.<sup>[13]</sup> Furthermore surfaces can be easily covered with it via dip-coating (ESI Figure S68).

Exposing the dried gel materials to DCM (a good solvent for the parent polymer) resulted in swelling but not dissolution, as expected. Determination of the sol-gel fraction suggested that the gel contained 85 wt % of the initial material while the soluble portion contained the dt-c5c by-product from the ROTERP stage (ESI Figure S69). Although covalent network structures (usually) impede solution processing, we thought that here thermal reprocessing could be feasible due to the dynamic nature of the polysulfide bonds. Indeed, hot-pressing of the granulated material could be achieved at 80 °C to yield a self-standing



**Figure 8.** Gelation of diluted ROTERP reaction mixture with tetrafunctional thiol and thermal reprocessing of dried network via polysulfide reaction.

and homogeneous film (see Figure 7). Adding an extra Lewis base such as  $\text{NEt}_3$  to the network promoted faster reprocessing at a given temperature and pressure (ESI Figure S60).<sup>[50,51]</sup> The possible thermal reprocessing further implies that these disulfide-crosslinked materials should be degradable by similar exchange reactions with small molecules. Accordingly, treatment of a crosslinked sample, which remained stable in DCM for weeks, with  $\text{tBuSH}$  and  $\text{NEt}_3$  caused break down of the network within minutes (see supplementary video in the ESI), a property which is for example also useful in the context of thiol sensing.<sup>[52]</sup>

## Conclusions

In conclusion, we introduced a ring-opening terpolymerisation (ROTERP) process to produce sulfur-containing polymer materials from commercially relevant epoxides, carbon disulfide and elemental sulfur waste. The process requires trace amounts of a cheap lithium alkoxide catalyst and occurs without external heating. Mechanistic investigations showed that  $\text{S}_8$  insertion leads to more facile propagation thereafter which enables the sequence selectivity. As the  $\text{R-S-S-R}$  links in the polymer remain susceptible towards nucleophilic attack by thiolate intermediates one can cross-link the chains in situ with multifunctional thiols producing reprocessable and degradable networks. Our report demonstrates how mechanistic understanding in alkali metal catalysis can turn waste  $\text{S}_8$  with commercially viable comonomers into complex polymers with tunable properties, reprocessability and degradability.

## Acknowledgements

The VCI is acknowledged for a Liebig Fellowship for A. J. P. and a Ph.D. scholarship for C.G. Dr. Patrick Pröhm is thanked for valuable consultation. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

There are no conflicts of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** sulfur waste · ring-opening polymerisation · degradable polymers · alkali metal catalysis

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Manuscript received: December 22, 2023

Accepted manuscript online: February 29, 2024

Version of record online: March 18, 2024



## Supporting Information

### **Ring-Opening Terpolymerisation of Elemental Sulfur Waste with Propylene Oxide and Carbon Disulfide via Lithium Catalysis**

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**Supporting information**

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## Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are referenced to the residual proton resonance of the deuterated solvents.  $\text{CS}_2$  and Epoxides were dried over calcium hydride at room temperature for 3 days followed by distillation under argon atmosphere.  $\text{BnOH}$  was dried over 4Å molecular sieves and degassed. Elemental sulfur (99.99% purity) was sublimed under dynamic vacuum at 100°C. All other reagents were used as received if not stated otherwise. All reagents were stored and used inside an Ar filled glovebox.

Gas IR measures were run on a Bruker Vector 22 FTIR spectrometer (gas IR cell: 10 cm, silicon windows)

Raman spectra were recorded on a Bruker MultiRAM II equipped with a low-temperature Ge detector (1064 nm, 30-80 mW, resolution 4  $\text{cm}^{-1}$ ).

TGA data was measured using a Netzsch TG 209. DSC was measured on a Netzsch 204 F1 "Phoenix" at 10 K/min heating rate.

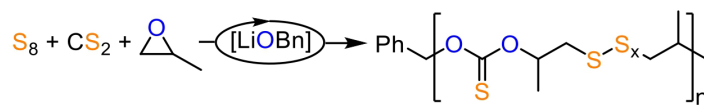
Films were prepared by hot-pressing 1.5 g of polymer between two aluminum plates covered with Teflon sheets heated with two LLG hotplates (held in place by a 15 kg weight put on top). The molecular mass and polydispersity of the polymers were determined by a Waters 1515 size exclusion chromatography (SEC) instrument equipped with two linear PLgel columns (Mixed-C) following a guard column and a differential refractive index as well as a UV detector using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 30°C and a series of narrow polystyrene standards for the calibration of the columns. Each polymer sample was dissolved in HPLC-grade THF (6 mg/mL) and filtered through a 0.10  $\mu\text{m}$  porous filter frit prior to analysis. Macro rheology was measured using a "Kinexus Pro +" rheometer (NETZSCH GmbH, Selb, Germany) at 25 °C. The films were measured using a plate–plate stainless steel geometrical setup. A 25 mm upper rotating plate diameter was used for all measurements with constant applied force of 0.1N.

## Section S2: Polymerisation procedure

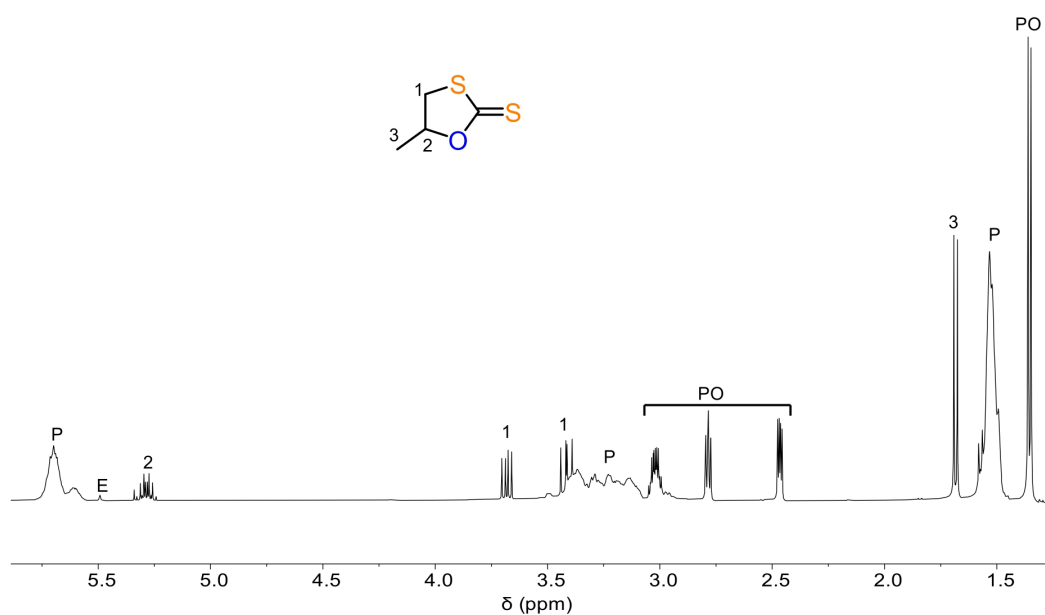
### General polymerisation protocol:

Inside an argon-filled glovebox, LiHMDS and BnOH were dissolved in the epoxide and the mixture was transferred to an oven dried vial equipped with an oven dried stirrer bar. S<sub>8</sub> and CS<sub>2</sub> were then added, and the vial was sealed with a melamine cap containing a Teflon inlay, brought outside the glovebox, and placed in a pre-heated aluminum block at the specified temperature for the specified time. To ensure reproducibility, we opted to run the polymerisation at 30°C as “room temperature” representing room temperature in the summer. At the end point of the reaction, the polymer was isolated by dilution in DCM (5 mL) and successive addition of the polymerisation mixture to 40 mL of MeOH resulting in the precipitation of the polymer which was isolated by centrifugation. This was followed by additional precipitation from DCM/Et<sub>2</sub>O for some samples. To ensure the stability of the samples during GPC measurements, Ellman’s reagent (ca. 10 mg/mL) was added to the THF solutions analysed to quench reactive thiol chain ends.<sup>[1][2]</sup> Note that if this is not done, slow depolymerisation occurs, presumably due to the high dilution during GPC measurements.

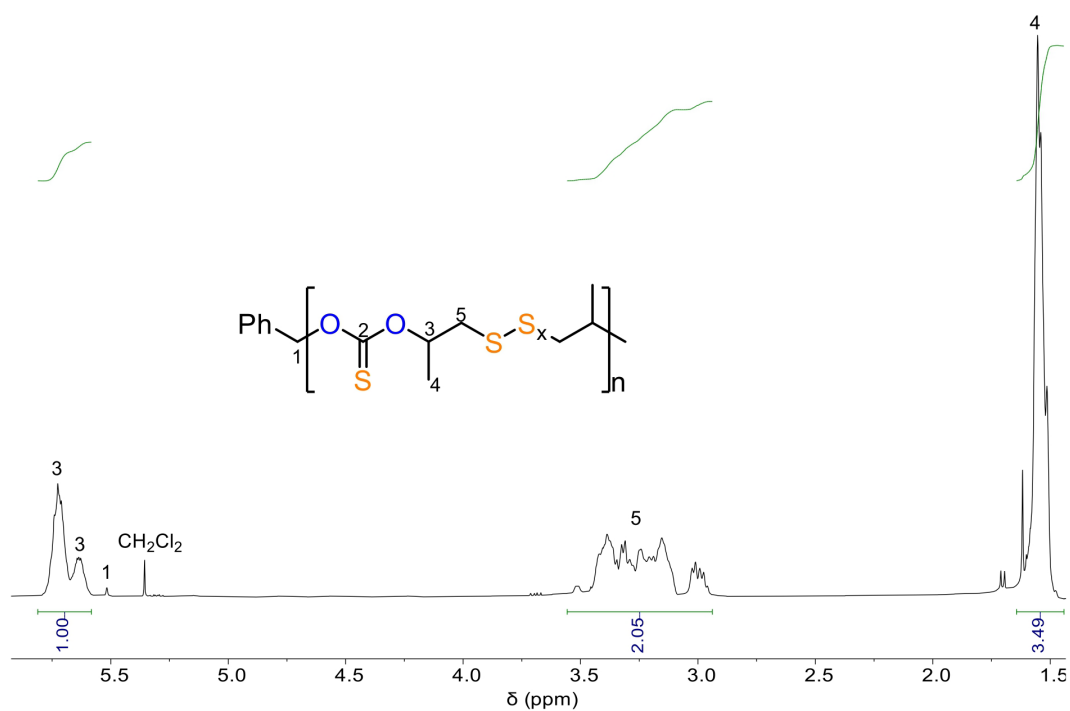
### Section S3: S<sub>8</sub>/CS<sub>2</sub>/PO ROTERP



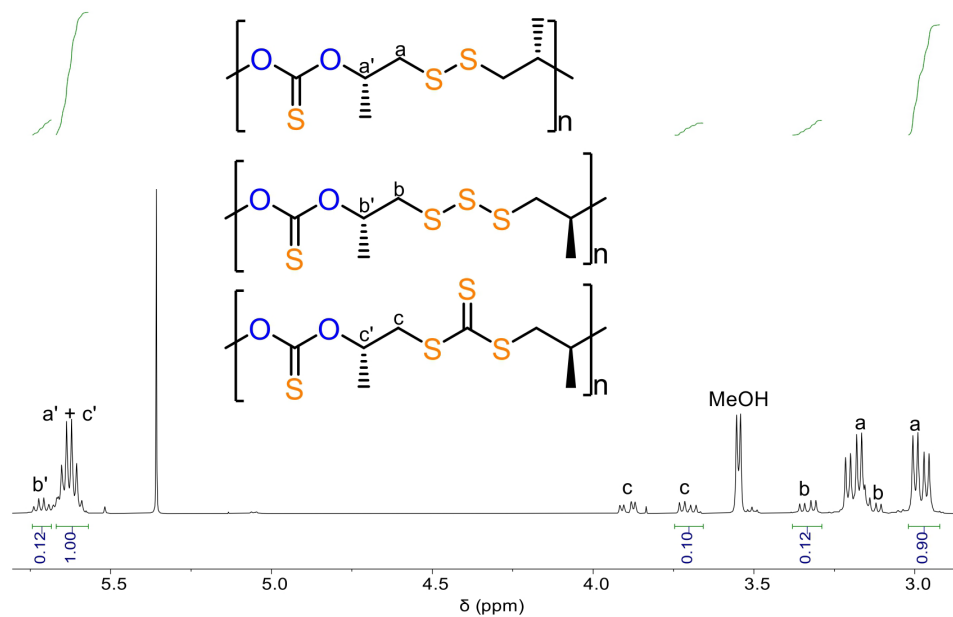
**Scheme S 1:** Synthesis of S<sub>8</sub>/CS<sub>2</sub>/PO terpolymer.



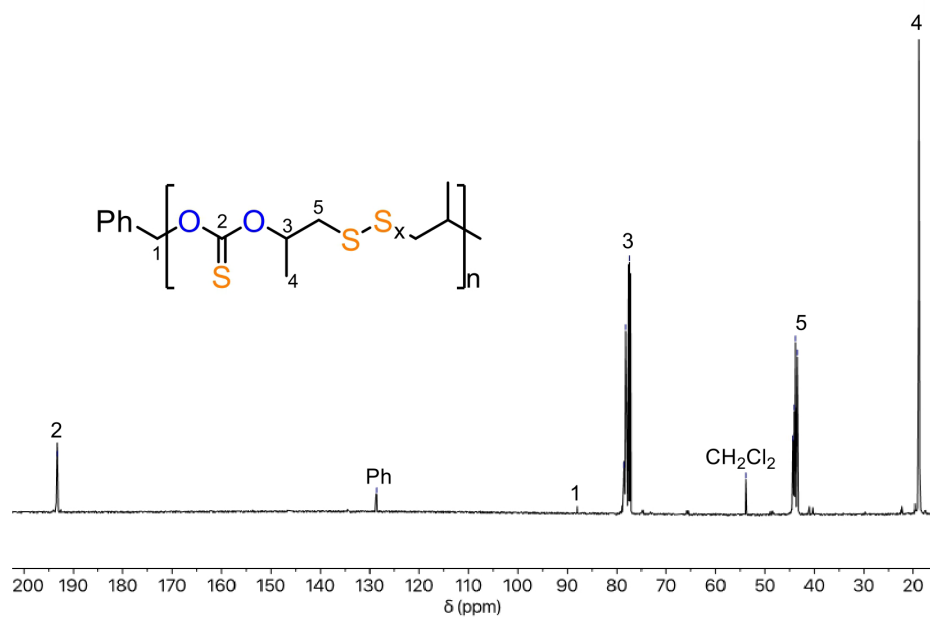
**Figure S 1:** Example <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C) spectrum of the crude reaction mixture (table 1 entry #9). P denotes resonances from polymer, PO denotes resonances from residual propylene oxide. E denotes CH<sub>2</sub> resonances from BnO initiator.



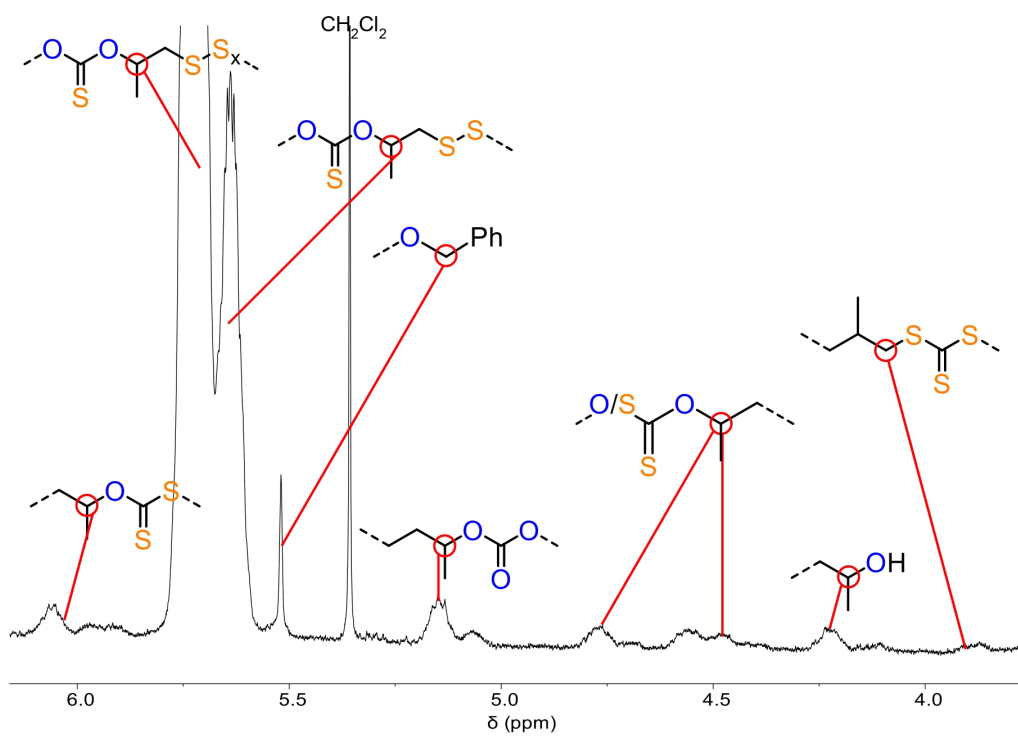
**Figure S 2:**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 entry #3.



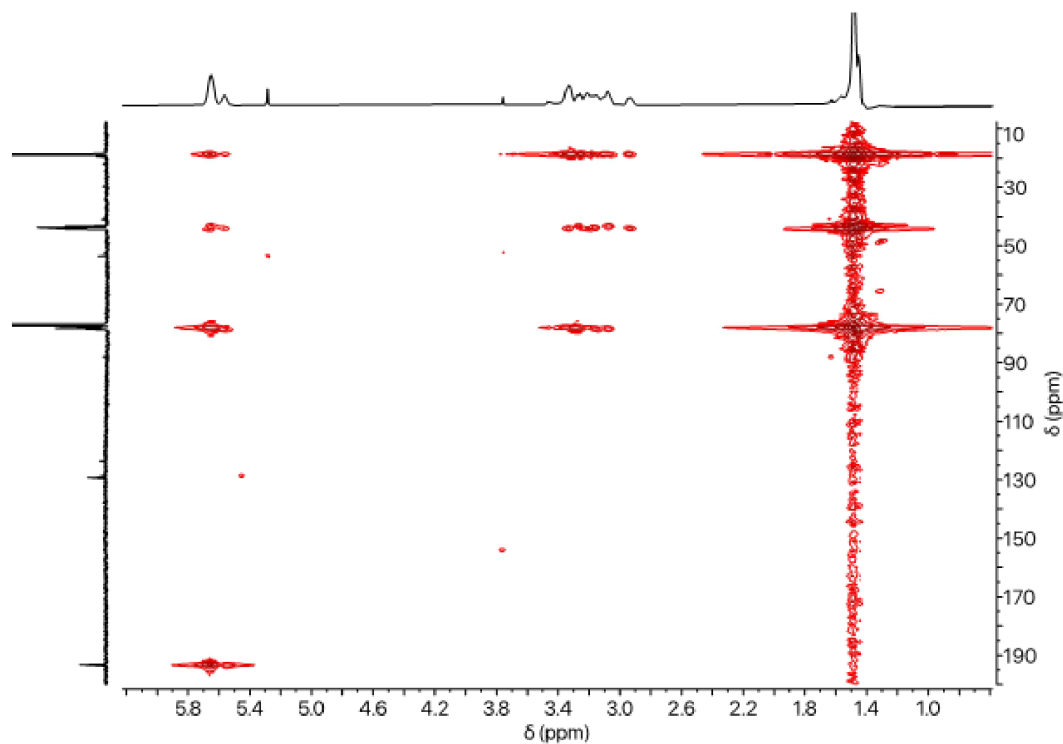
**Figure S 3:**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of a precipitated polymer from a ROTERP conducted with enantiopure R-PO in place of the racemic mixture (loading 1 eq. LiHMDS: 1 eq. BnOH: 250 eq. R-PO: 250 eq.  $\text{CS}_2$ : 90 eq. S) allowing for differentiation between  $\text{CH}_2$  groups next to disulfide and trisulfide links.



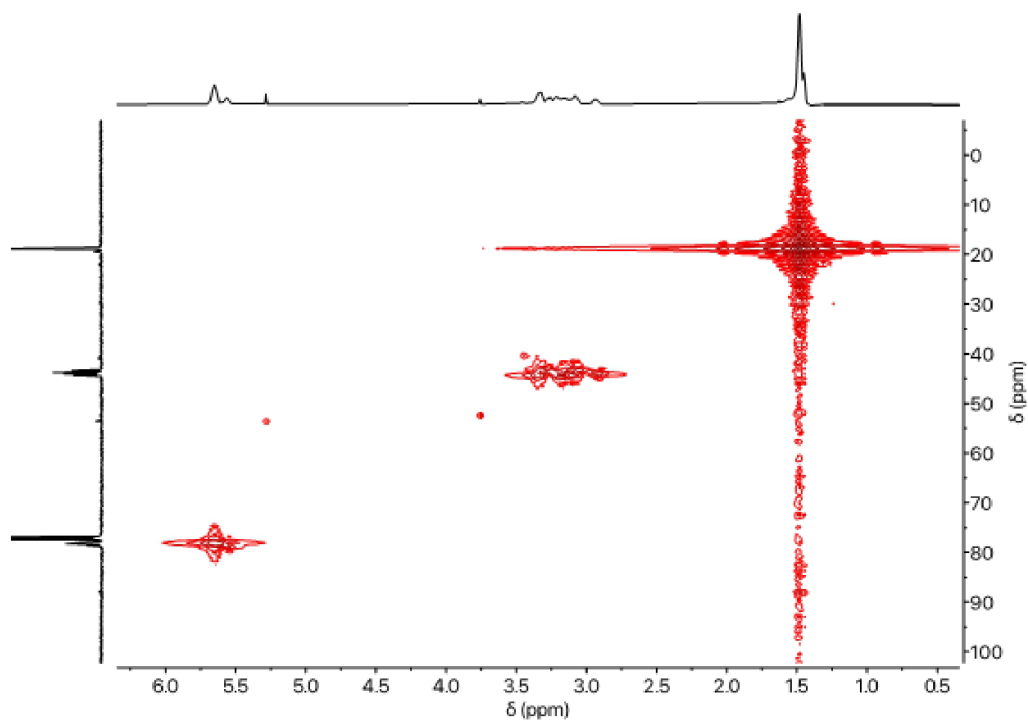
**Figure S 4:**  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 entry #3.



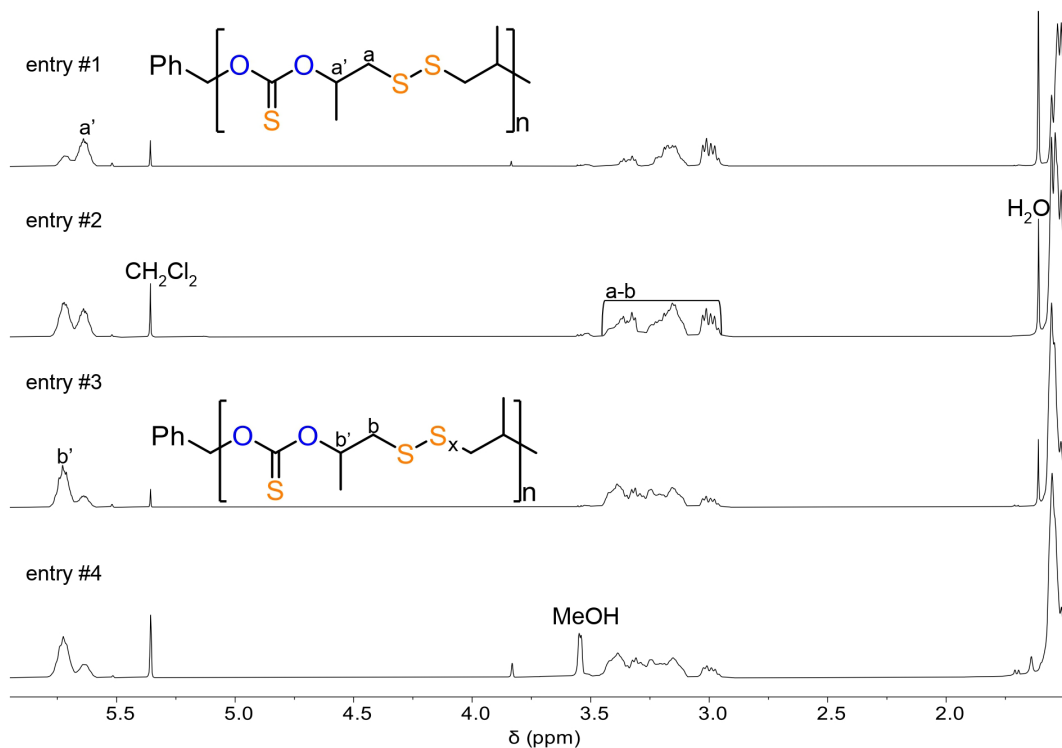
**Figure S 5:** Zoom into the  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 entry #3 depicting minor side links produced. Assignment by 2D NMR and in reference to Werner and coworkers.<sup>[3]</sup>



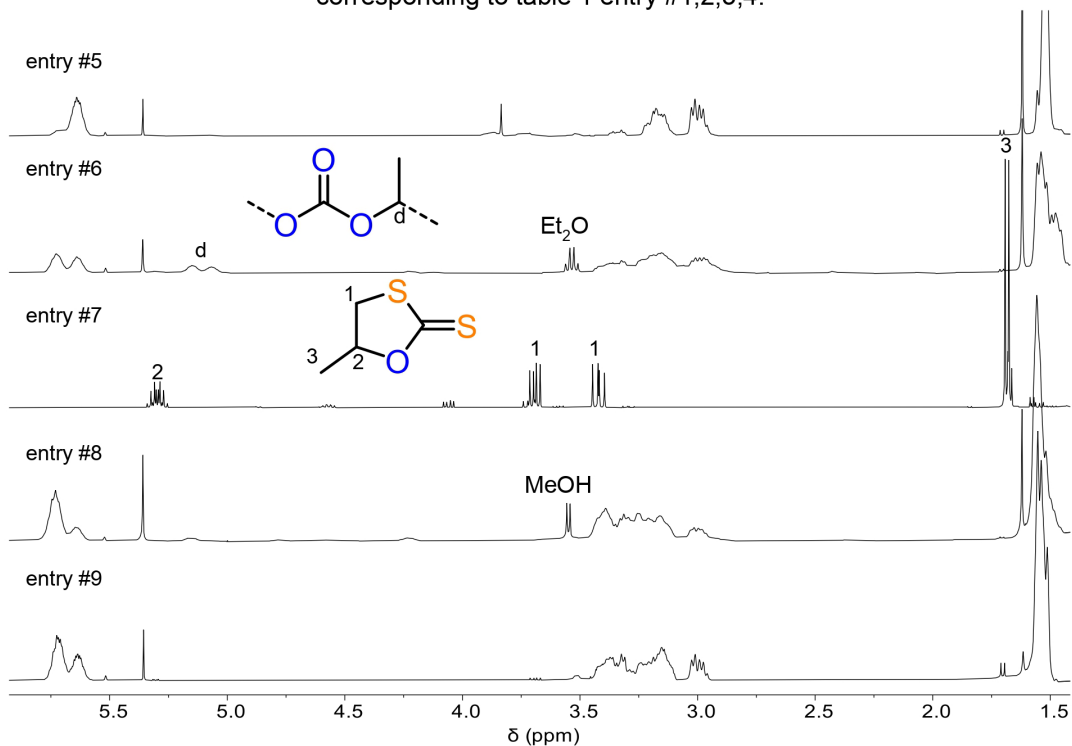
**Figure S 6:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 entry #4



**Figure S 7:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 entry #4.

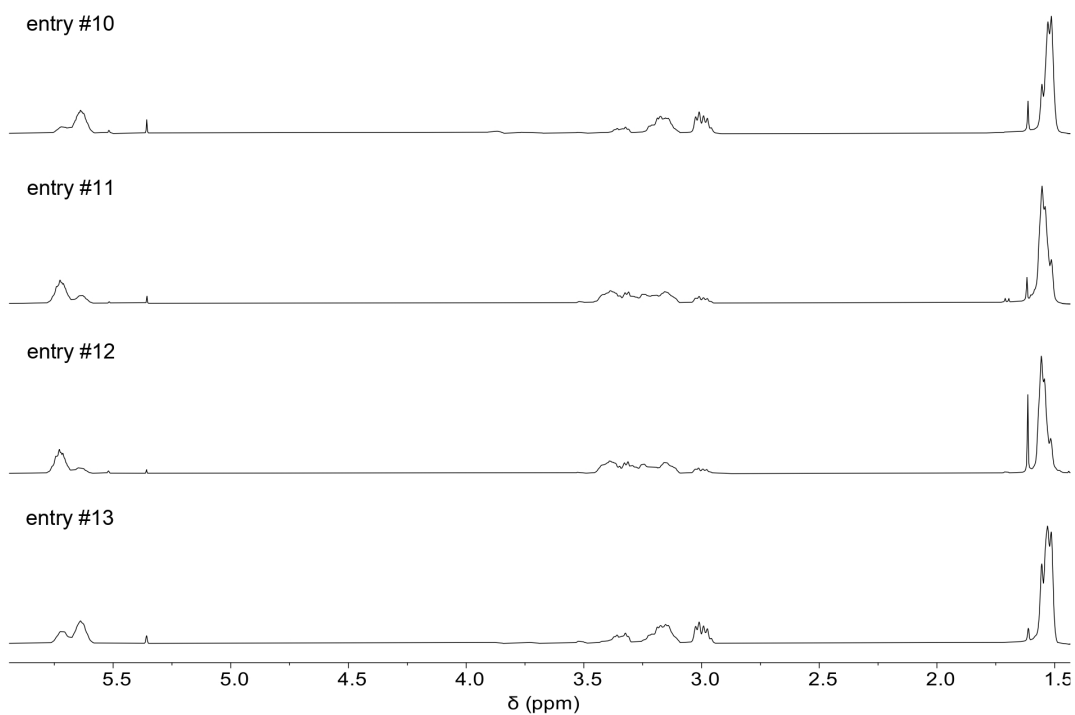


**Figure S 8:** Overlaid  $^1\text{H}$ -NMR spectra (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to table 1 entry #1,2,3,4.

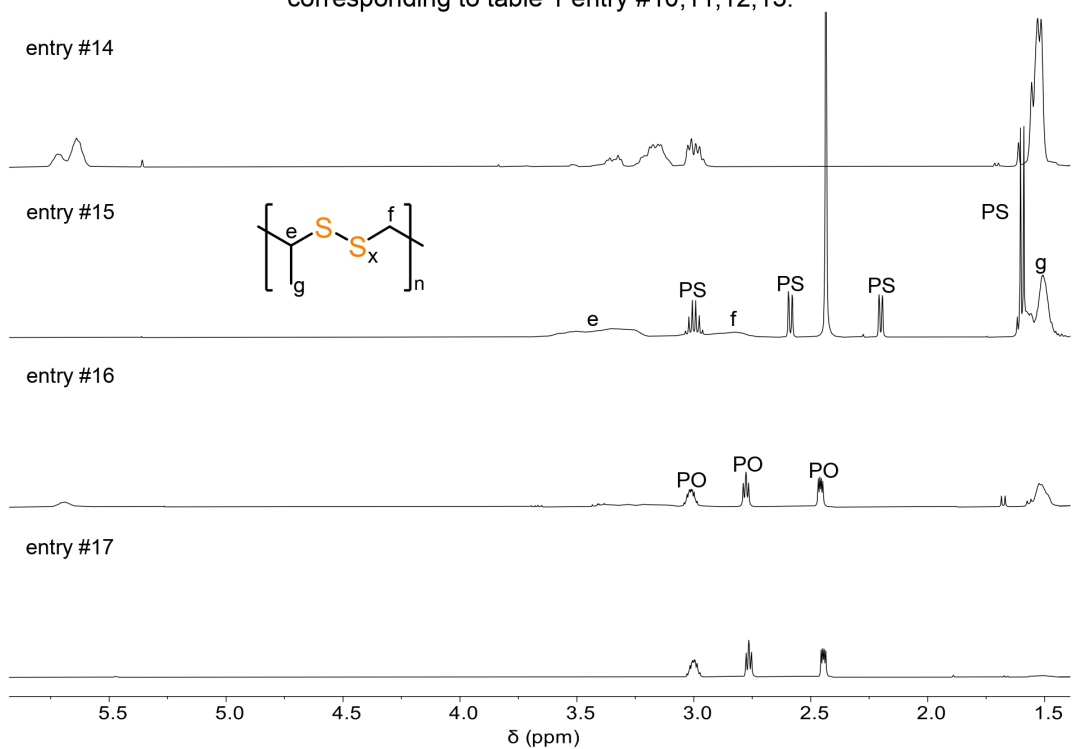


**Figure S 9:** Overlaid  $^1\text{H}$ -NMR spectra (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to table 1 entry #5,6,7 (crude mixture),8,9.

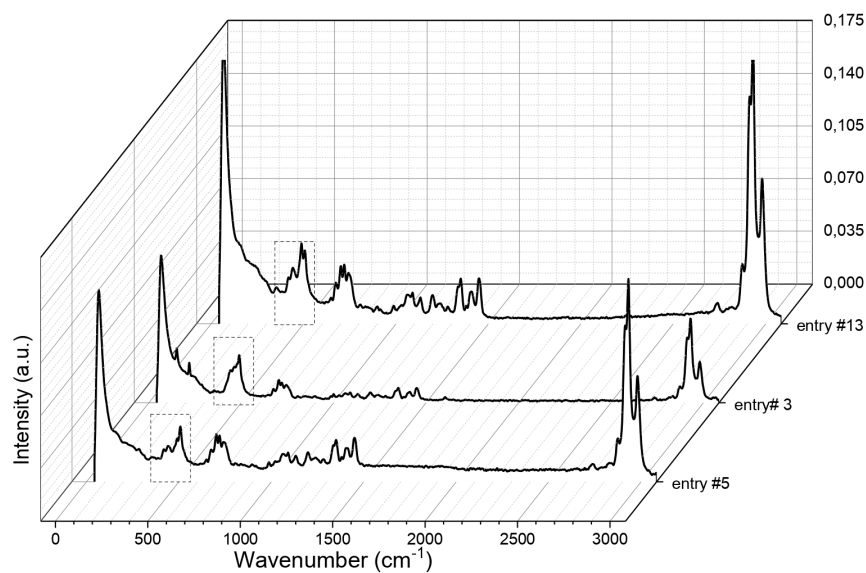




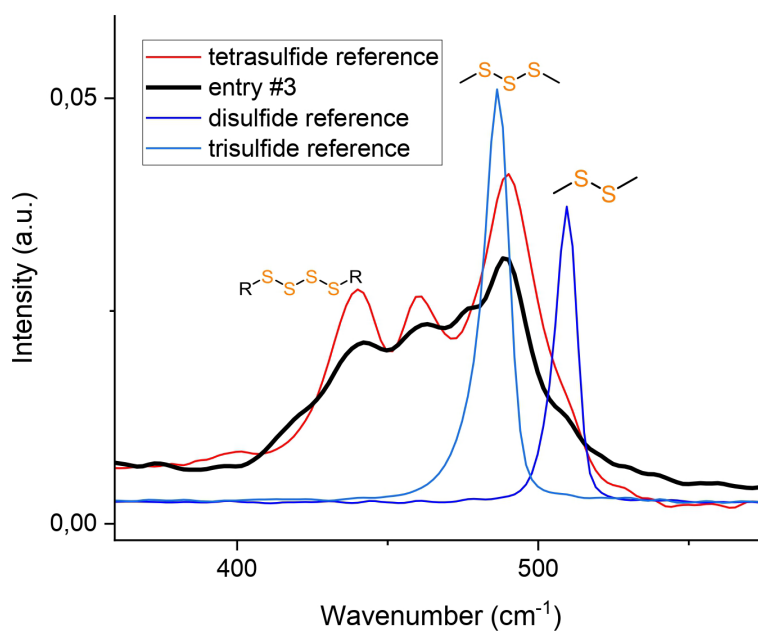
**Figure S 10:** Overlaid <sup>1</sup>H-NMR spectra (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymers corresponding to table 1 entry #10,11,12,13.



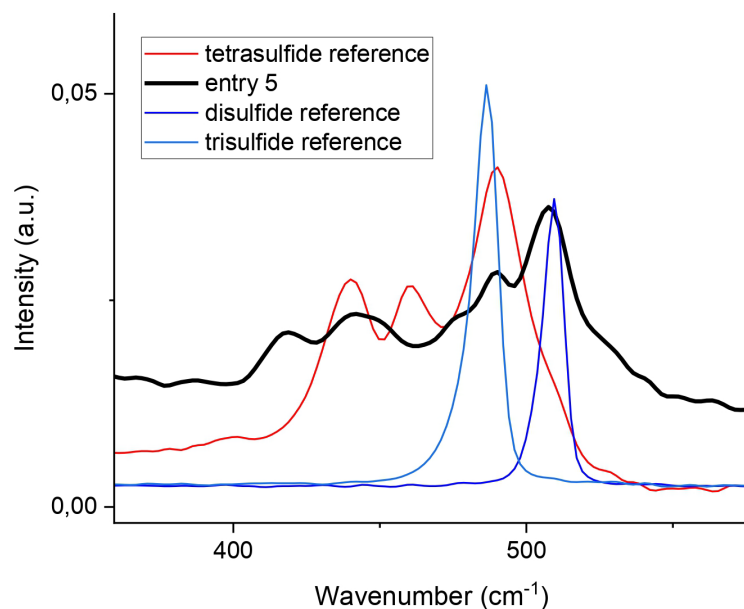
**Figure S 11:** overlaid <sup>1</sup>H-NMR spectra (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 entry #14 and the crude mixture corresponding to table 1 entry #15, 16, 17. PS/PO denotes unconsumed propylene sulfide/oxide.



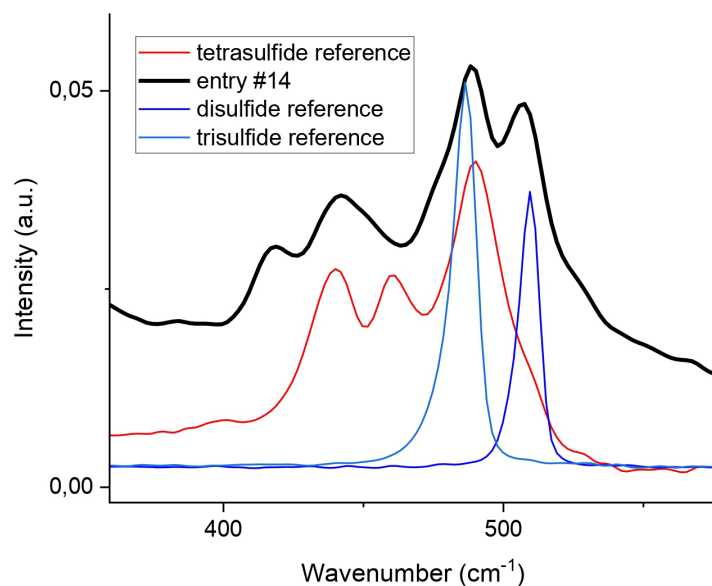
**Figure S 12:** Overlaid Raman spectra the polymers corresponding to table 1 entry #3,5,14. C-S<sub>x</sub>-C stretching vibrations highlighted by dashed box.



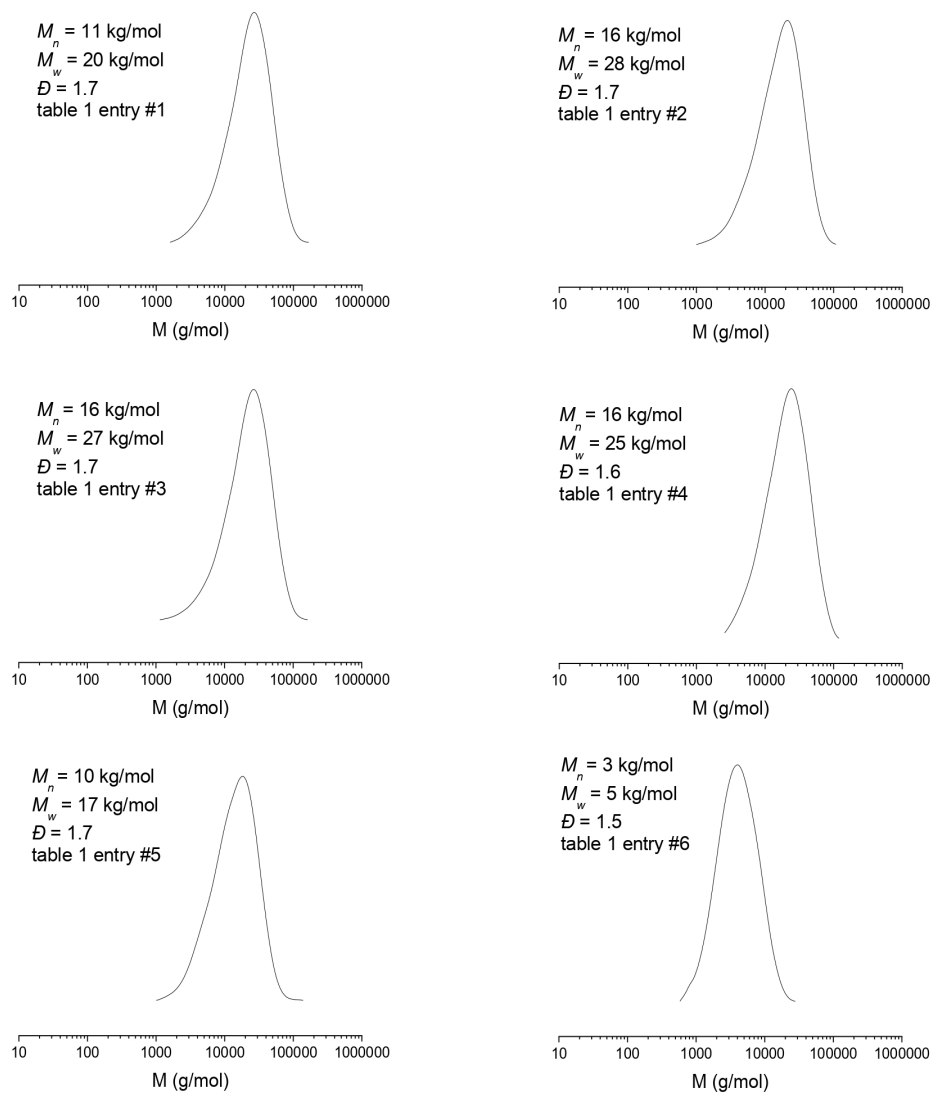
**Figure S 13:** Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectrum of the polymer corresponding to table 1 entry #3 compared with dimethyldisulfide, dimethyltrisulfide, and R<sub>2</sub>-tetrasulfide [R= -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference compounds.



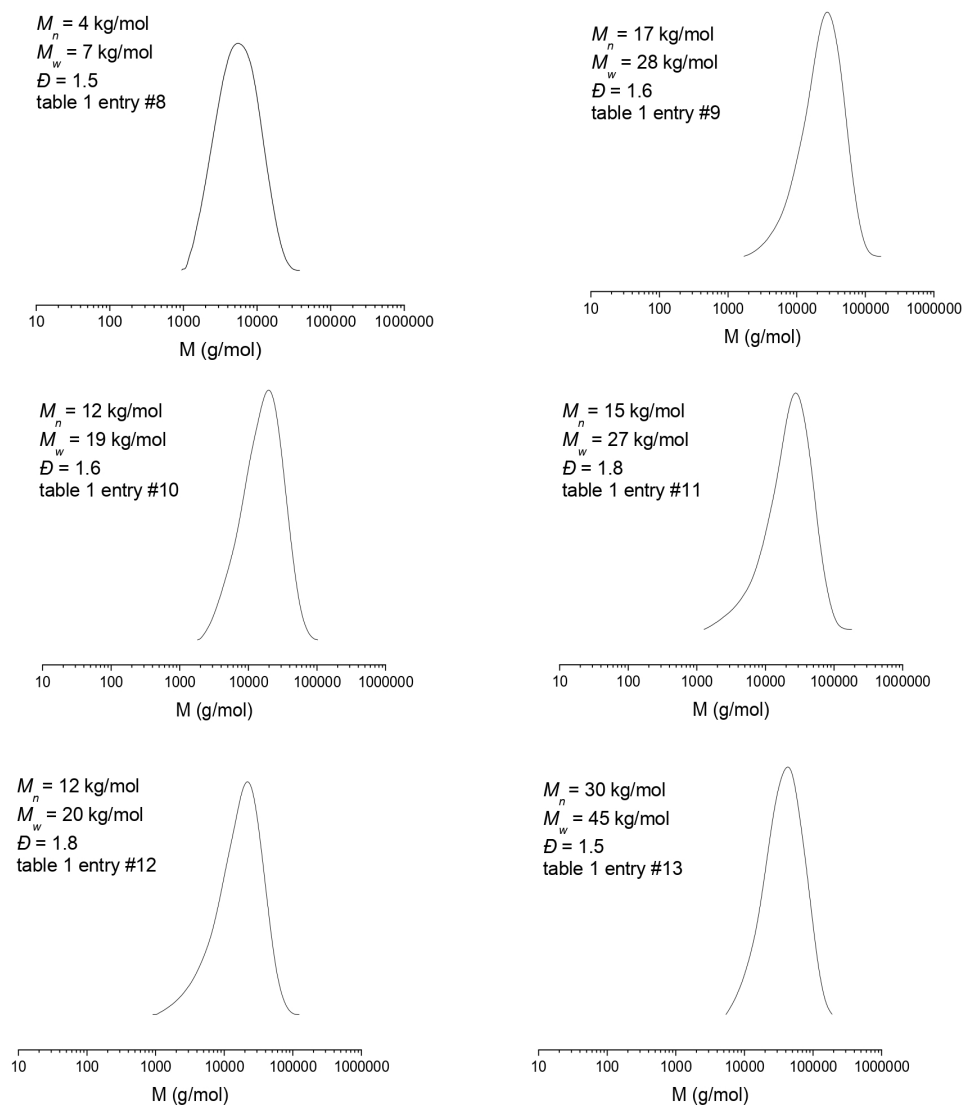
**Figure S 14:** Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectrum of the isolated polymer corresponding to table 1 entry #5, compared with dimethyldisulfide, dimethyltrisulfide, and R<sub>2</sub>-tetrasulfide [R= -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference compounds.



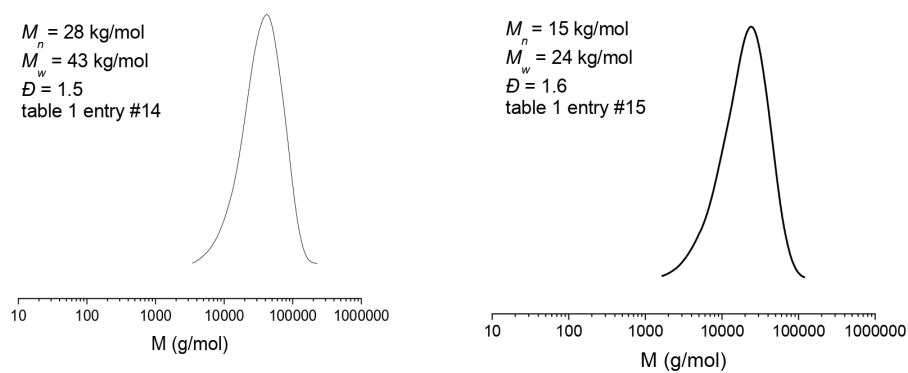
**Figure S 15:** Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectrum of the isolated polymer corresponding to table 1 entry #14, compared dimethyldisulfide, dimethyltrisulfide, and R<sub>2</sub>-tetrasulfide [R= -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference compounds.



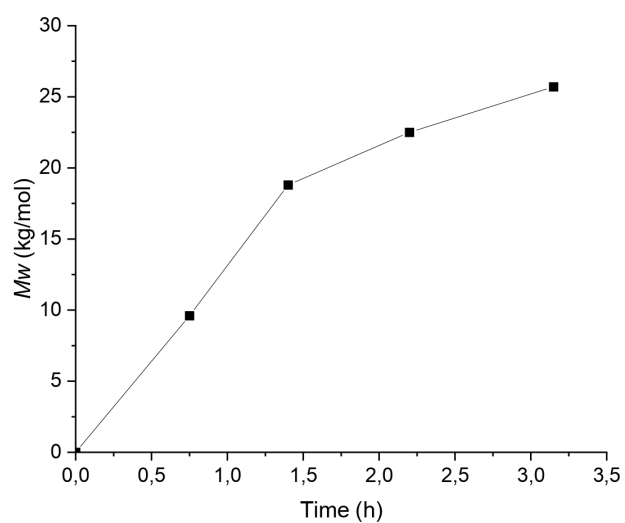
**Figure S 16:** GPC curves corresponding to table 1 entry #1,2,3,4,5,6.



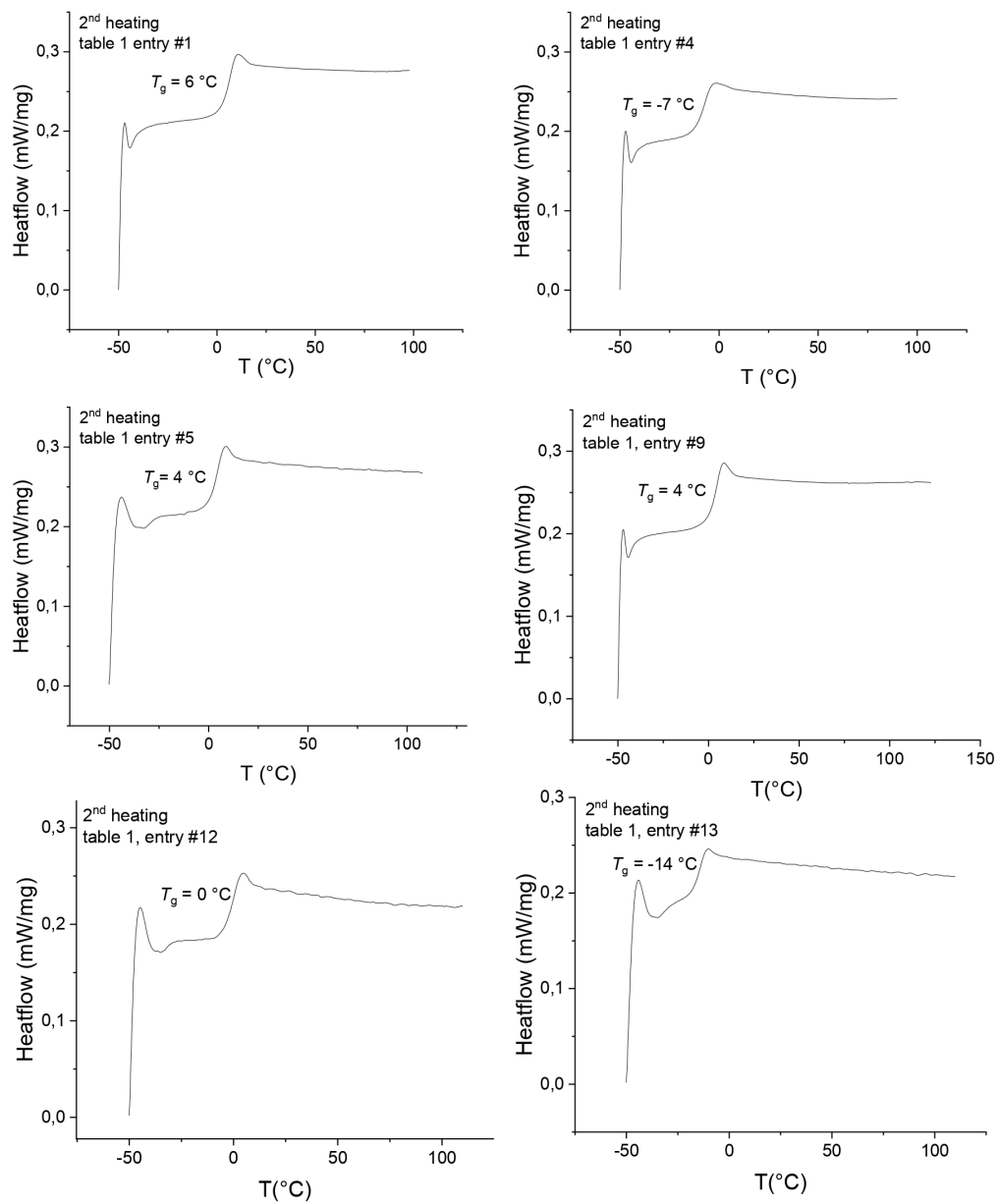
**Figure S 17:** GPC curves corresponding to table 1 entry #8,9,10,11,12,13.



**Figure S 18:** GPC curves corresponding to table 1 entry #14,15



**Figure S 19:** GPC analysis of aliquots removed at a regular time (45 min).



**Figure S 20:** DSC heating curves of the polymers corresponding to table 1 entry #1,4,5,9,12,13.

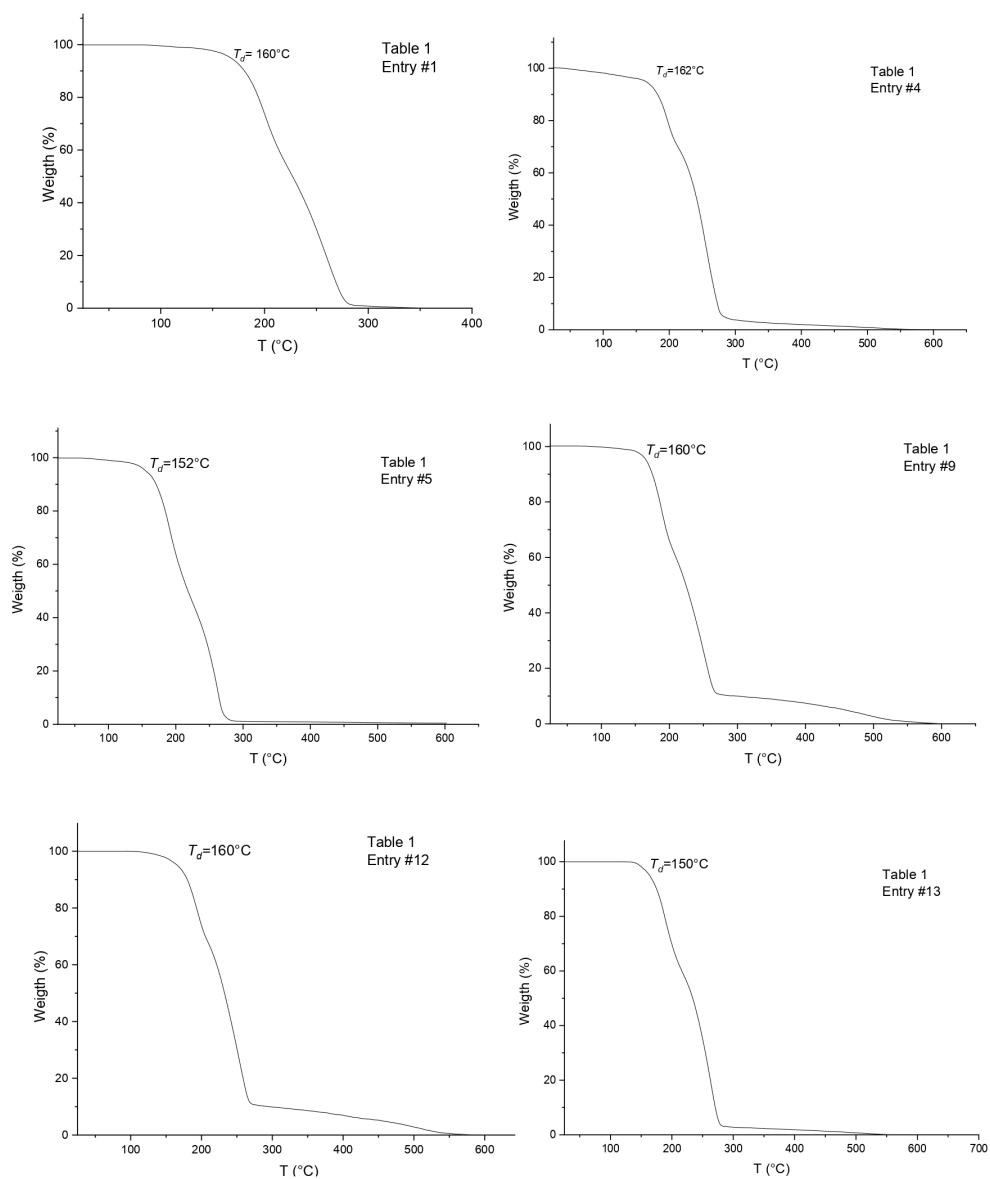
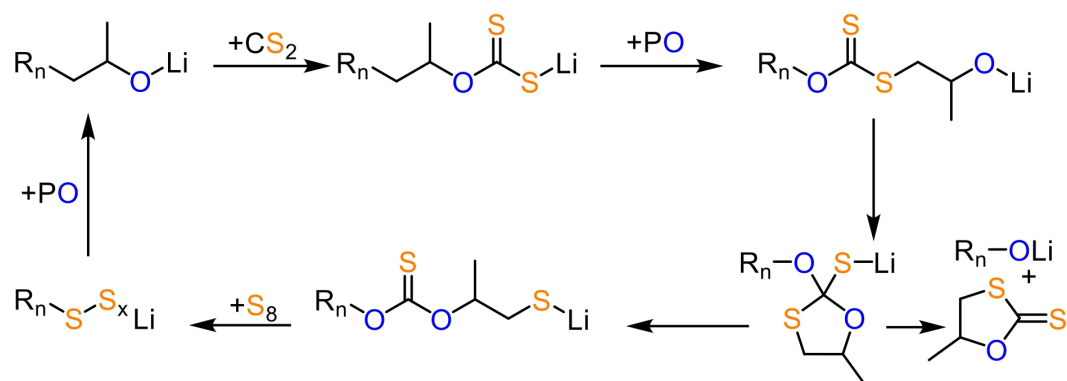


Figure S 21: TGA data of the polymers corresponding to table 1 entry #1,4,5,9,12,13.



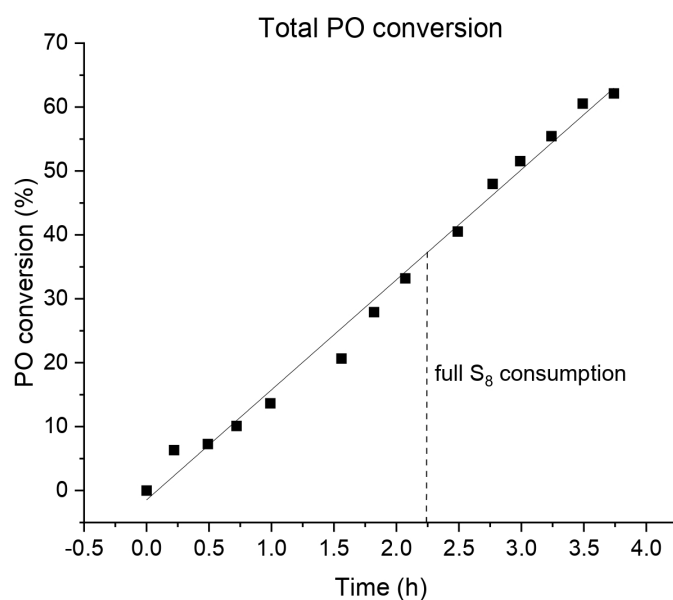
### Section S4: Mechanistic studies



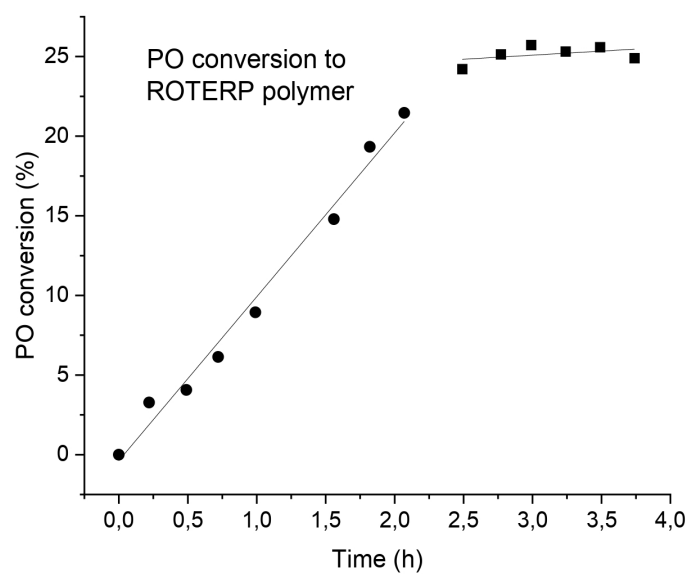
**Scheme S 2:** Mechanistic hypothesis.

### Reaction kinetics

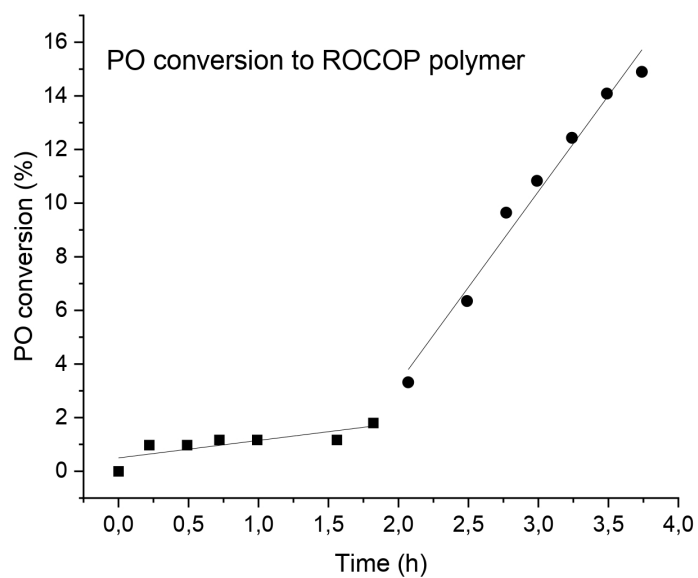
The monomer conversion was followed by integration of the proton signals around 5.7 ppm. (-CH next to thiocarbonate) in relation to the CH proton of PO at 2.75 ppm. To investigate how the depletion of sulfur affects the reaction rate, a stoichiometry of 1 eq. LiHMDS: 1 eq. BnOH: 500 eq. PO: 500 eq. CS<sub>2</sub>: 70 eq. S was chosen as the starting monomer feed conducting a ROTER inside an NMR tube. Once all the sulfur is consumed the polymerisation switches to a PO/CS<sub>2</sub> ROCOP. The graph in Figure S 19 shows a 0<sup>th</sup> order dependence in sulfur. Note that this occurs at 35% rather than the theoretical 28% PO conversion (from 70 eq. S per 500 eq. PO with two PO insertions occurring per S insertion in ROTERP) due to co-occurring consumption of PO via cyclic dithiocarbonate formation and formation of erroneous thiocarbonate links which is somewhat more pronounced in this case than in table 1.



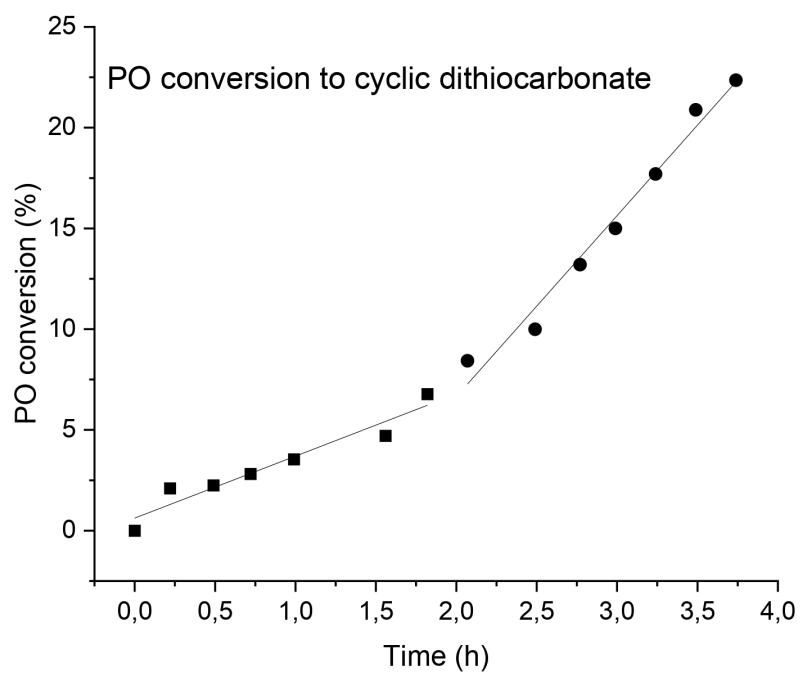
**Figure S 22:** PO conversion versus time for ROTERP inside NMR tube as outlined above.



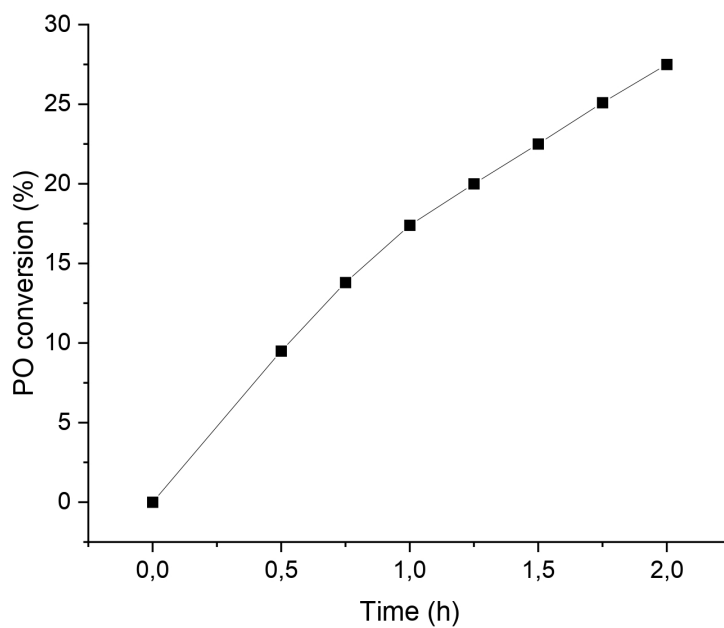
**Figure S 23:** PO conversion versus time to ROTERP polymer for polymerisation outlined above.



**Figure S 24:** PO conversion versus time to ROCOP polymer for polymerisation outlined above.



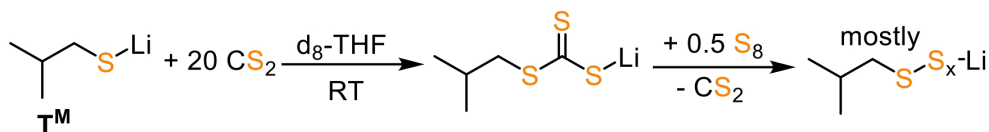
**Figure S 25:** PO conversion versus time to cyclic dithiocarbonate for polymerisation outlined above.



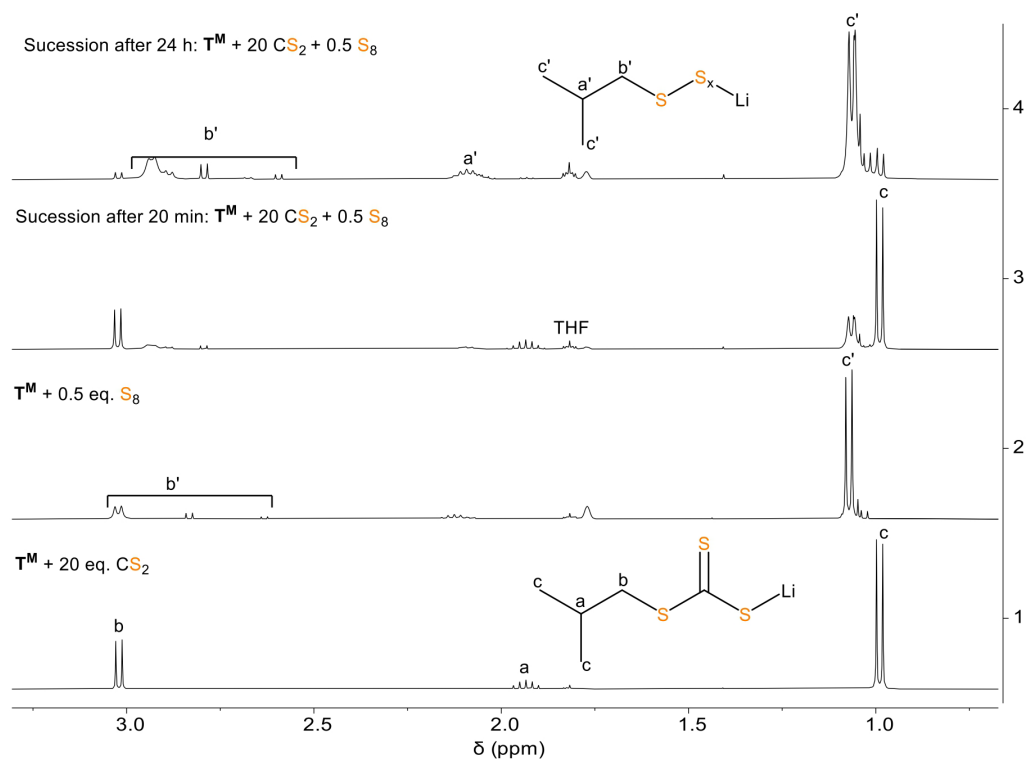
**Figure S 26:** PO conversion versus time at 1 eq. LiHMDS: 1 eq. BnOH: 500 eq. PO: 75 eq. CS<sub>2</sub>: 90 eq. S. Polymerisation conducted inside an NMR tube.

### Competition and succession experiments

**Succession experiment:** Inside an Argon filled glovebox, 1 eq. of **T<sup>M</sup>** in d<sup>8</sup>-THF (0.4 mL) was added to CS<sub>2</sub> (20 eq. per **T<sup>M</sup>**) according to Scheme S3. The reaction mixture was transferred to an NMR tube and analysed by <sup>1</sup>H NMR spectroscopy after 20 min. Thereafter S<sub>8</sub> (0.5 eq. = 4 eq. S per **T<sup>M</sup>**) was added, and the reaction mixture was analysed by <sup>1</sup>H NMR spectroscopy after 20 min and 24h.



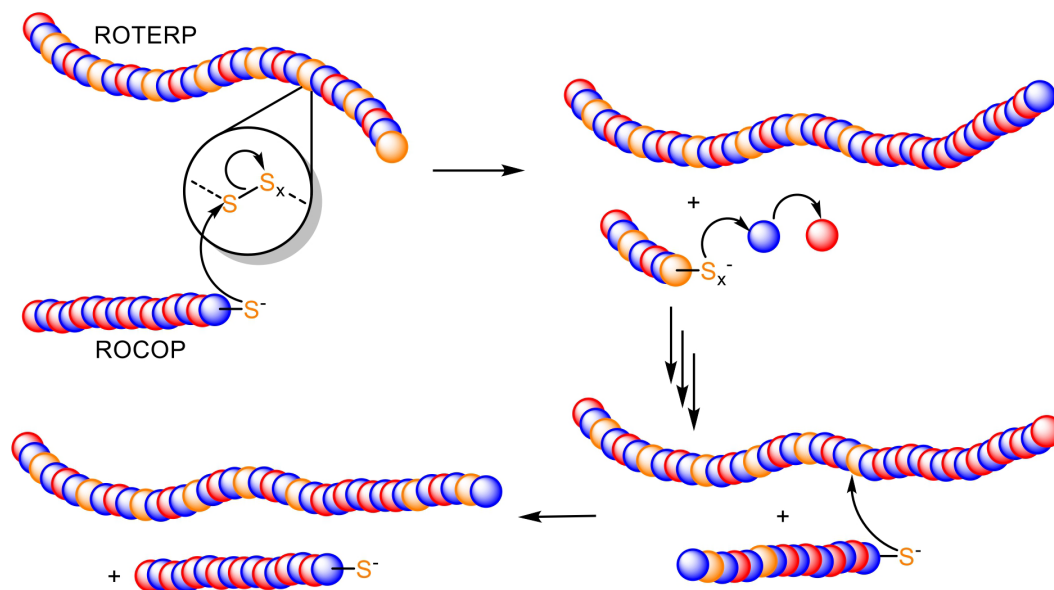
**Scheme S 3:** Succession experiment. Prepared accordingly to literature<sup>[4]</sup>.



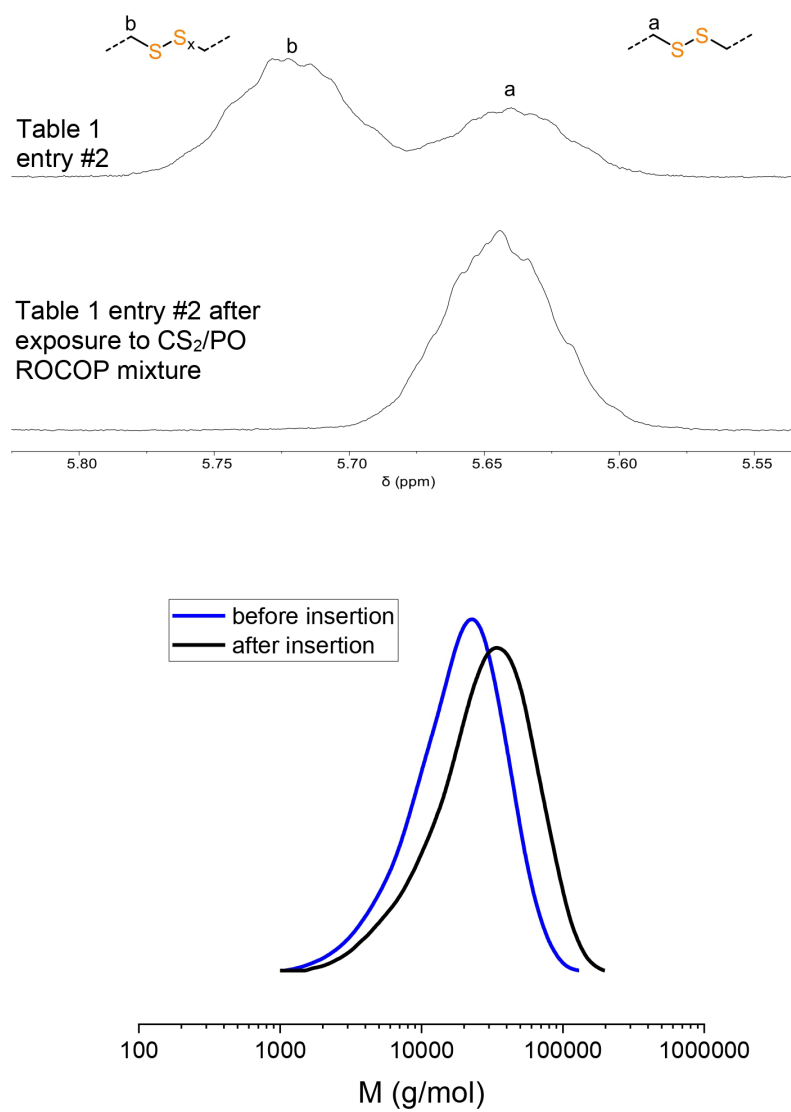
**Figure S27:** Overlaid <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>, 25°C) of reaction mixture produced by competition experiment and reference spectra of **T<sup>M</sup>** and the insertion products with only S<sub>8</sub> or CS<sub>2</sub> respectively. Residual THF from **T<sup>M</sup>** starting material.

### Section S5: PO/CS<sub>2</sub> insertion

An isolated ROTERP polymer (table 1 entry #2, 750 mg) was dissolved in a solution containing 1 eq. LiOBn, 500 eq. PO and 1000 eq. CS<sub>2</sub> in which ROCOP occurs. Analysis of the crude reaction mixture by <sup>1</sup>H NMR after 3 h reveals disappearance of the signal at 5.73 ppm (from CH protons in repeat units featuring polysulfide links) in favor of the signal at 5.65 ppm (from a CH proton in repeat units featuring disulfide and trithiocarbonate links). Moreover, GPC shows a slight increase of molecular weight from 23 to 32 kDa.



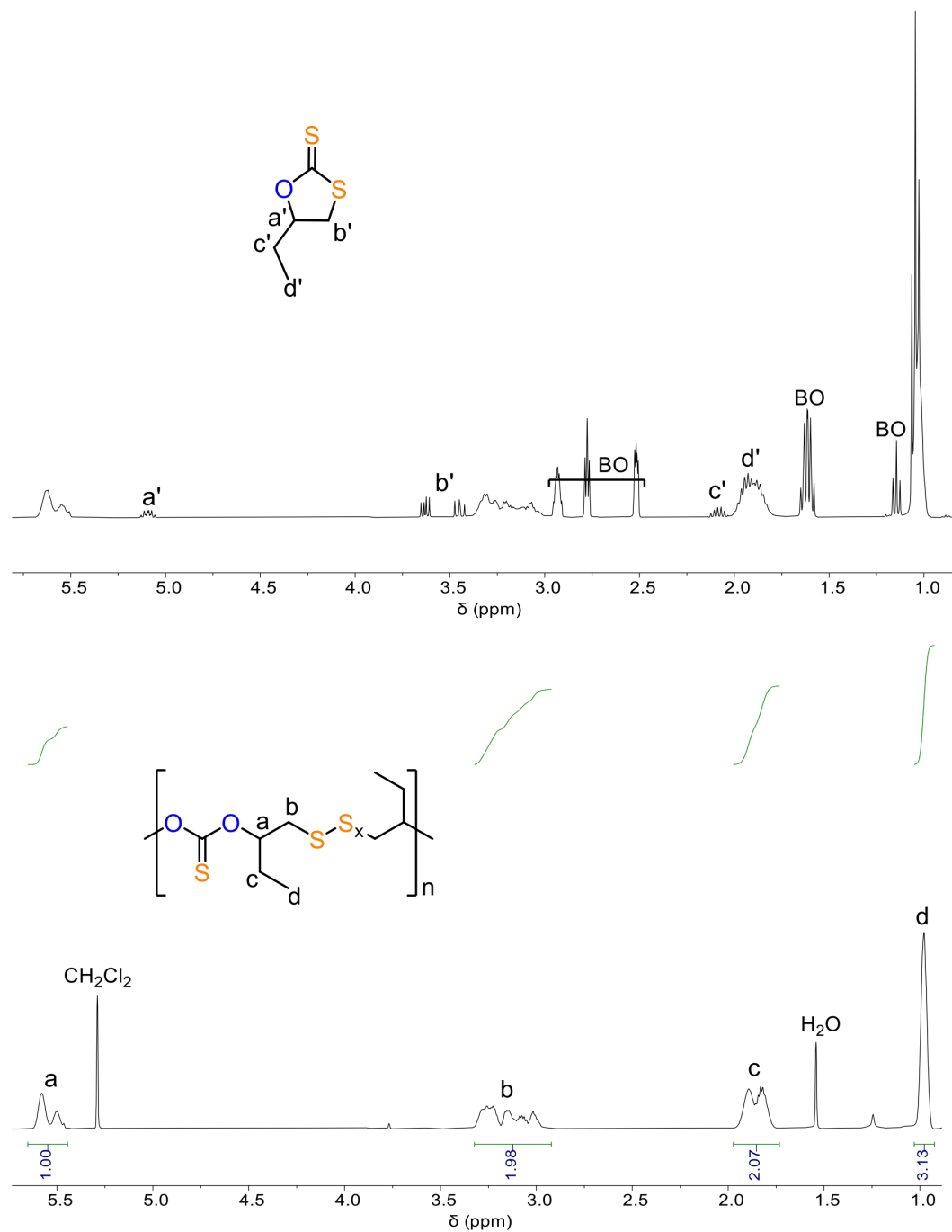
**Scheme S 4:** ROCOP polymer insertion into ROTERP polymer.



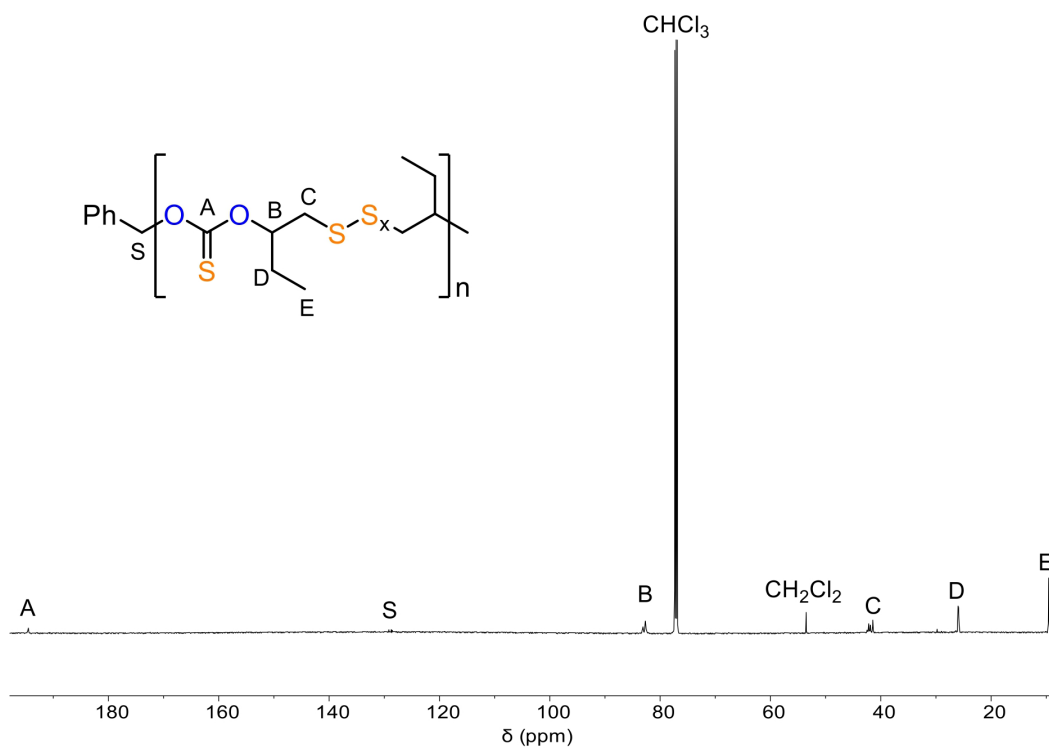
**Figure S28:** (top)  $^1\text{H}$ -NMR of before and after the insertion experiment. (bottom) GPC curve of the polymer before and after the insertion experiment.

### Section S6: Monomer scoping

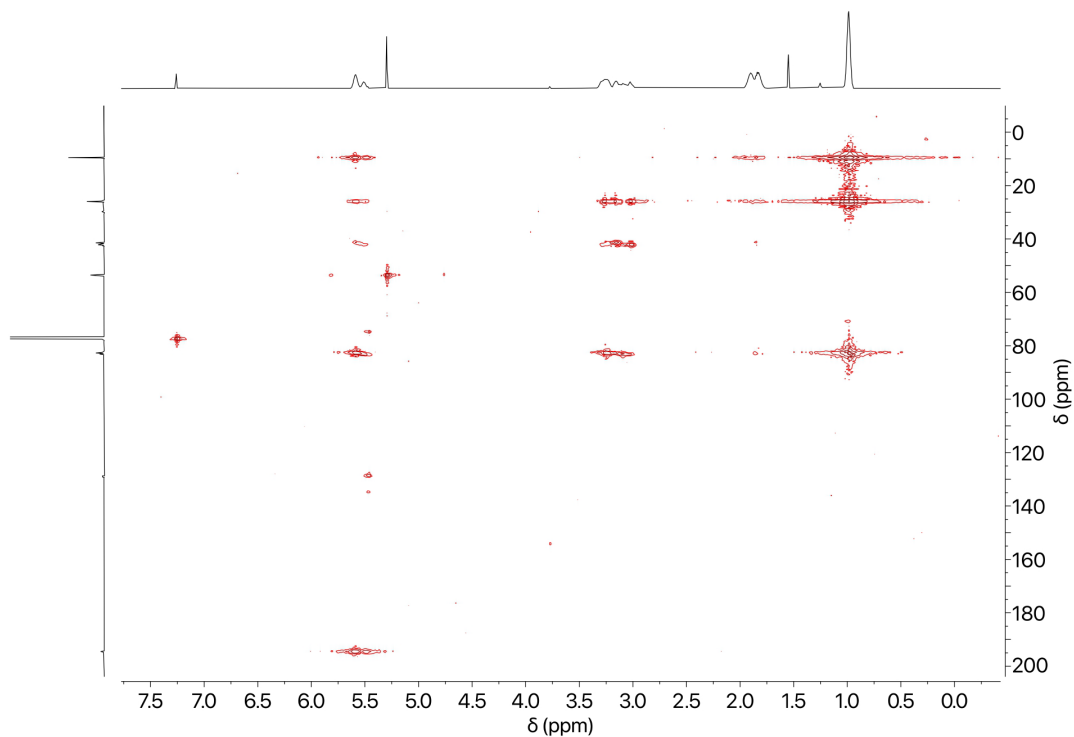
Monomer scoping was conducted with the same polymerisation methodology described in Section S 2.



**Figure S29:** <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>, 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #2.

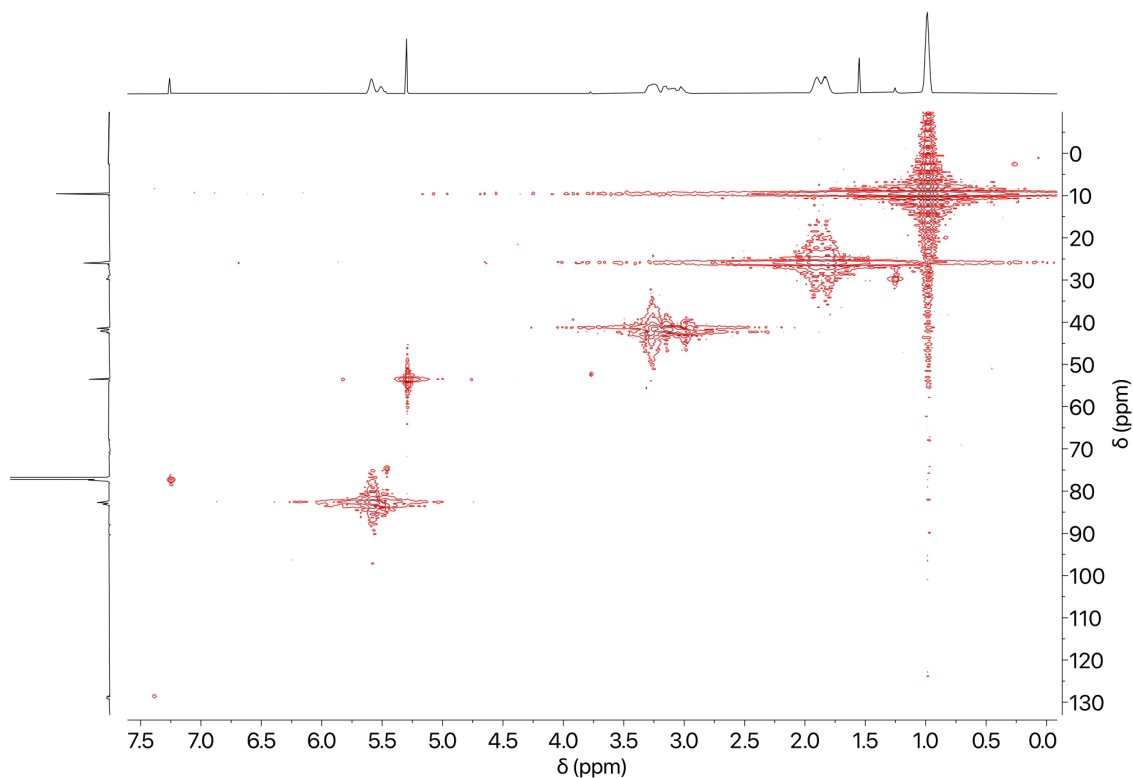


**Figure S30:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #2.

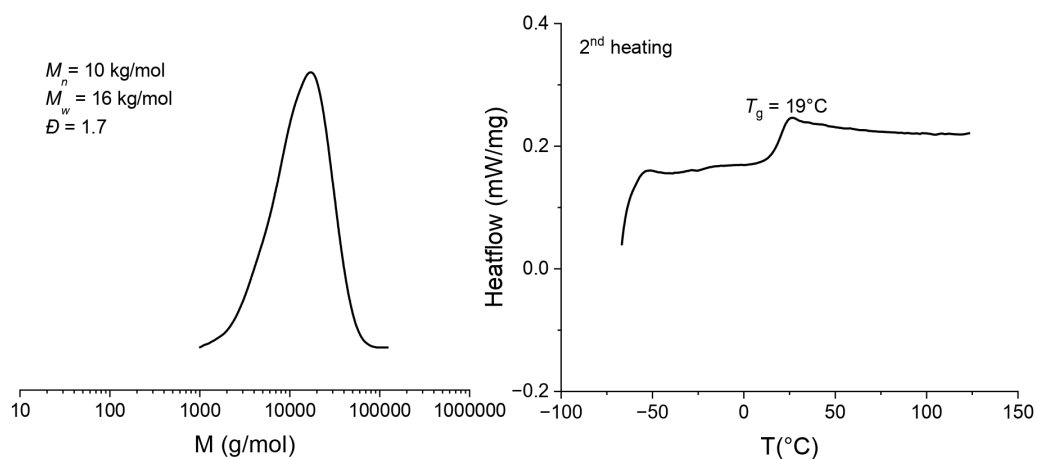


**Figure S31:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #2.

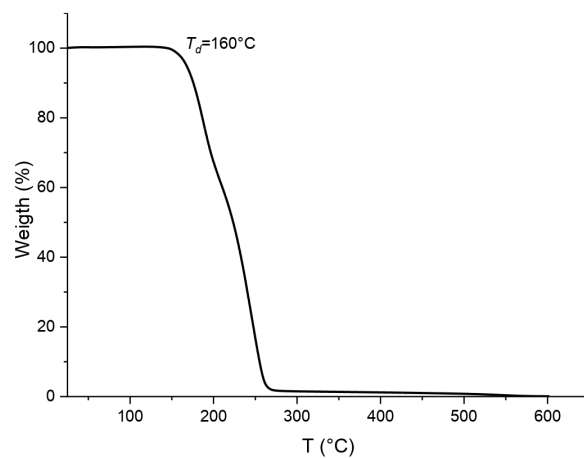




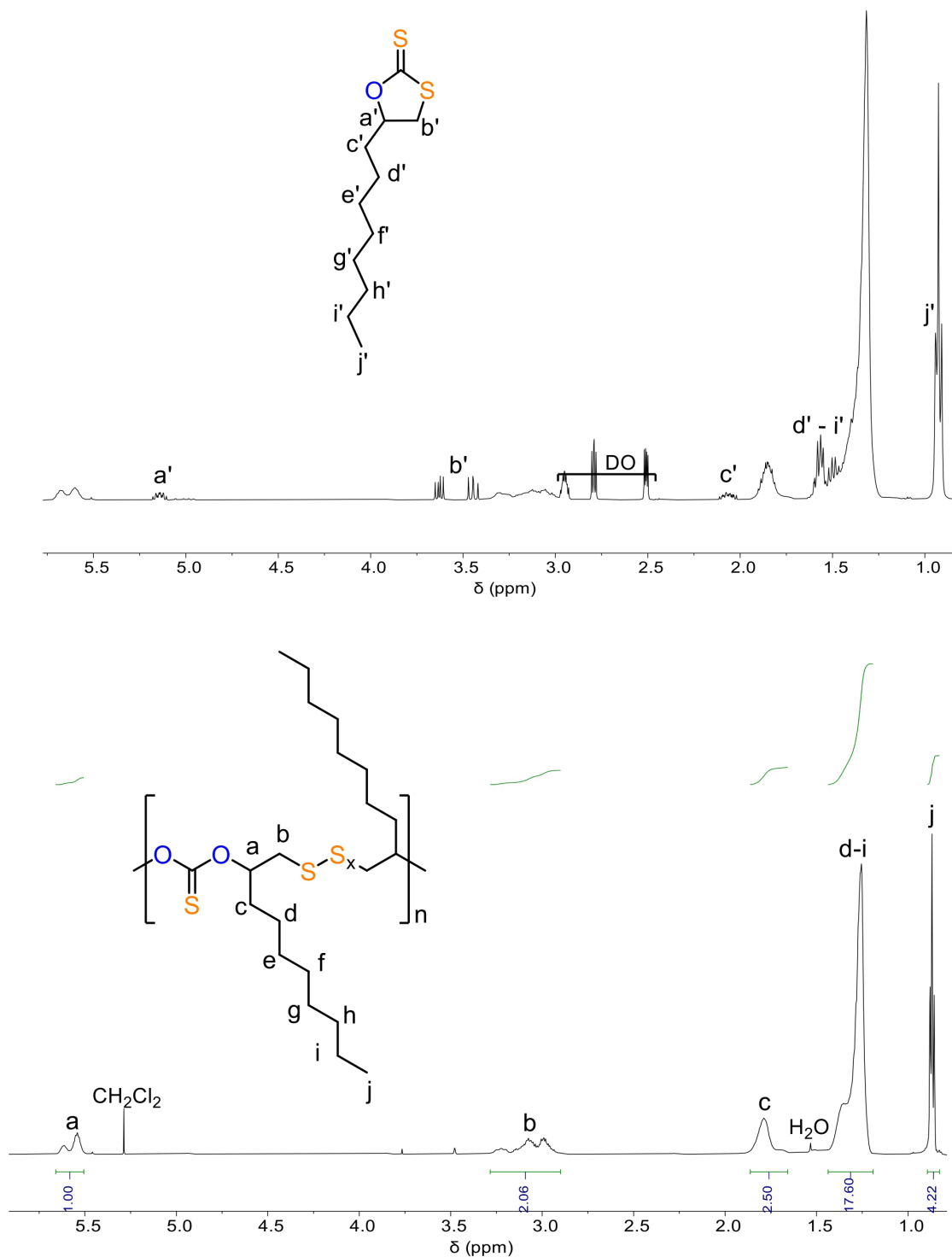
**Figure S32:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #2.



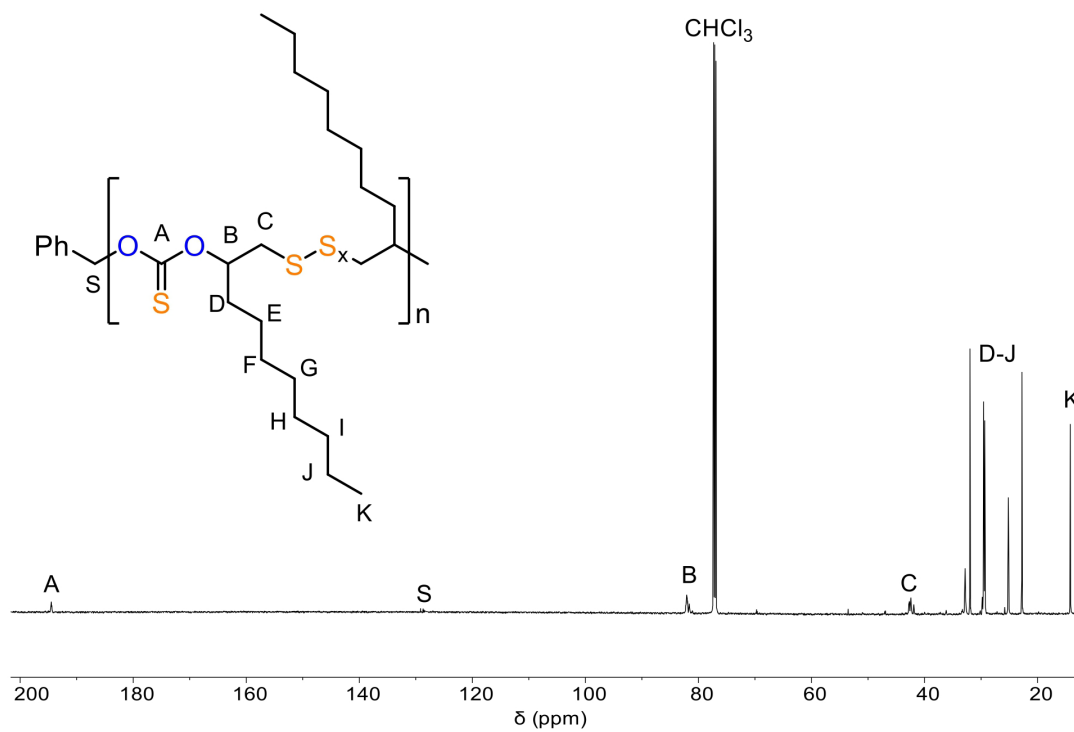
**Figure S33:** (left) GPC curve and (right) DSC heating curve of the precipitated polymer corresponding to table 2 entry #2.



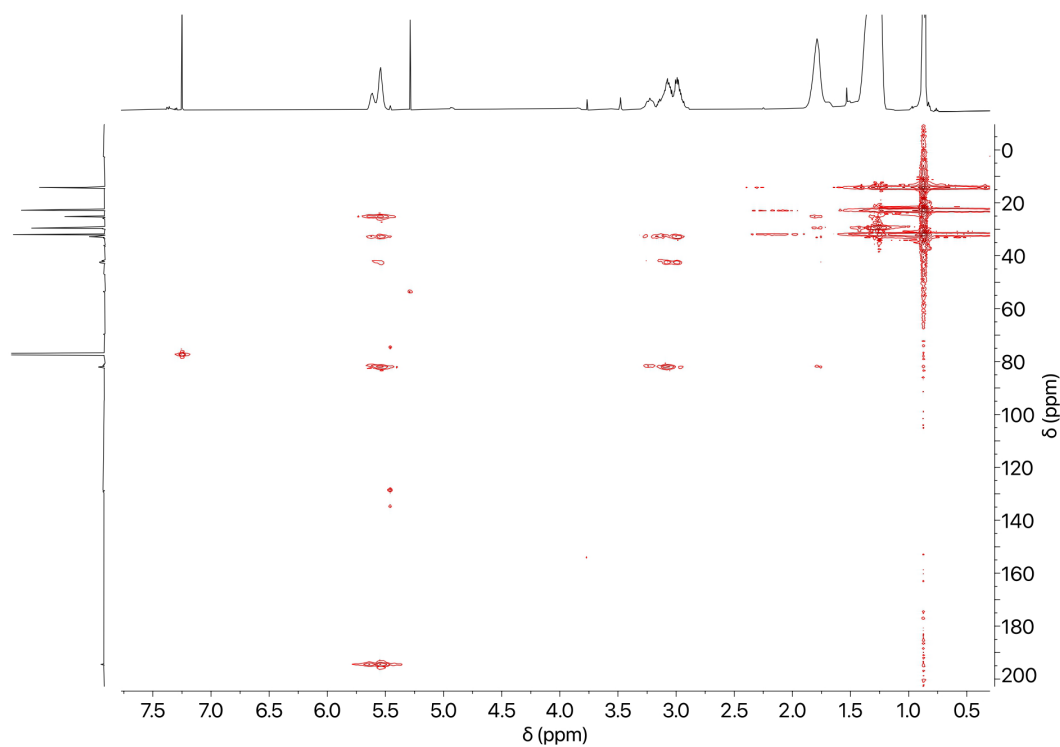
**Figure S34:** TGA data of the precipitated polymer corresponding to Table 2 run #2.



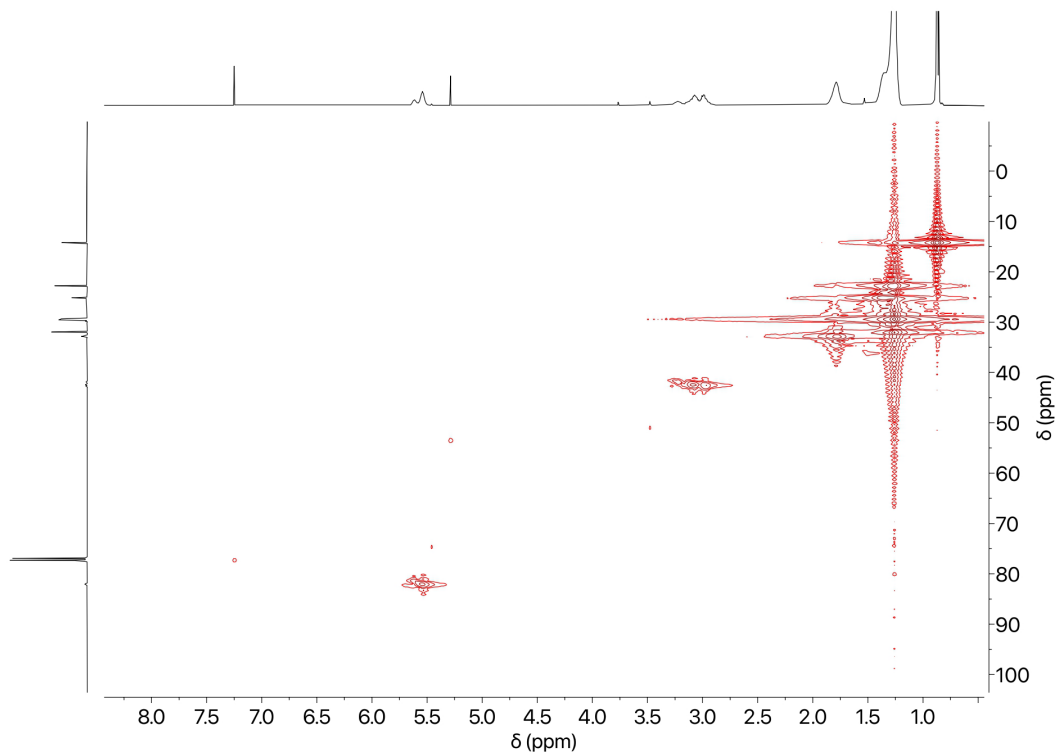
**Figure S35:** <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>, 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #3.



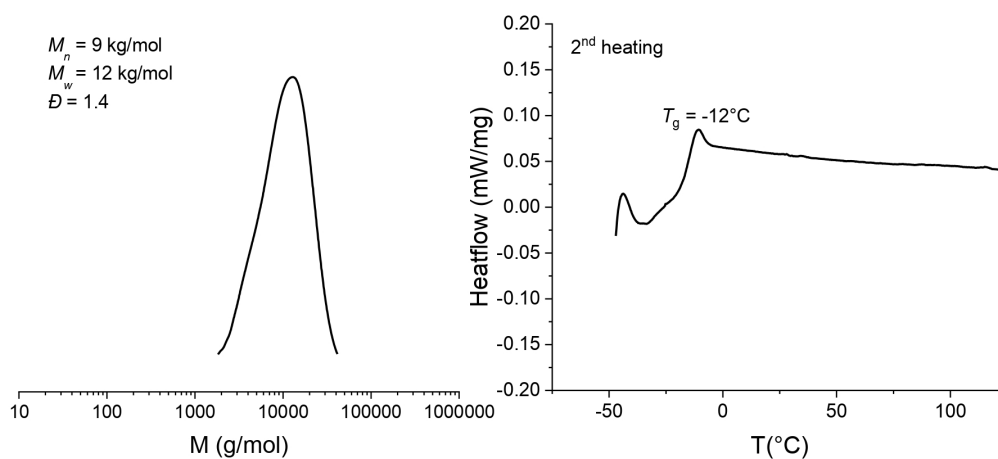
**Figure S36:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #3.



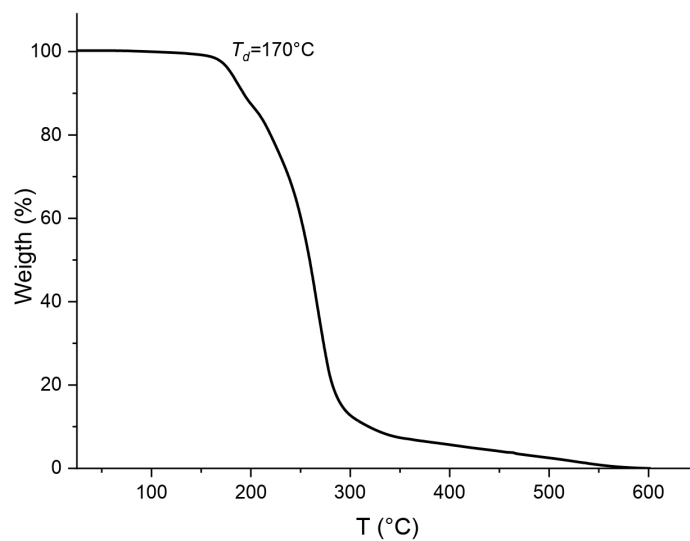
**Figure S37:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #3.



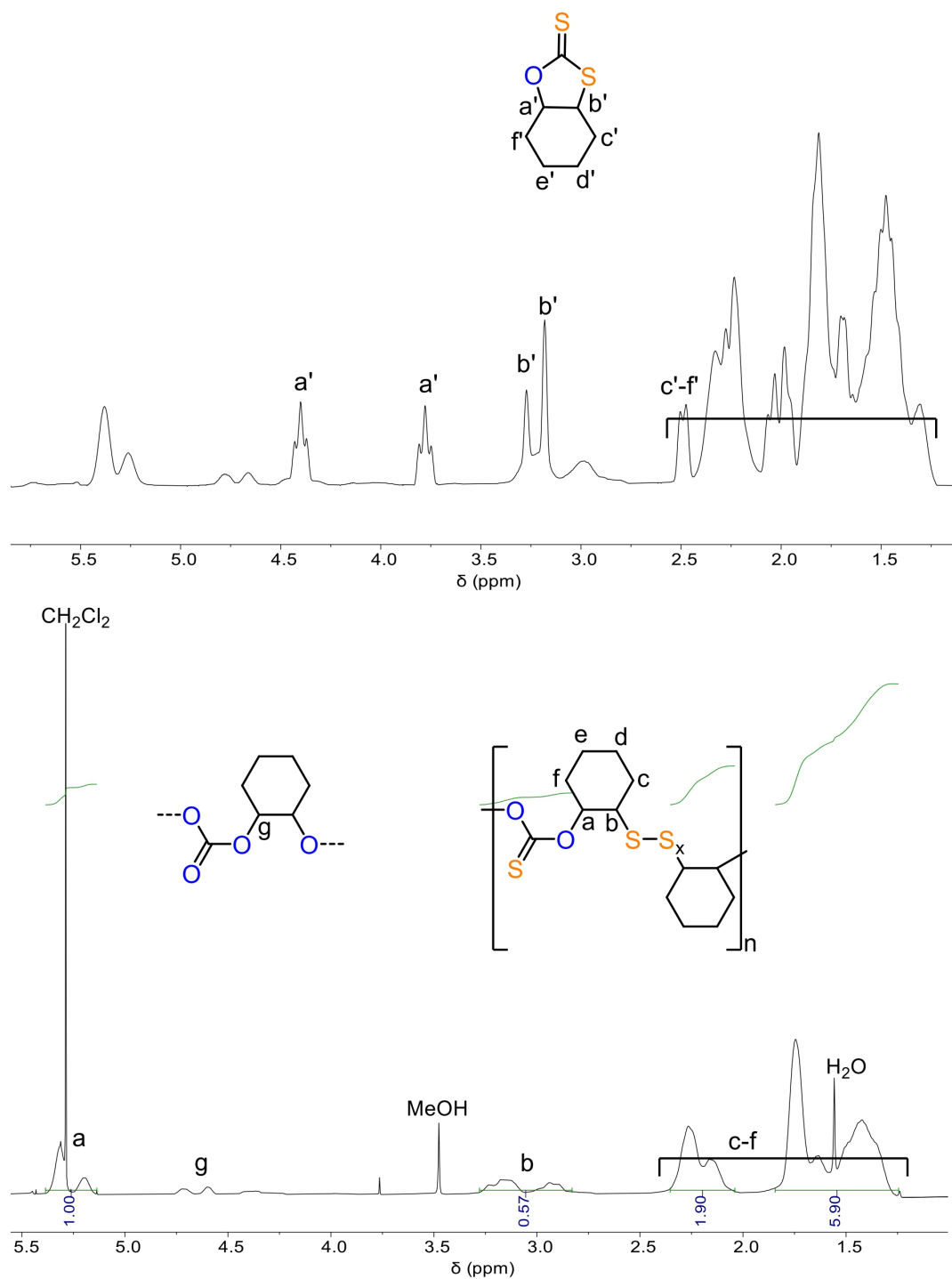
**Figure S38:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #3.



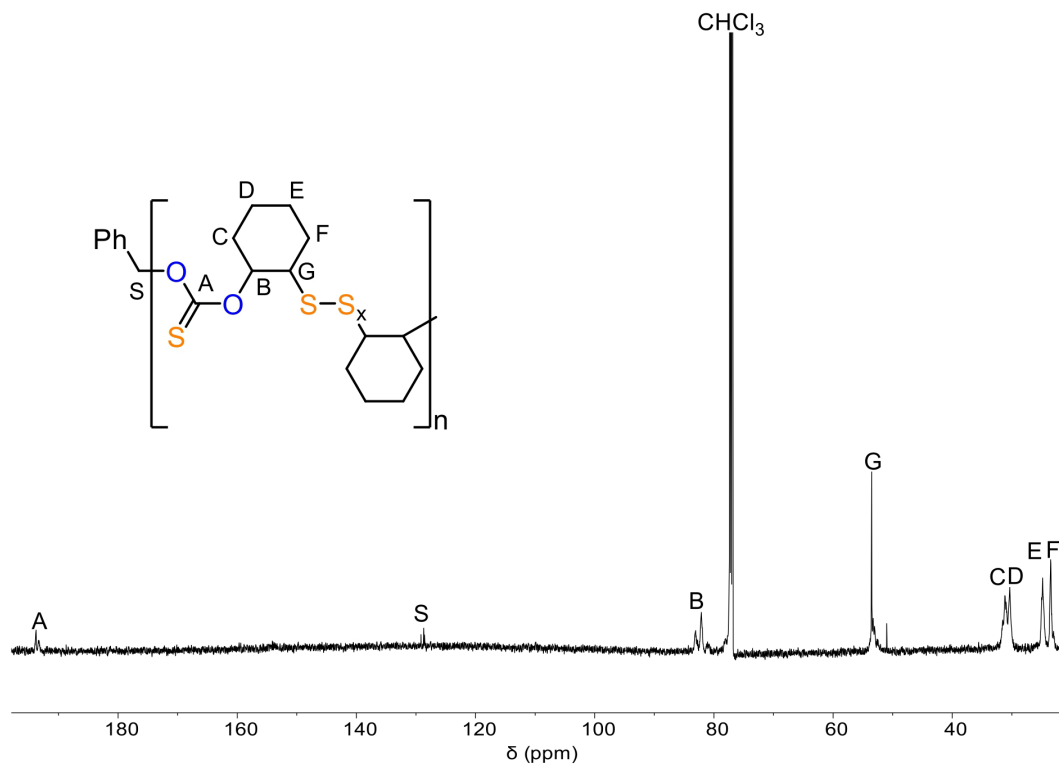
**Figure S39:** (left) GPC curve and (right) DSC heating curve of the precipitated polymer corresponding to table 2 entry #3.



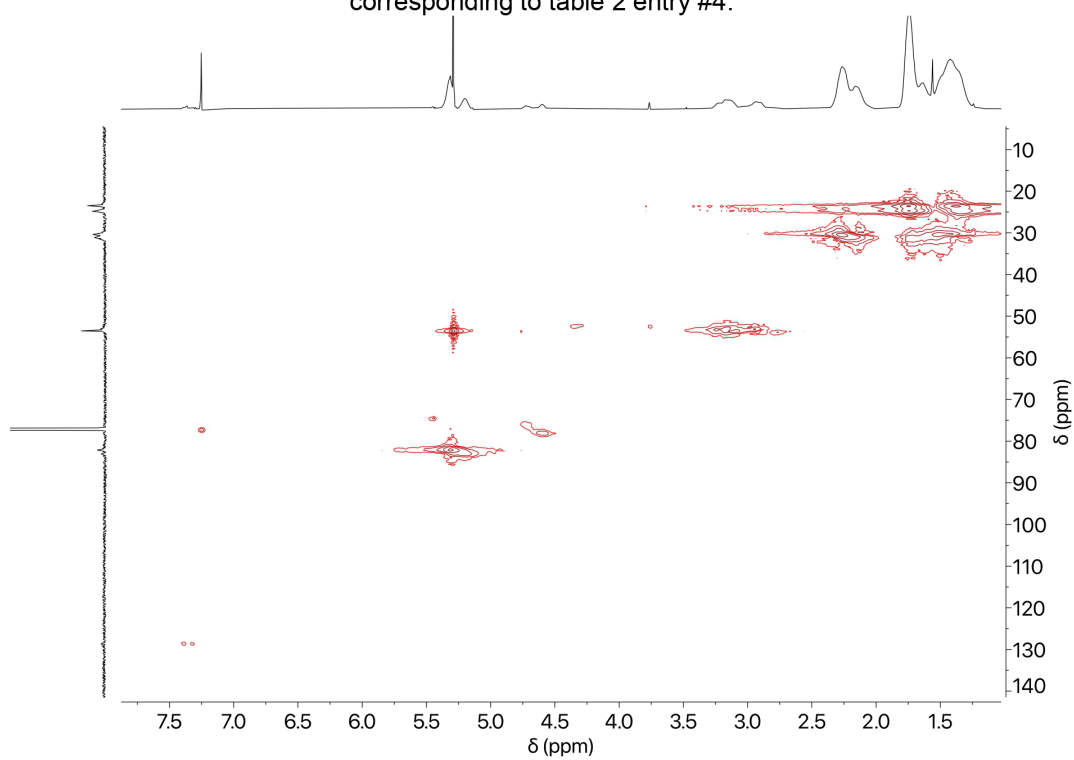
**Figure S40:** TGA data of the precipitated polymer corresponding to Table 2 run #3.



**Figure S41:** <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>, 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #4.

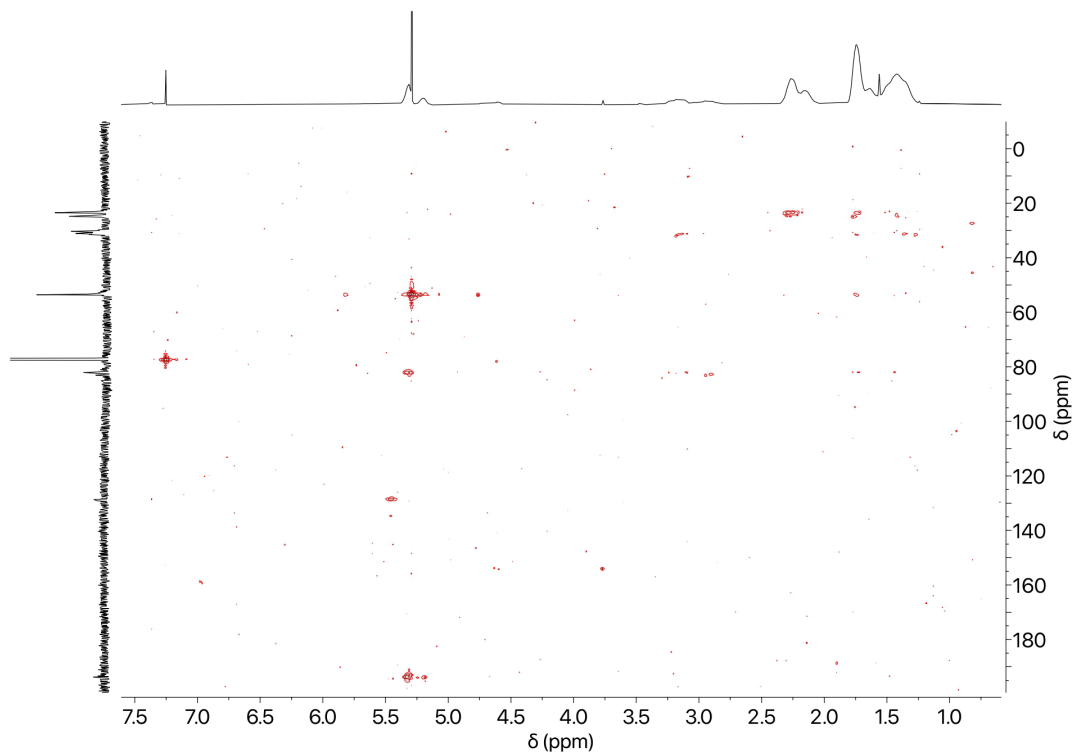


**Figure S42:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #4.

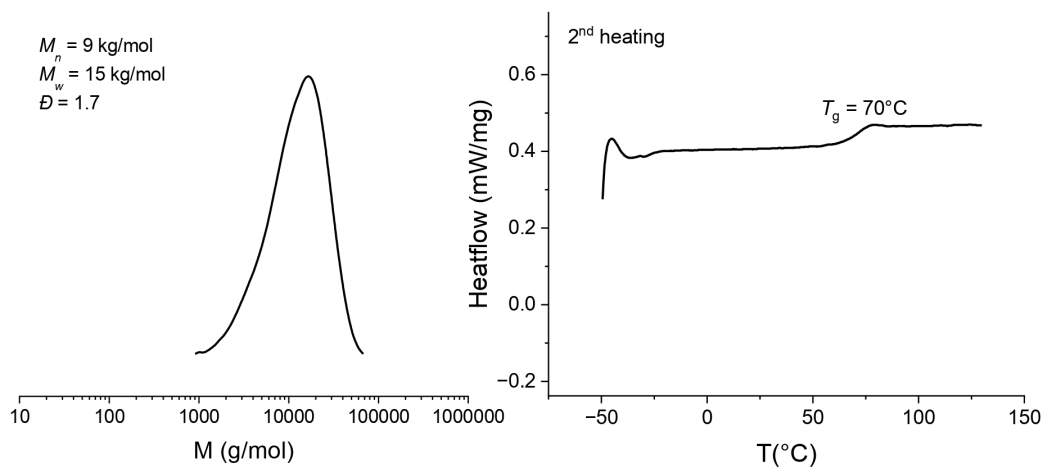


**Figure S43:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #4.

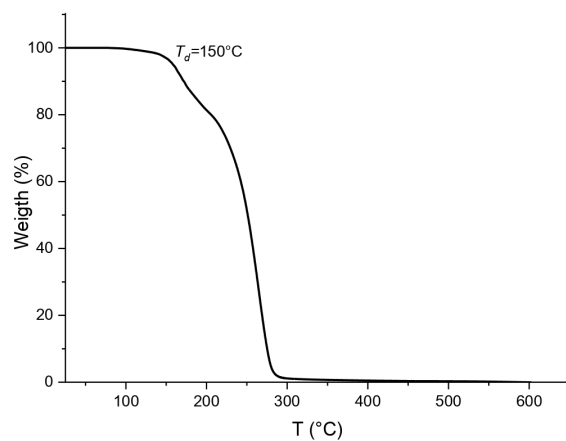




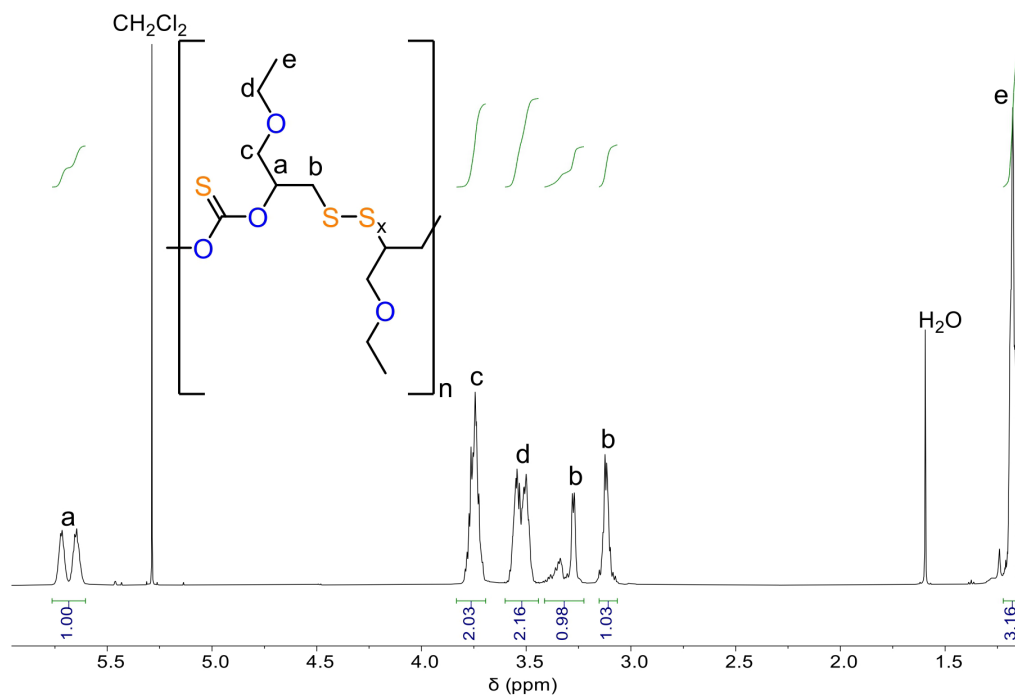
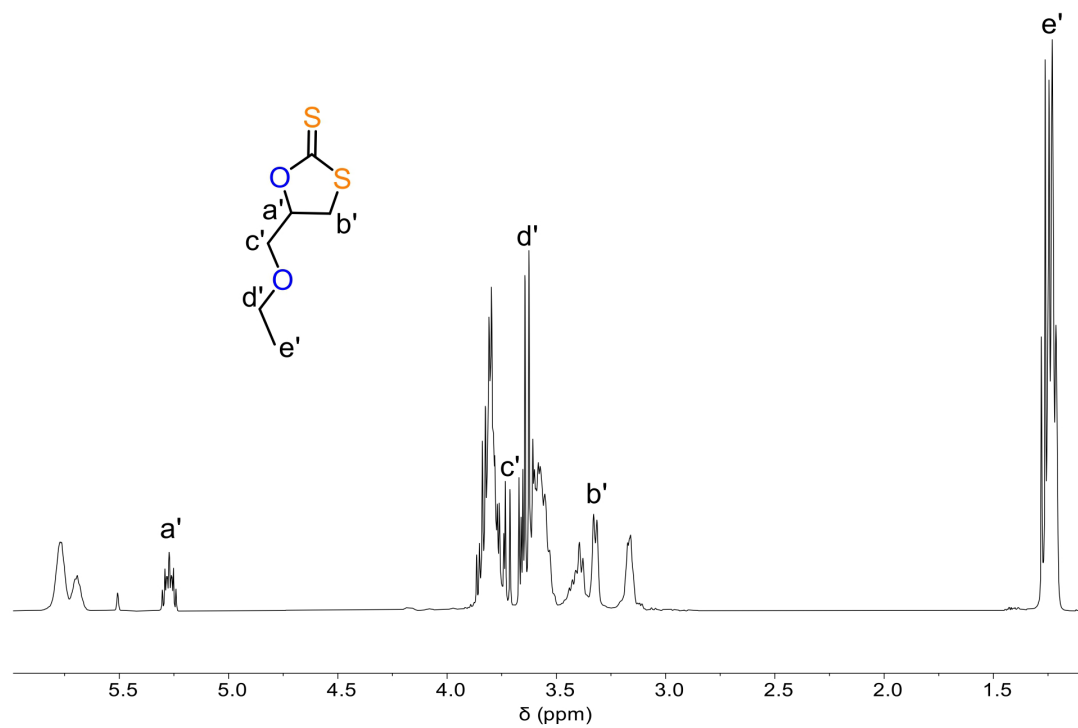
**Figure S44:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #4.



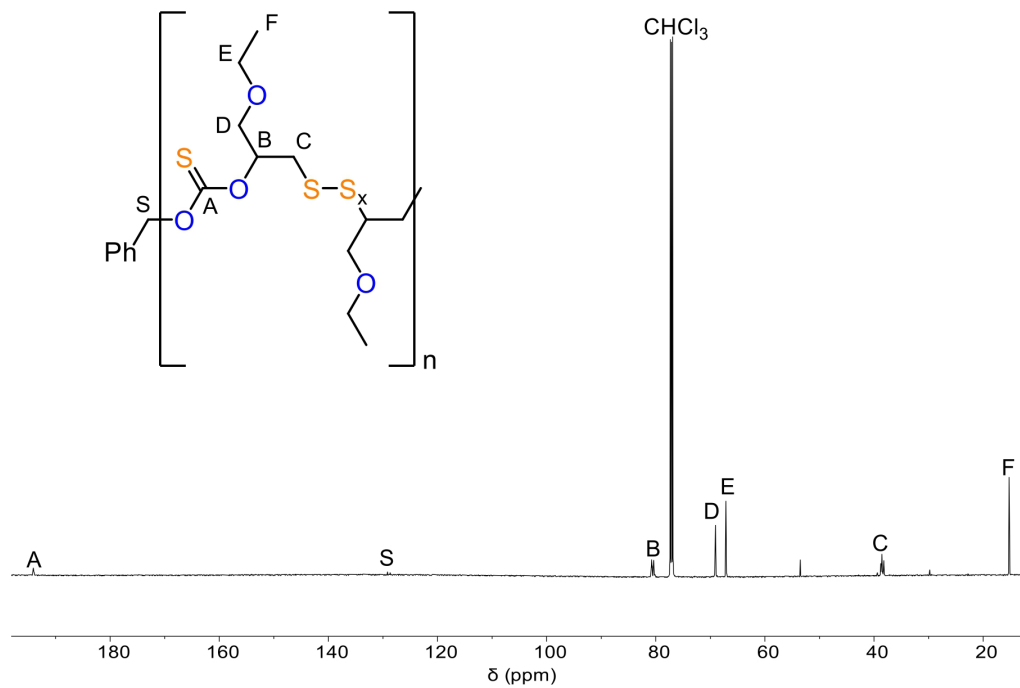
**Figure S45:** (left) GPC curve and (right) DSC heating curve of the precipitated polymer corresponding to table 2 entry #4.



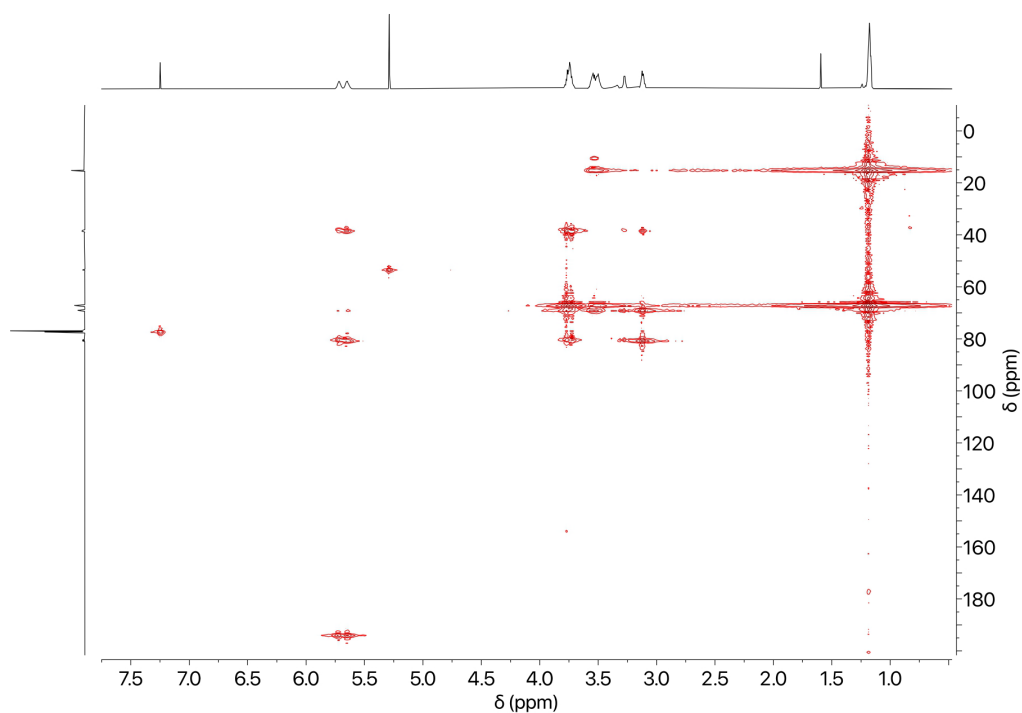
**Figure S46:** TGA data of the precipitated polymer corresponding to Table 2 run #4.



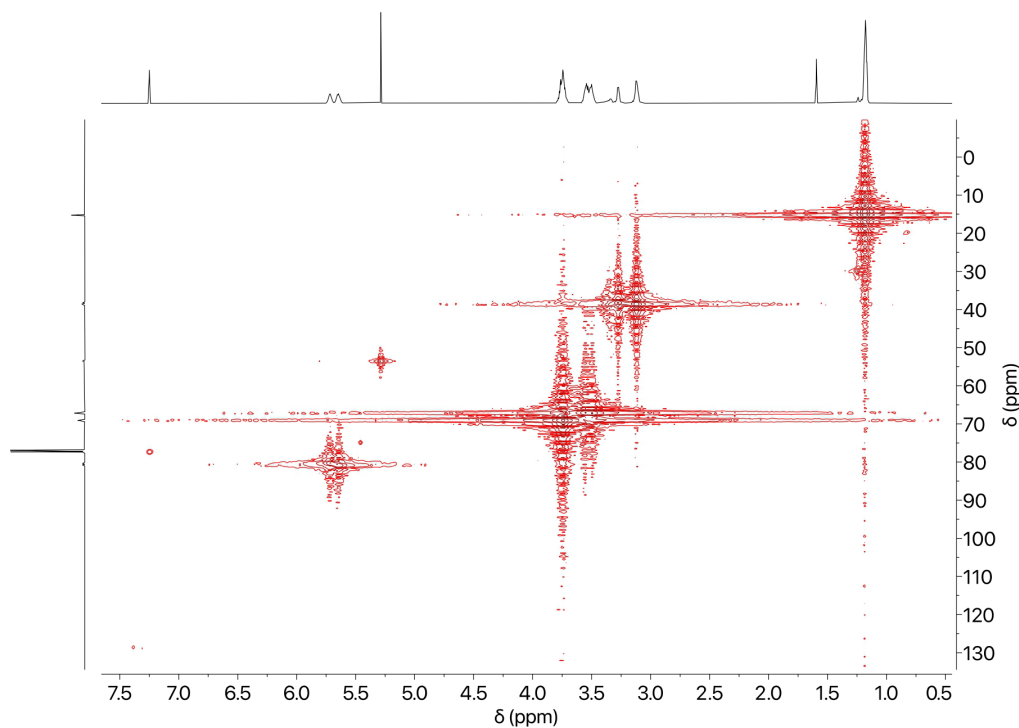
**Figure S47:**  $^1\text{H}$ -NMR spectra (600 MHz,  $\text{CDCl}_3$ , 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #5.



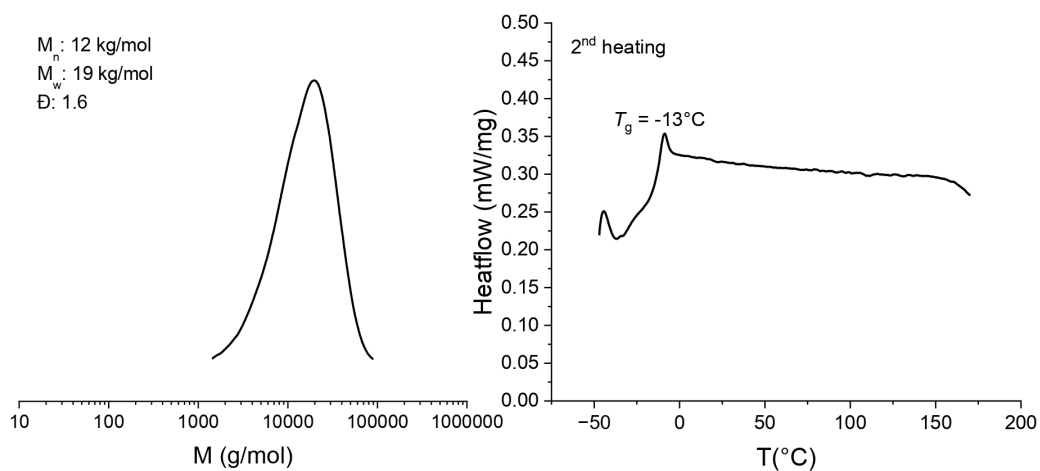
**Figure S48:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #5.



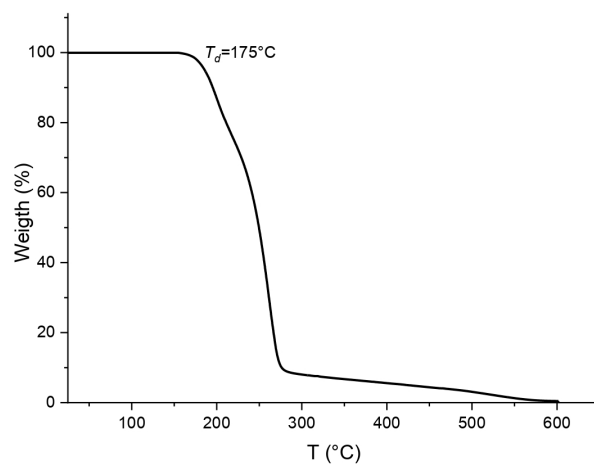
**Figure S49:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #5.



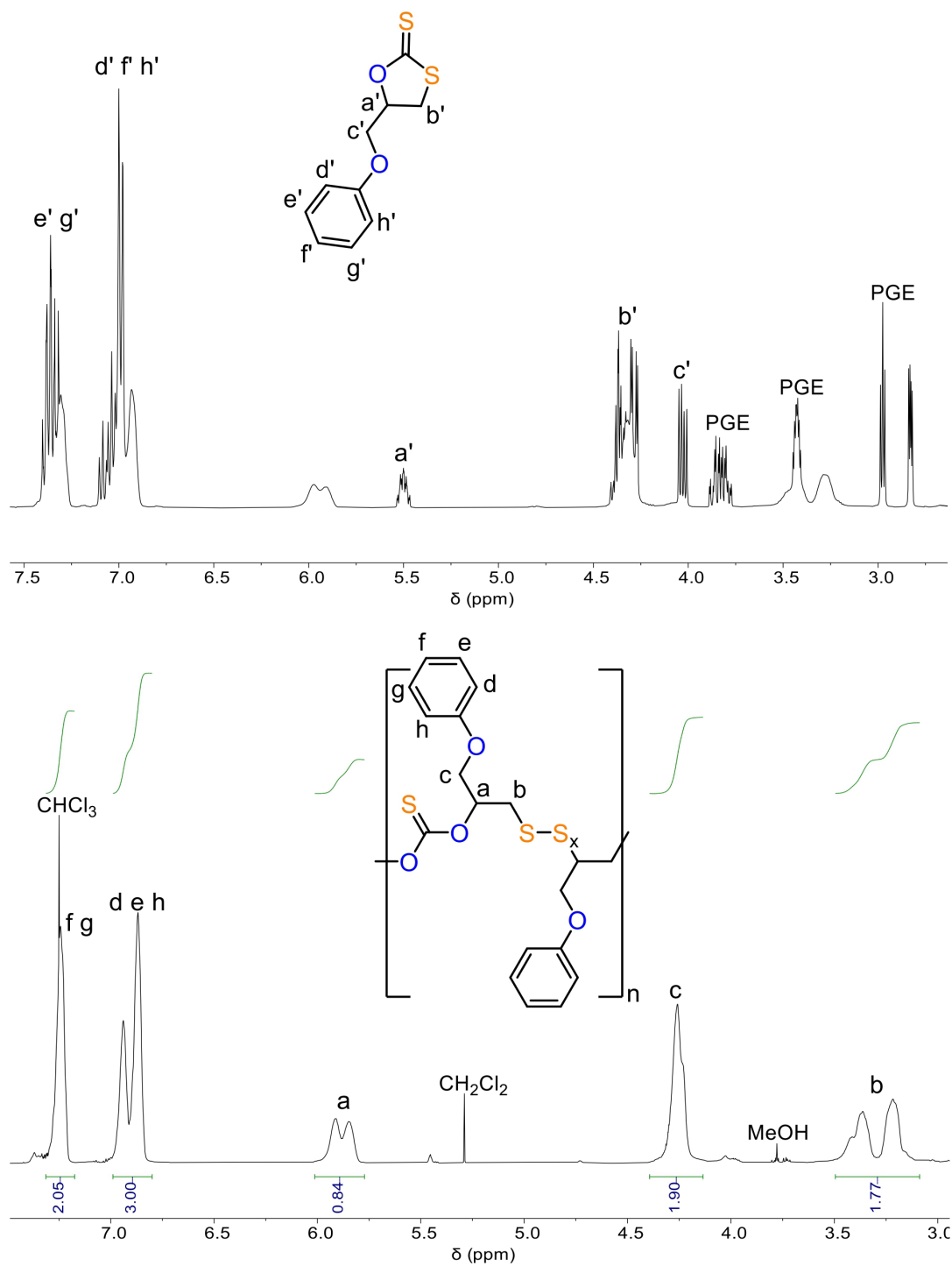
**Figure S50:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #5.



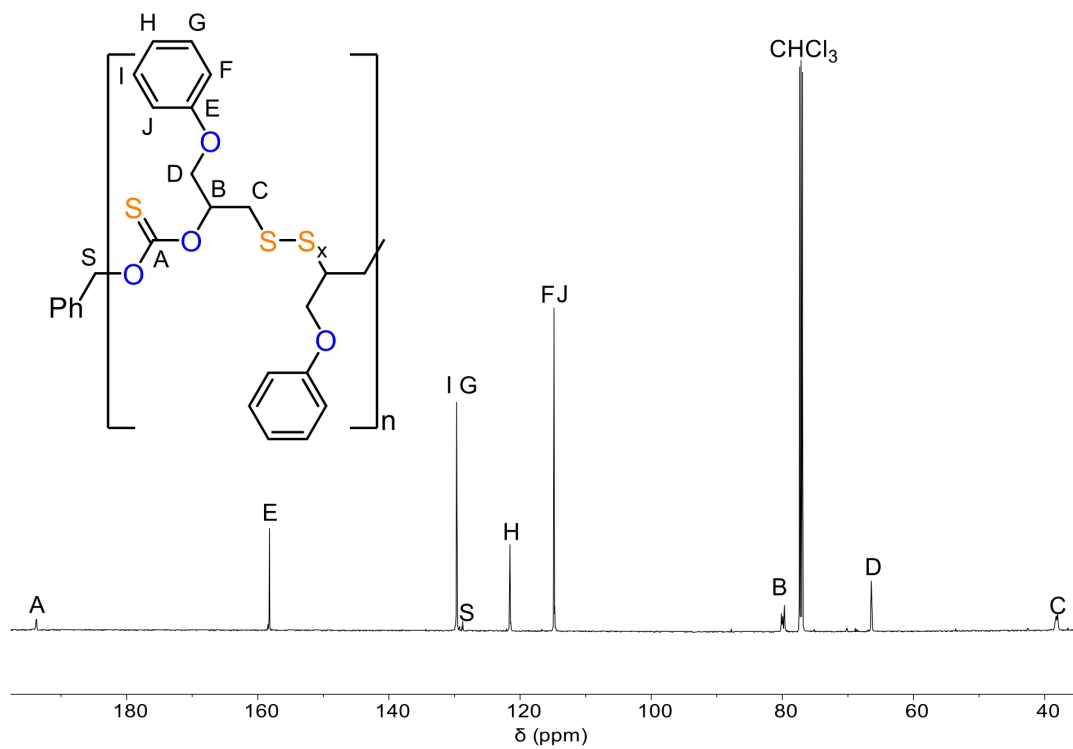
**Figure S51:** (left) GPC curve and (right) DSC heating curve of the precipitated polymer corresponding to table 2 entry #5.



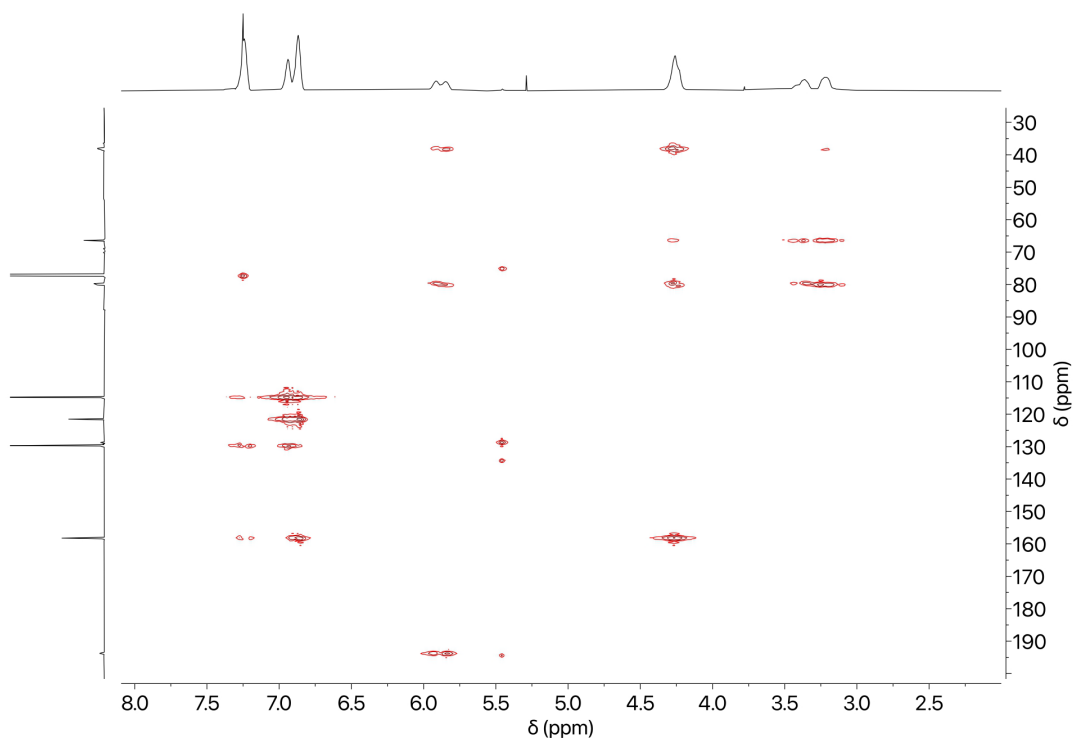
**Figure S52:** TGA data of the precipitated polymer corresponding to Table 2 run #5.



**Figure S53:** <sup>1</sup>H-NMR spectra (600 MHz, CDCl<sub>3</sub>, 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #6.

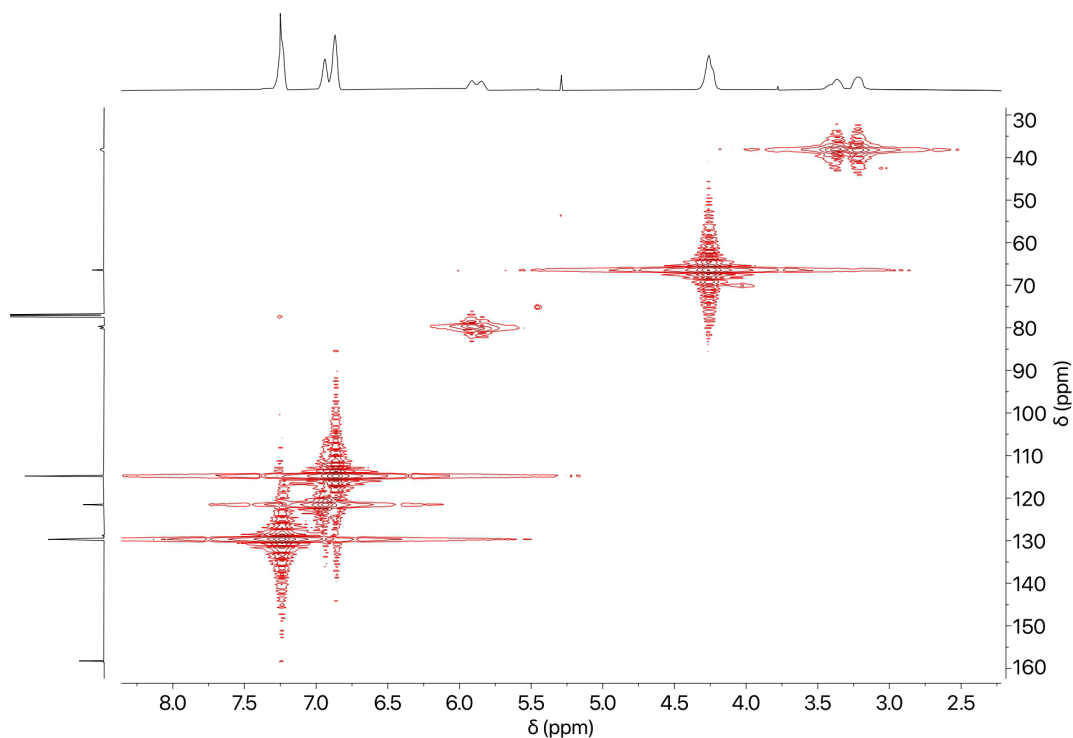


**Figure S54:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #6.

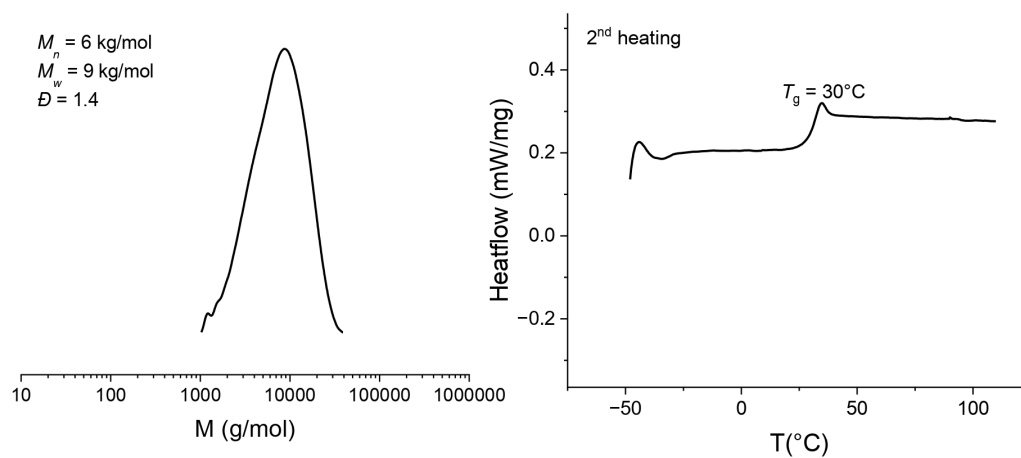


**Figure S55:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 2 entry #6.

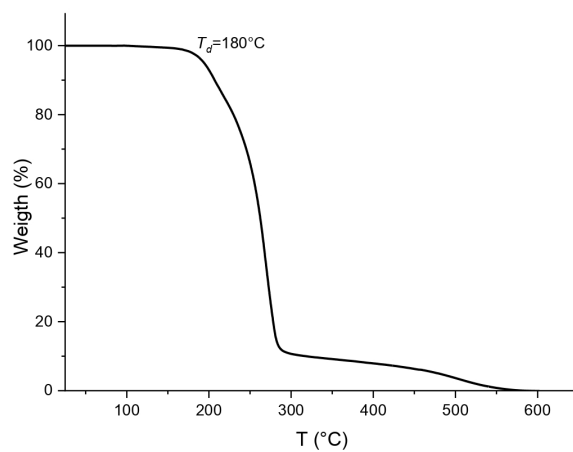




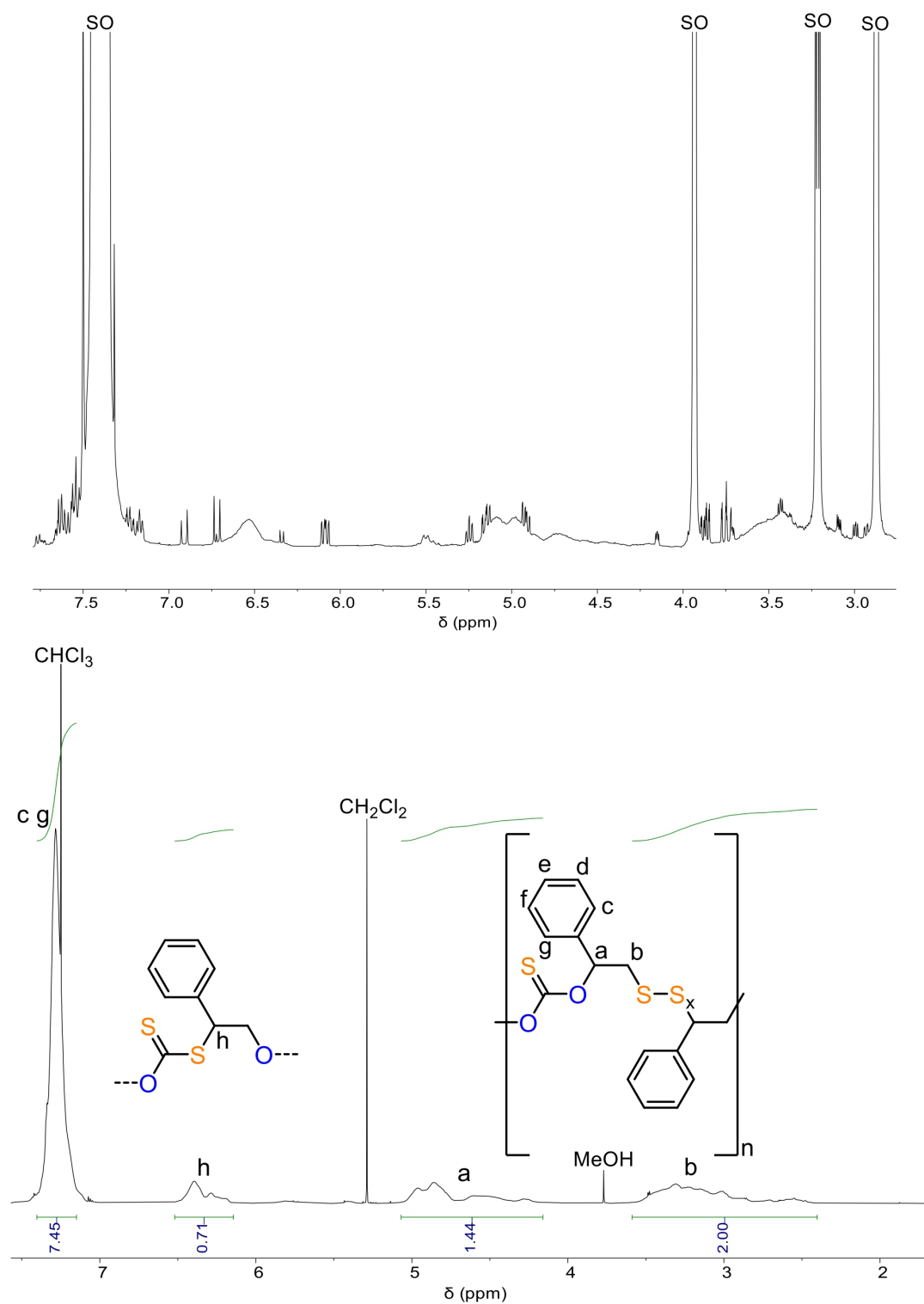
**Figure S56:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #6.



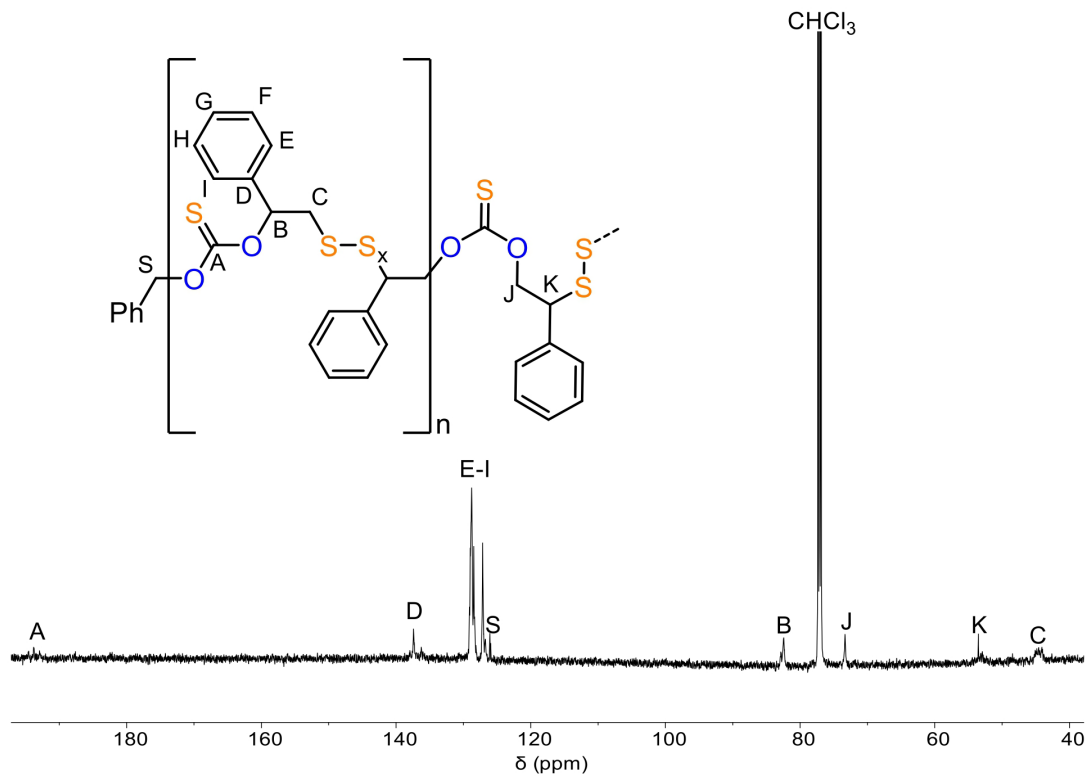
**Figure S57:** (left) GPC curve and (right) DSC heating curve of the precipitated polymer corresponding to table 2 entry #6.



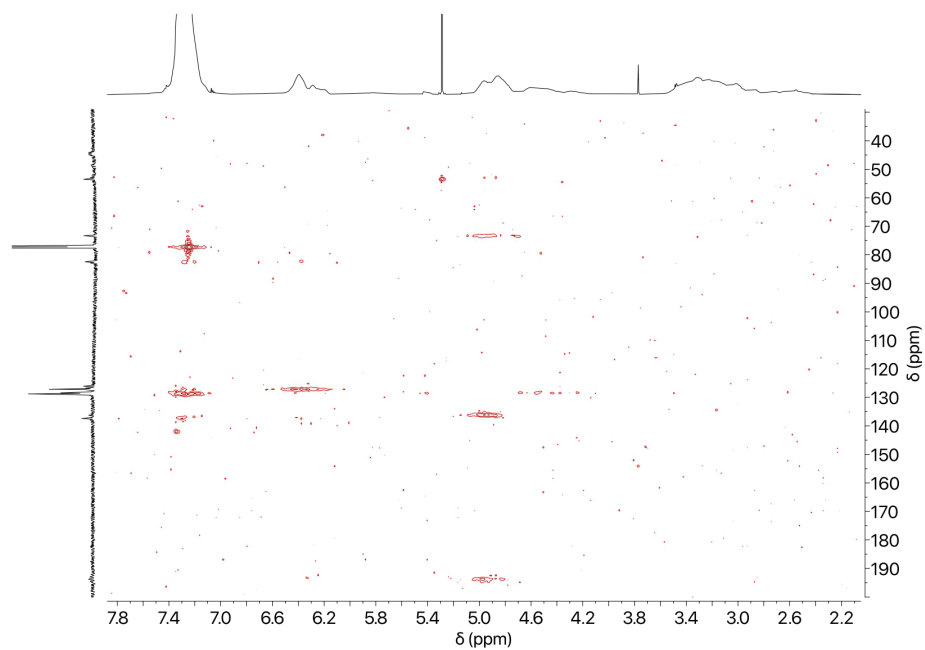
**Figure S58:** TGA data of the precipitated polymer corresponding to Table 2 run #6.



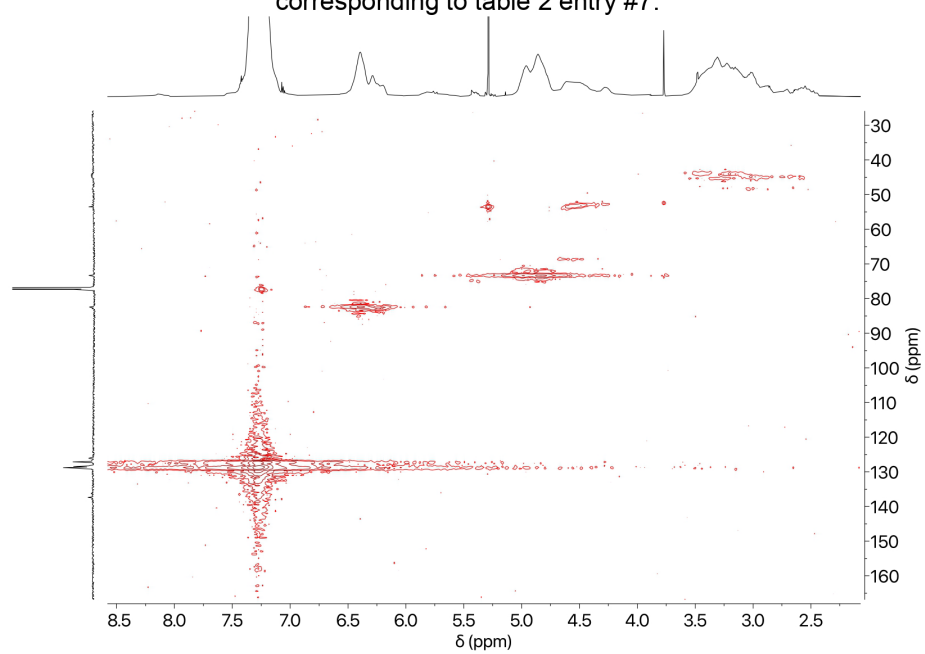
**Figure S59:**  $^1\text{H}$ -NMR spectra (600 MHz,  $\text{CDCl}_3$ , 25°C) of the crude mixture (top) and precipitated polymer (bottom) corresponding to table 2 entry #7. Decreased polymer and sequence selectivity prevented quantification.



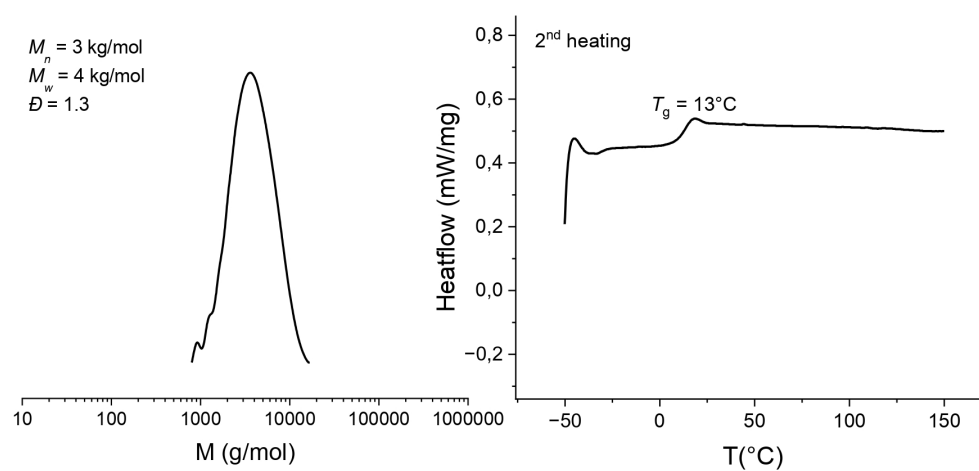
**Figure S60:**  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #7.



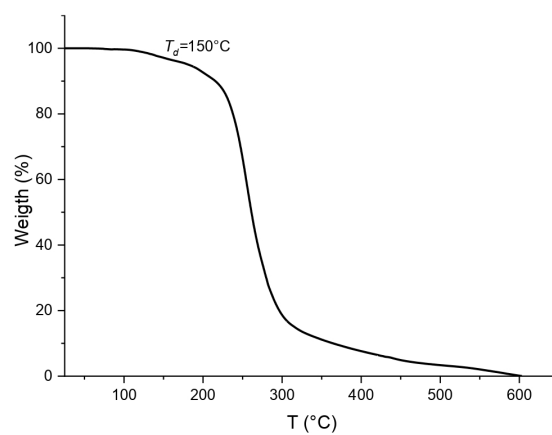
**Figure S61:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #7.



**Figure S62:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 2 entry #7.



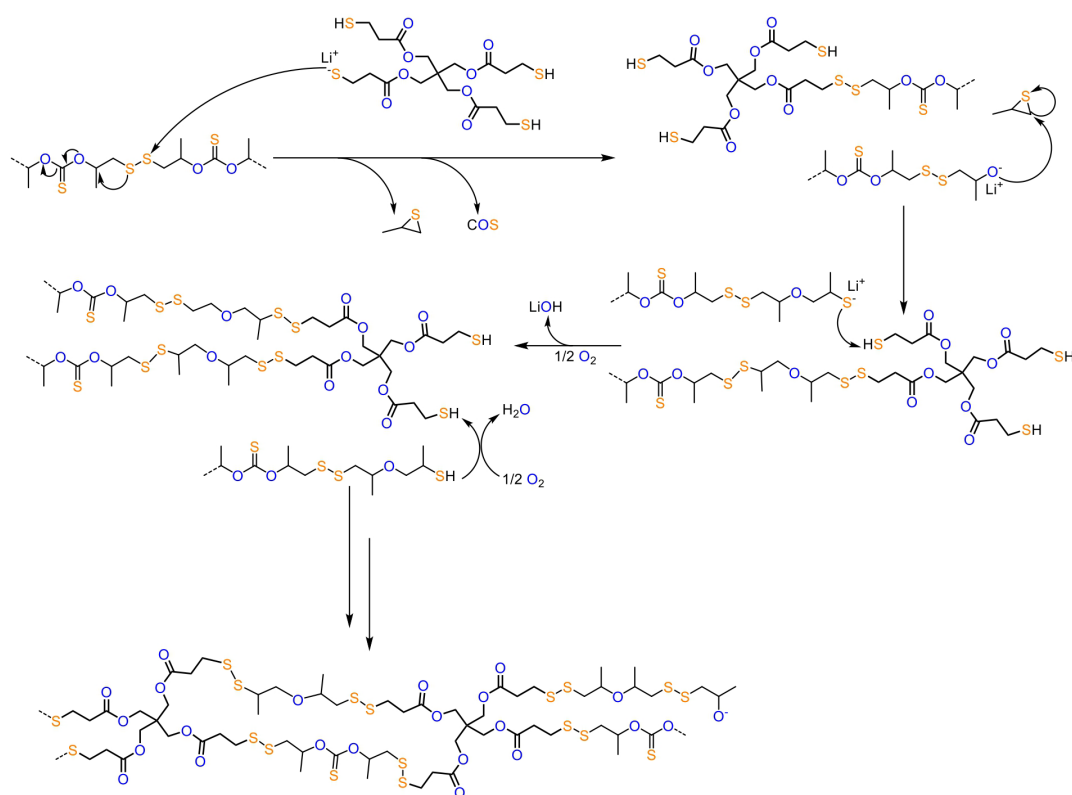
**Figure S63:** GPC curve corresponding to the polymer from table 2 entry #7.  
 (right) DSC heating curve of the polymer from table 2 entry #7.



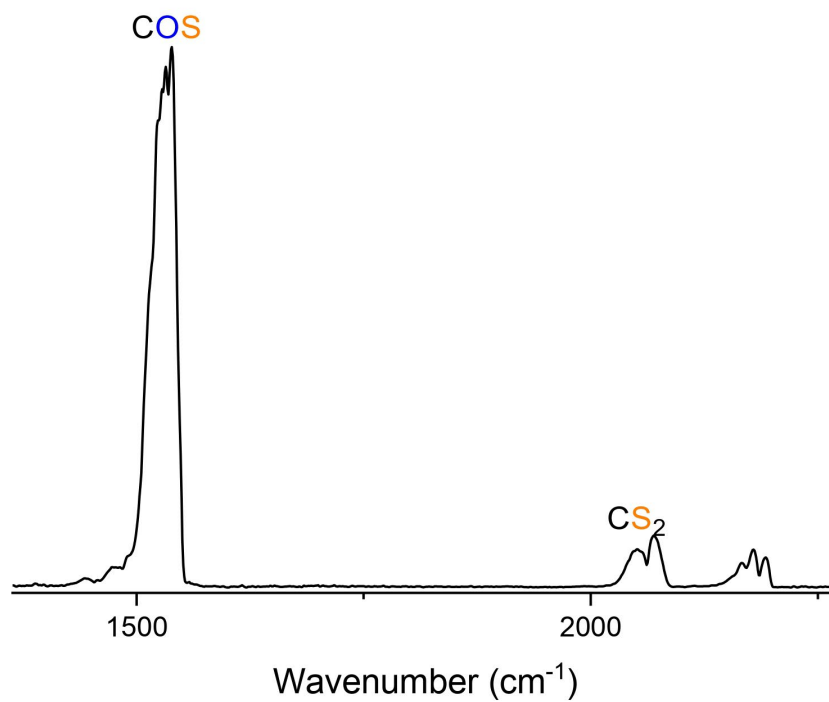
**Figure S64:** TGA data of the precipitated polymer corresponding to Table 2 run #7.

### Section S7: Cross-linking

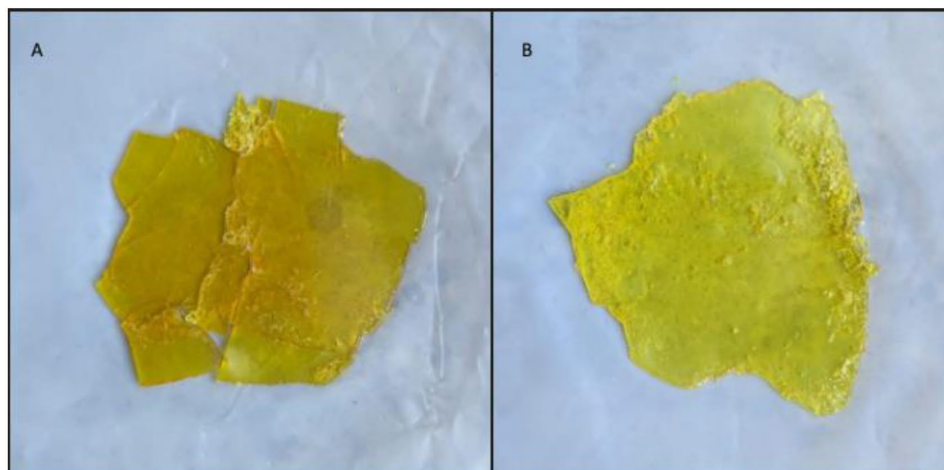
After the polymerisation (according to Section S2) went to completion (PO consumption 99% established by  $^1\text{H}$  NMR aliquot analysis), Pentaerythritol tetrakis(3-mercaptopropionate) (PTM, 25 w%) was added to the crude mixture and the reaction was let react open to air overnight causing gelation as shown in Figure 6 of the main manuscript. Residual volatiles were removed at  $80^\circ\text{C}$  prior to processing of the material into films and further analysis. In a control experiment crosslinking was attempted under an Argon atmosphere which did not result in gelation.



**Scheme S 5:** Mechanistic hypothesis for the cross-linking reaction.



**Figure S 65:** Gas phase IR of the atmosphere of the crosslinking reaction.

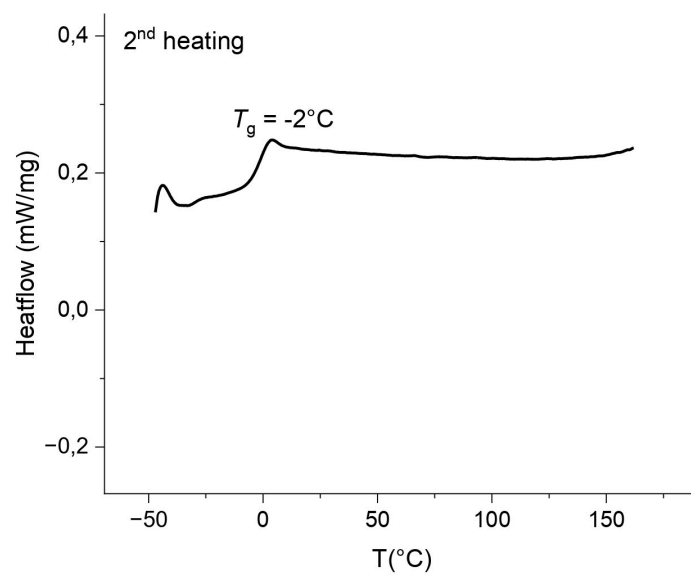


**Figure S 66:** Cross-linked materials pressed under the same conditions (90 min, 80°C, 15 kg) (A) without and (B) with additional NEt<sub>3</sub> (1w% with respect to PTM) in the network (introduced during cross-linking) showing the benefits on reprocessing.

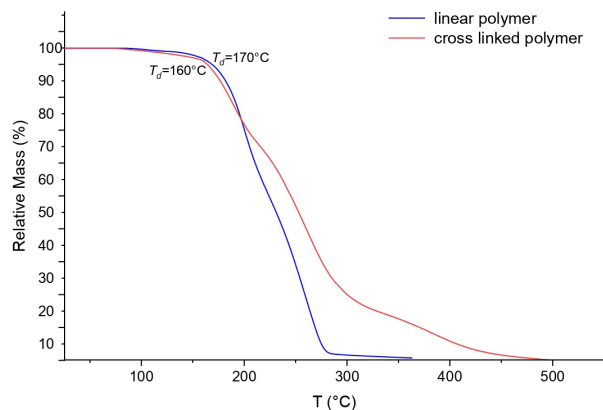




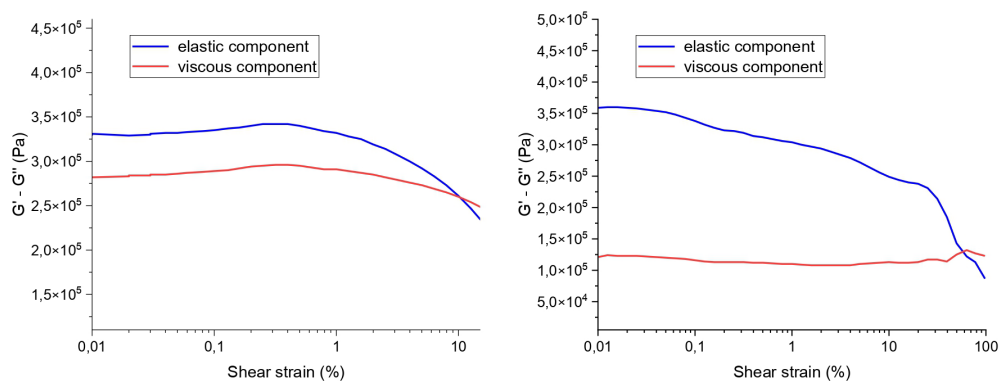
**Figure S 67:** Vial inversion test of polymerisation mixture after crosslinking.



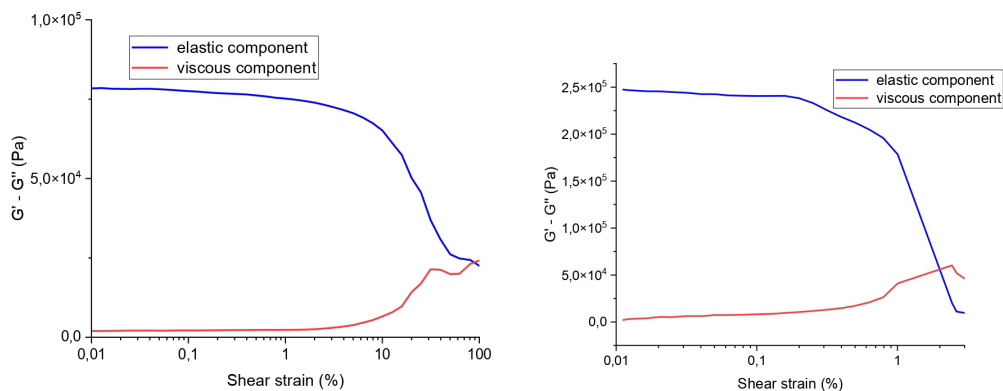
**Figure S 68:** DSC heating curve of the cross-linked material after drying from 1 eq. LiHMDS:  
1 eq. BnOH: 2000 eq. PO: 1000 eq. CS<sub>2</sub>: 1000 eq. S and 25 w% PTM.



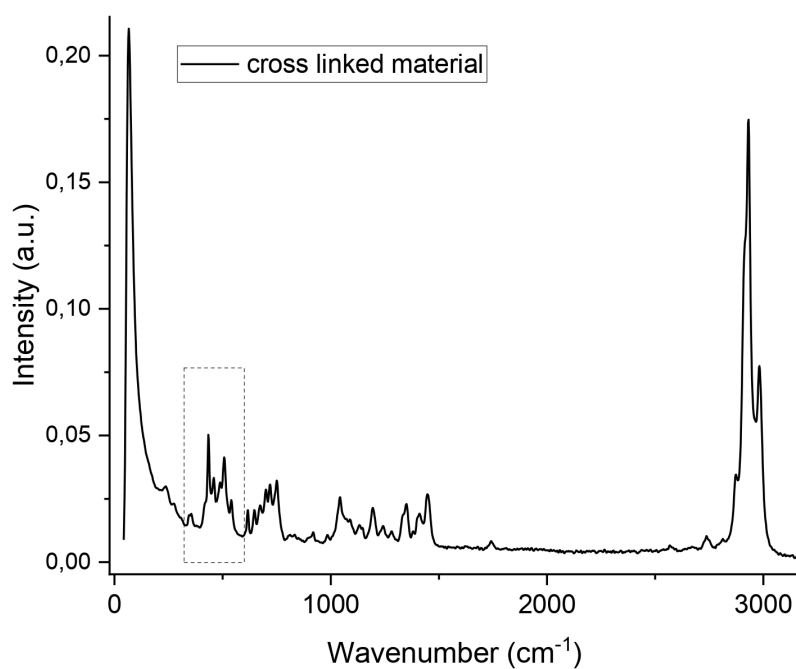
**Figure S69:** Overlaid TGA data a linear polymer (table 1 entry #1) and the cross-linked material after drying from 1 eq. LiHMDS: 1 eq. BnOH: 2000 eq. PO: 1000 eq. CS<sub>2</sub>: 1000 eq. S and 25 w% PTM.



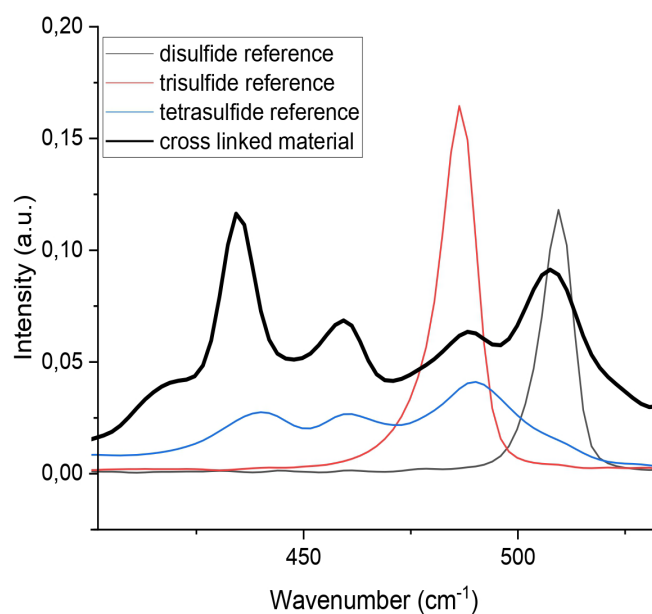
**Figure S70:** Comparison of amplitude sweep tests on (left) a linear polymer (table 1 entry #5) and (right) and the cross-linked material after drying from 1 eq. LiHMDS: 1 eq. BnOH: 2000 eq. PO: 1000 eq. CS<sub>2</sub>: 1000 eq. S: 25 w% PTM.



**Figure S71:** Amplitude sweep tests of cross-linked material after drying from 1 eq. LiHMDS: 1 eq. BnOH: 2000 eq. PO: 1000 eq. CS<sub>2</sub>: 1000 eq. S and (left) 10 w% PTM or (right) 50 w% PTM.



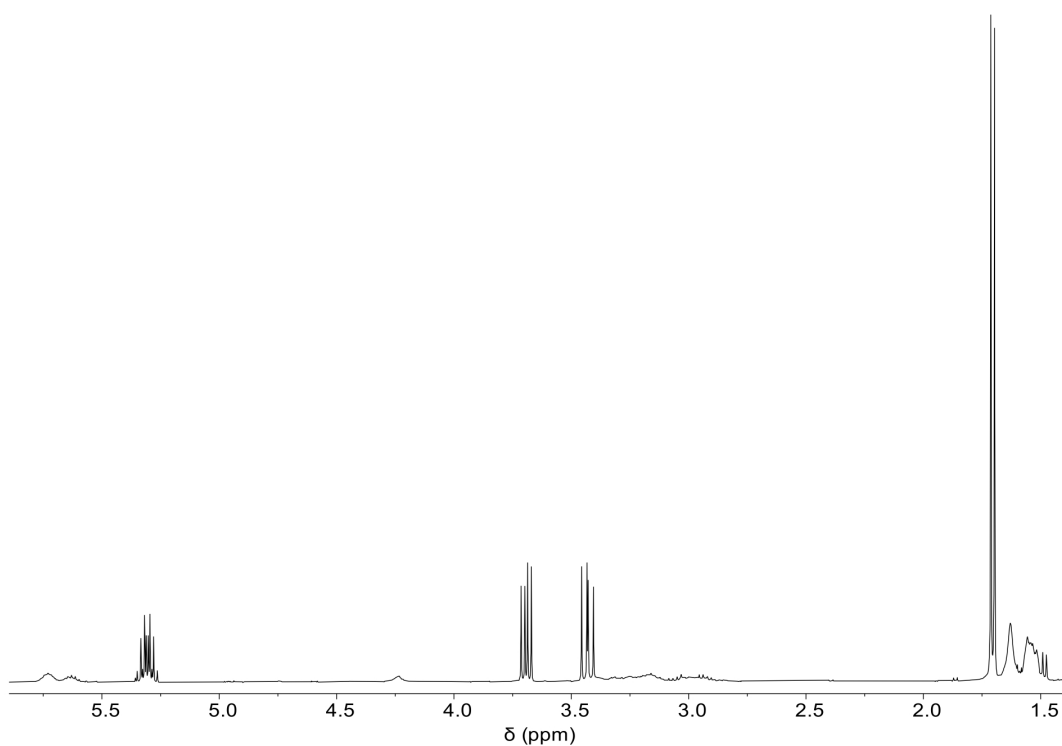
**Figure S 72:** Raman spectrum of cross-linked material after drying from 1 eq. LiHMDS: 1 eq. BnOH: 2000 eq. PO: 1000 eq. CS<sub>2</sub>: 1000 eq. S and 25w% PTM



**Figure S 73:** Zoom in of the highlighted C-S<sub>x</sub>-C stretching region of the Raman spectrum above compared to dimethyldisulfide, dimethyltrisulfide and R<sub>2</sub>-tetrasulfide [R = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference.



**Figure S 74:** Water drops on glass slide. The left slide underwent a dip-coating procedure, involving immersion in the cross-linking mixture for a duration of 5 seconds. Subsequently, the coated slide underwent air-drying overnight leading to an increase in hydrophobicity.



**Figure S 75:**  $^1\text{H}$ -NMR spectra (600 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the solution fraction of the sol-gel test.

## Section S8: DFT calculations

Final DFT single-point energy calculations (in the vacuum) were performed with the meta-hybrid functional M06-2X employing a def2-TZVPD basis set, whereas structures were obtained with the TPSSH functional and a def-TZVP basis set, using the solvation model COSMO with a dielectric constant of infinity.<sup>5-9</sup> For all DFT calculations the program package TURBOMOLE was used.<sup>10</sup>

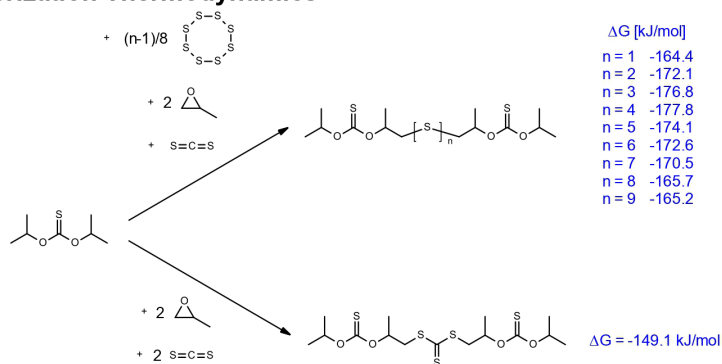
The final solvation treatment to solvate the species from single-point calculations was done with the COSMO-RS solvation model, using the software COSMOtherm in its BP\_TZVPD\_FINE\_C30\_1801 parameterization. As solvent, a 1:1 (wrt mol fraction) mixture of CS<sub>2</sub> and PO was assumed.<sup>11</sup>

For both computations of thermodynamic functions in the gas phase (within the RRHO approximation) as well as for COSMO-RS solvation, a temperature of 30 °C was chosen.

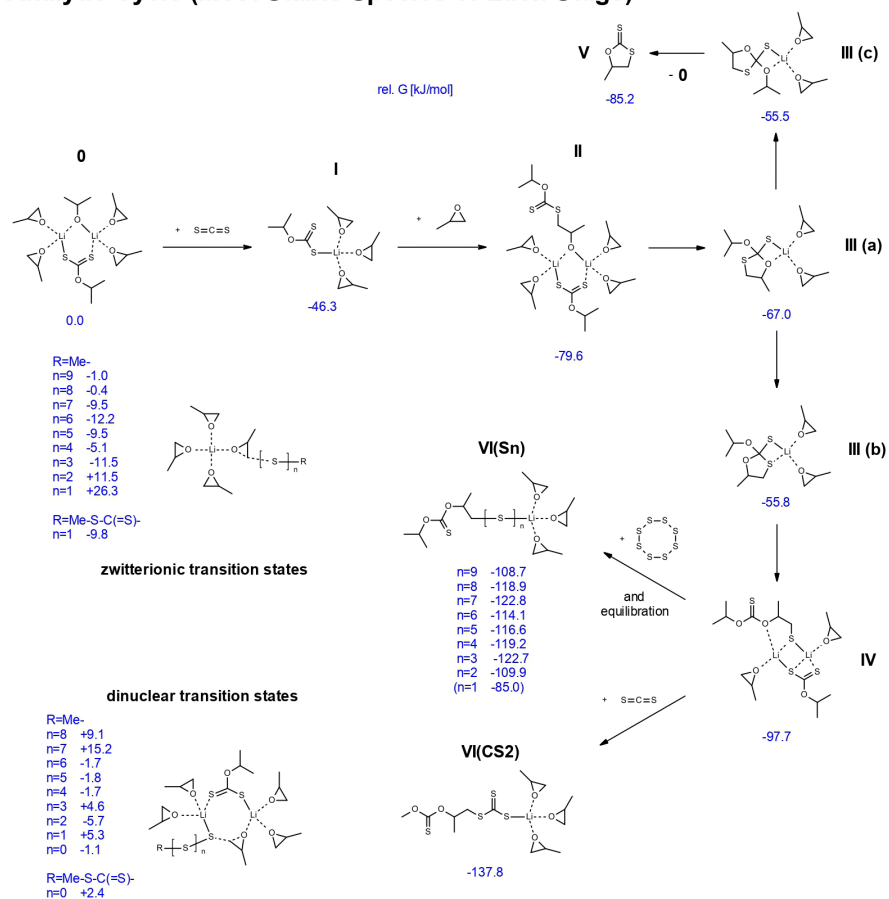
It was tried, to take into account all probable and not too complicated species for each step of the catalytic cycle, i.e. typically mononuclear Li-species were studied as well as dimeric ones (the latter also as models for not-explicitly studied higher oligomers), and for all species variable numbers of PO ligands were tried (the latter turned out in a previous work to be the most probable donors at Li) as well as the possibility that neutral donors from the growing polymer chain interact with Li as well. Furthermore, for each species generated according to these principles, conformer searches (with the optimization criterion of a minimal TPSSH/def-TZVP energy) were performed.

For the explicitly studied transition states, the PO ring opening which concludes the catalytic cycle, smaller models for the propagating polymer chain end (with the chain end of T modeled as methyl thiolate) had to be used to minimize noise in vibrational spectra of the otherwise too large and flexible structures.

## 2 Polymerization Thermodynamics

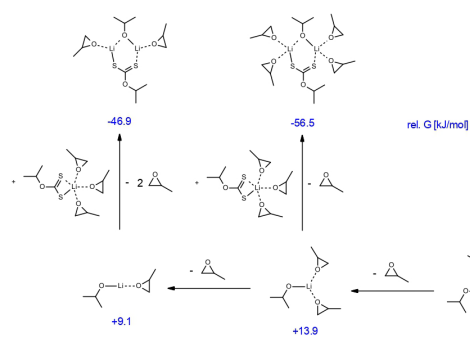


### 3 Catalytic Cycle (Most Stable Species of Each Stage)

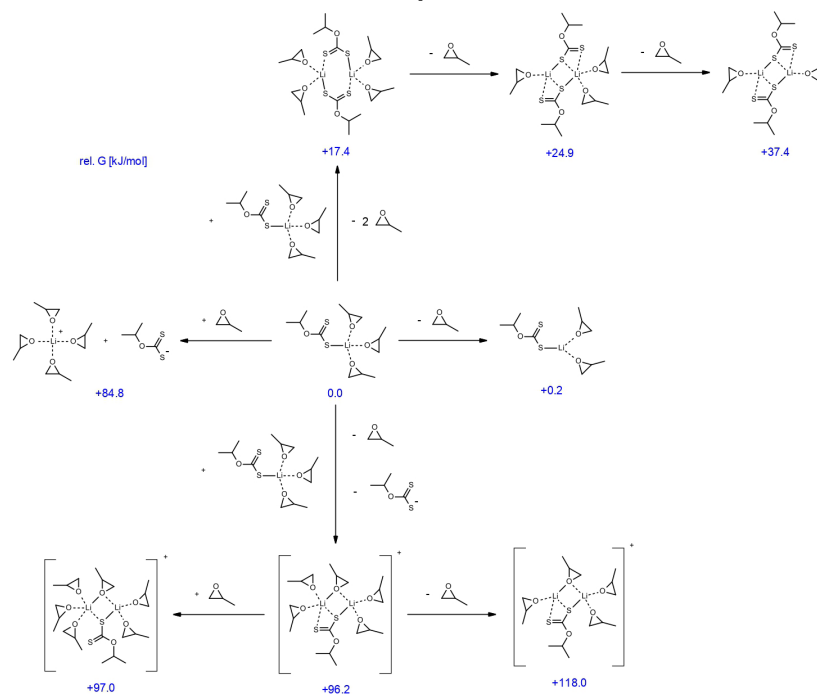


#### 4 Speciation of Intermediates and Transition States

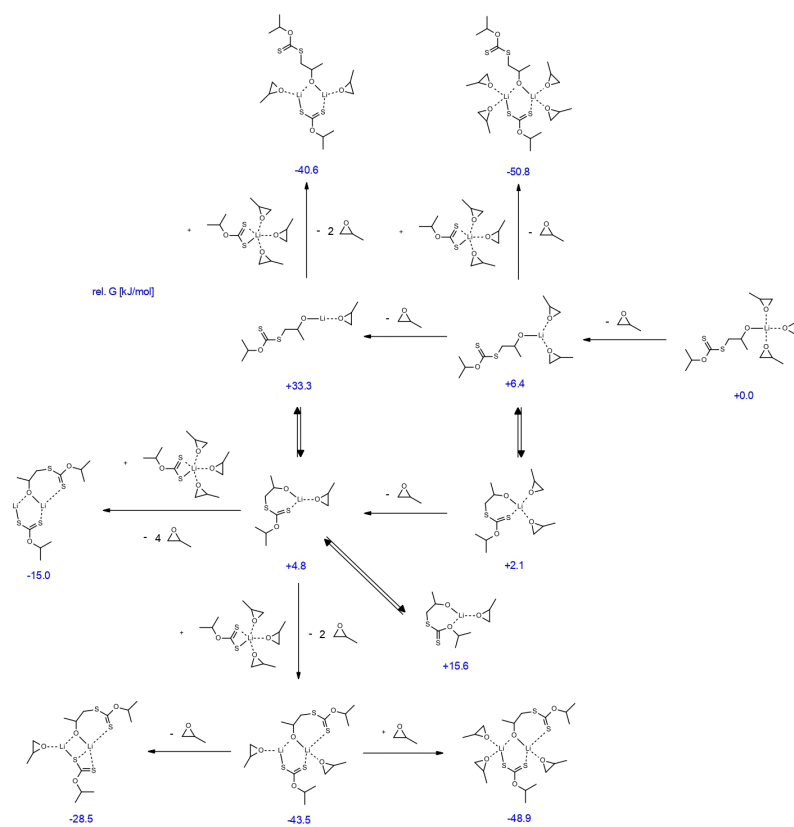
0



I

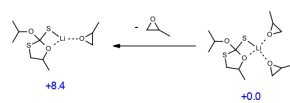


## II



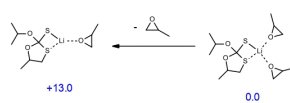
## III(a)

rel. G [kJ/mol]

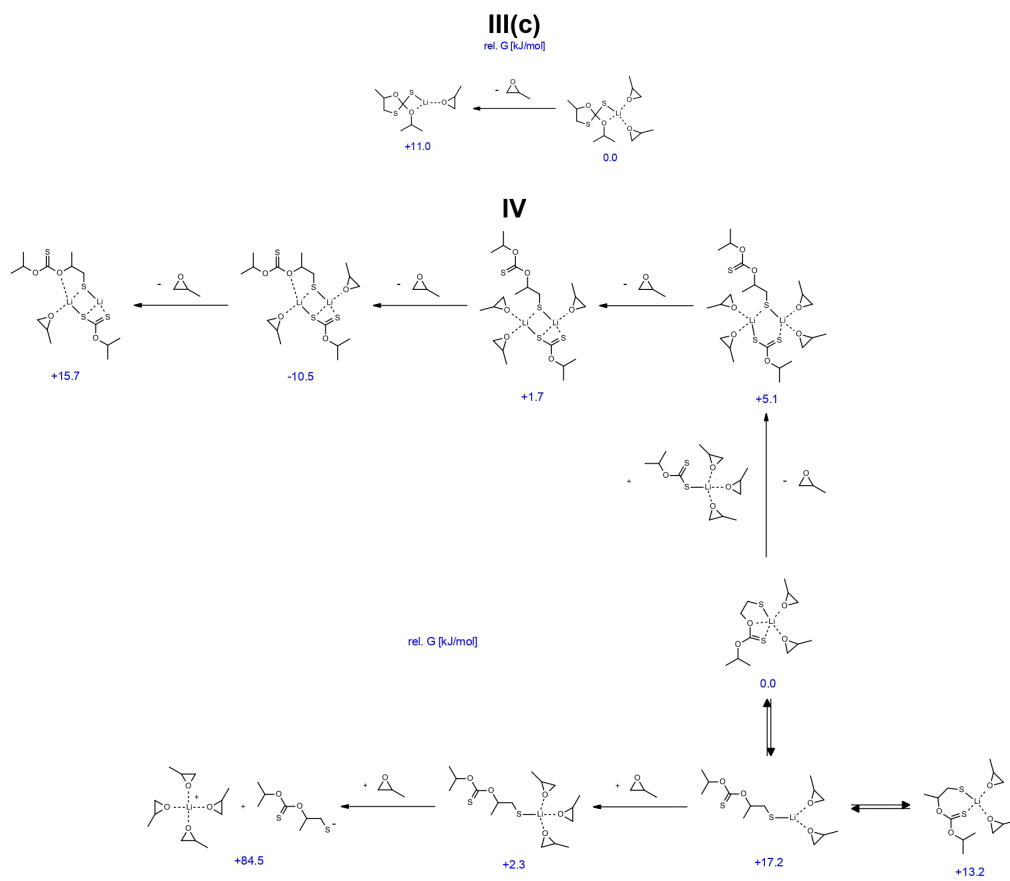


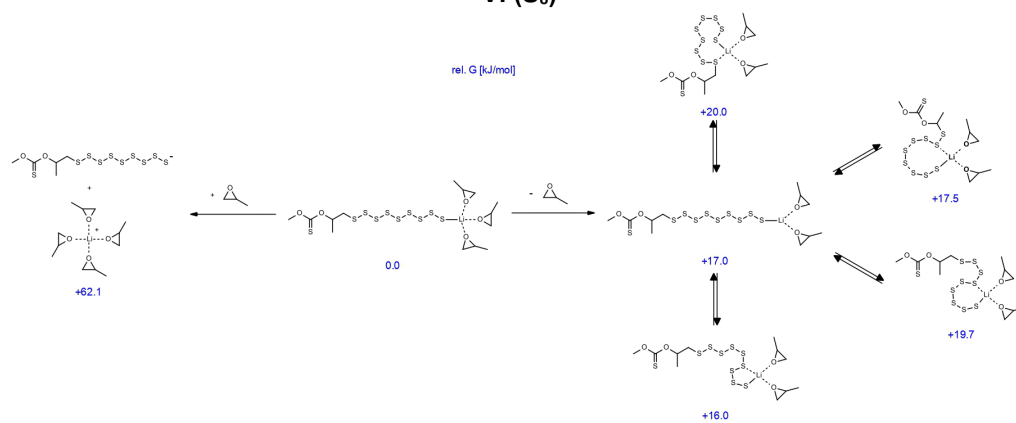
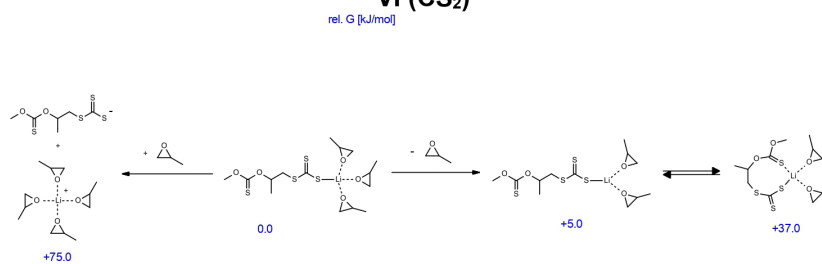
## III(b)

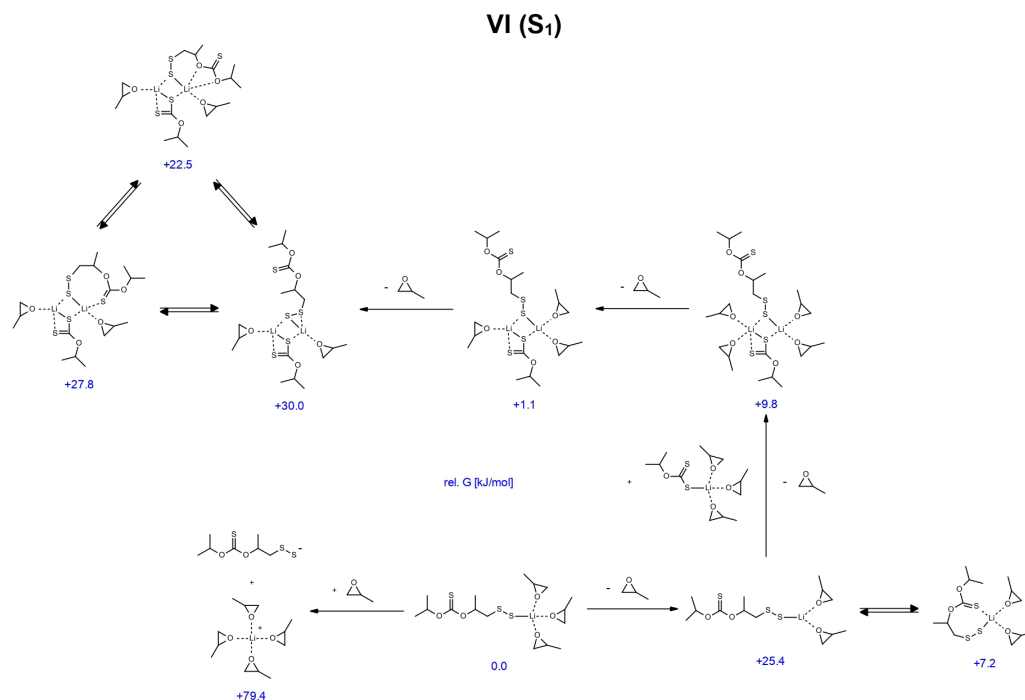
rel. G [kJ/mol]







VI (S<sub>8</sub>)VI (CS<sub>2</sub>)



## 5 Structures

**A**  
67

Energy = -2010.298630844

|    |           |            |            |
|----|-----------|------------|------------|
| Li | 4.3716451 | 1.4576979  | -0.0658468 |
| H  | 3.7631103 | 2.4866831  | 4.2350211  |
| Li | 1.4270652 | 1.4833549  | 0.2852764  |
| C  | 3.5399747 | 2.5552797  | 3.1636708  |
| H  | 4.3929693 | 3.0206454  | 2.6619183  |
| H  | 2.6711836 | 3.2080684  | 3.0296094  |
| C  | 3.2523577 | 1.1766423  | 2.5485832  |
| H  | 4.1458977 | 0.5492150  | 2.7407194  |
| O  | 3.0175090 | 1.2702872  | 1.1748391  |
| C  | 2.0759166 | 0.5071432  | 3.2755365  |
| H  | 1.8805032 | -0.4806501 | 2.8473997  |
| H  | 2.2741596 | 0.3871975  | 4.3468205  |
| H  | 1.1705781 | 1.1133626  | 3.1587759  |
| S  | 1.7359736 | 2.4326619  | -2.1053825 |
| S  | 4.0212601 | 0.4523400  | -2.3930399 |
| C  | 2.7893241 | 1.4470653  | -3.0360679 |
| O  | 2.5664909 | 1.5405493  | -4.3559481 |
| C  | 3.3587689 | 0.7813606  | -5.3424759 |
| O  | 5.2736320 | 3.2678256  | -0.3386533 |
| C  | 4.5738746 | 4.5371488  | -0.3169519 |
| C  | 5.3010596 | 4.1207302  | -1.5180274 |
| H  | 5.0177707 | 5.2746151  | 0.3448144  |
| H  | 3.4937632 | 4.4450504  | -0.2874256 |
| H  | 4.7076093 | 3.7106437  | -2.3304510 |
| C  | 6.6390138 | 4.6919383  | -1.8866116 |
| H  | 7.2602547 | 3.9358992  | -2.3740160 |

|   |            |            |            |
|---|------------|------------|------------|
| H | 6.5034323  | 5.5207213  | -2.5871611 |
| H | 7.1602125  | 5.0629051  | -1.0017327 |
| O | -0.0515260 | 2.7704968  | 0.9088586  |
| C | -0.0672075 | 4.2156952  | 1.0732596  |
| C | -0.9914991 | 3.5649110  | 0.1408417  |
| H | 0.8121620  | 4.6908192  | 0.6460746  |
| H | -0.7934970 | 3.5902841  | -0.9257871 |
| H | -2.0275198 | 3.4262966  | 0.4337991  |
| C | -0.5099226 | 4.7259713  | 2.4135633  |
| H | -0.7603062 | 5.7876293  | 2.3353830  |
| H | -1.3901443 | 4.1828760  | 2.7630843  |
| H | 0.2889714  | 4.6193086  | 3.1514666  |
| O | 6.0556130  | 0.3582123  | 0.3987265  |
| O | 0.2173991  | -0.1381154 | -0.0134225 |
| C | 7.3293681  | 0.3898892  | -0.3055649 |
| C | 7.2280438  | 0.8936021  | 1.0661464  |
| C | -0.6239604 | -0.4186535 | -1.1689442 |
| C | 0.5692257  | -1.2270333 | -0.9056121 |
| H | -0.5353007 | 0.3493808  | -1.9328980 |
| H | 1.4751626  | -1.0564329 | -1.4785681 |
| H | 0.4555770  | -2.2118312 | -0.4630081 |
| H | 7.3404856  | 1.1282287  | -1.1030152 |
| H | 7.1879310  | 1.9626562  | 1.2446352  |
| H | 7.5874813  | 0.2785799  | 1.8851955  |
| C | 7.9354232  | -0.9440366 | -0.6296949 |
| H | 8.9880743  | -0.8140676 | -0.8960563 |
| H | 7.8714344  | -1.6172858 | 0.2275000  |
| H | 7.4241284  | -1.4017283 | -1.4803718 |
| C | -2.0099782 | -0.9095481 | -0.8689750 |
| H | -2.4473300 | -1.3473454 | -1.7706151 |
| H | -1.9925875 | -1.6686392 | -0.0841364 |
| H | -2.6507386 | -0.0834246 | -0.5492144 |
| H | 4.3410885  | 0.6129846  | -4.8996357 |
| C | 3.4553953  | 1.6772440  | -6.5631293 |
| H | 4.0440157  | 1.1737548  | -7.3338269 |
| H | 2.4636769  | 1.8900225  | -6.9703880 |
| H | 3.9464068  | 2.6206299  | -6.3154216 |
| C | 2.6626876  | -0.5426635 | -5.6076292 |
| H | 3.2361690  | -1.1132927 | -6.3425442 |
| H | 2.5941257  | -1.1326275 | -4.6920282 |
| H | 1.6575098  | -0.3773924 | -6.0041370 |

**DTC**

45

Energy = -1615.639560328

|    |            |            |            |
|----|------------|------------|------------|
| S  | 0.0609328  | 0.1518291  | 3.8309081  |
| Li | 0.3396630  | -1.0845308 | 1.6169211  |
| O  | 0.2435825  | -0.0282151 | -0.1076104 |
| C  | 0.2691524  | 1.4287601  | -0.1816177 |
| C  | 1.2836031  | 0.6326746  | -0.8749881 |
| H  | 0.5628955  | 1.8772034  | 0.7637105  |
| H  | 2.2763165  | 0.5425412  | -0.4477816 |
| H  | 1.1975710  | 0.4800231  | -1.9460304 |
| C  | -0.8811078 | 2.0713462  | -0.8994483 |
| H  | -0.6265485 | 3.1066570  | -1.1428786 |
| H  | -1.1081193 | 1.5395355  | -1.8257142 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -1.7728857 | 2.0818787  | -0.2676095 |
| C | 1.6990516  | 0.6579739  | 3.7064890  |
| O | -1.6251487 | -1.7504437 | 1.4278959  |
| C | -2.4973699 | -2.2321340 | 2.4895293  |
| C | -2.8105409 | -0.9912450 | 1.7766095  |
| H | -2.0412771 | -2.1348202 | 3.4713438  |
| H | -2.6072386 | -0.0335024 | 2.2448582  |
| H | -3.5804691 | -0.9987986 | 1.0112509  |
| C | -3.2212383 | -3.5183838 | 2.2180114  |
| H | -4.0377754 | -3.6370642 | 2.9358143  |
| H | -3.6386513 | -3.5236503 | 1.2090828  |
| H | -2.5462333 | -4.3708806 | 2.3286574  |
| O | 1.0909072  | -2.9540839 | 1.5413306  |
| C | 1.7749057  | -3.5772968 | 2.6603260  |
| C | 2.4535562  | -3.4406299 | 1.3700122  |
| H | 1.3616400  | -4.5392688 | 2.9459737  |
| H | 2.0167555  | -2.8932829 | 3.4673604  |
| H | 3.1684438  | -2.6274920 | 1.2785821  |
| C | 2.6199814  | -4.5923339 | 0.4230412  |
| H | 2.5618796  | -4.2495009 | -0.6133055 |
| H | 3.6011121  | -5.0513306 | 0.5736812  |
| H | 1.8502072  | -5.3480896 | 0.5913515  |
| O | 2.0776344  | 1.5061113  | 4.6744655  |
| S | 2.7487705  | 0.1275551  | 2.4721443  |
| C | 3.4331705  | 2.0896660  | 4.7073825  |
| H | 4.1028031  | 1.3609309  | 4.2487701  |
| C | 3.4261259  | 3.3805914  | 3.9058543  |
| H | 3.1525338  | 3.1877313  | 2.8669082  |
| H | 2.7225683  | 4.0977412  | 4.3364468  |
| H | 4.4256114  | 3.8227342  | 3.9218630  |
| C | 3.7577376  | 2.2837885  | 6.1767518  |
| H | 4.7613860  | 2.7053220  | 6.2705907  |
| H | 3.0494088  | 2.9724048  | 6.6445343  |
| H | 3.7318023  | 1.3317751  | 6.7104278  |

A'  
80

Energy = -3038.091792998

|    |           |            |            |
|----|-----------|------------|------------|
| Li | 4.4340593 | 1.5613114  | -0.0966136 |
| S  | 4.0000612 | 2.7076304  | 4.8659072  |
| Li | 1.4794604 | 1.5654317  | 0.3222704  |
| C  | 3.4553481 | 2.7075918  | 3.1042283  |
| H  | 4.1866272 | 3.2834569  | 2.5402291  |
| H  | 2.4852509 | 3.2010303  | 3.0470432  |
| C  | 3.3658049 | 1.2716638  | 2.5410336  |
| H  | 4.3446729 | 0.7871334  | 2.7198378  |
| O  | 3.1018814 | 1.3741170  | 1.1808618  |
| C  | 2.3000460 | 0.4444805  | 3.2704493  |
| H  | 2.2375933 | -0.5476340 | 2.8163048  |
| H  | 2.5250327 | 0.3209903  | 4.3354977  |
| H  | 1.3217754 | 0.9279810  | 3.1779680  |
| S  | 1.7342846 | 2.5124116  | -2.0555336 |
| S  | 4.0212017 | 0.5374451  | -2.3862999 |
| C  | 2.7460370 | 1.4960558  | -3.0004863 |
| O  | 2.4514513 | 1.5322720  | -4.3080670 |
| C  | 3.1969346 | 0.7392152  | -5.3049937 |

|   |            |            |            |
|---|------------|------------|------------|
| O | 5.3099751  | 3.3776354  | -0.3660927 |
| C | 4.6171663  | 4.6506671  | -0.4204600 |
| C | 5.3900169  | 4.1871476  | -1.5746309 |
| H | 5.0392448  | 5.4091971  | 0.2316007  |
| H | 3.5362104  | 4.5655359  | -0.4320341 |
| H | 4.8291928  | 3.7486696  | -2.3953803 |
| C | 6.7445577  | 4.7394008  | -1.9090210 |
| H | 7.3813537  | 3.9640674  | -2.3429476 |
| H | 6.6407544  | 5.5420777  | -2.6445421 |
| H | 7.2311671  | 5.1412342  | -1.0180776 |
| O | 0.0627824  | 2.8642469  | 1.0188246  |
| C | -0.0692520 | 4.3082454  | 0.8897273  |
| C | -1.0916575 | 3.4171504  | 0.3357158  |
| H | 0.6492501  | 4.7276474  | 0.1897928  |
| H | -1.1186345 | 3.2236662  | -0.7315768 |
| H | -2.0256922 | 3.2846758  | 0.8723869  |
| C | -0.2763522 | 5.0725258  | 2.1643960  |
| H | -0.6534990 | 6.0725190  | 1.9324025  |
| H | -0.9984886 | 4.5653849  | 2.8071056  |
| H | 0.6663434  | 5.1834799  | 2.7062640  |
| O | 6.1164960  | 0.4737281  | 0.3831491  |
| O | 0.2905306  | -0.0741038 | 0.0825506  |
| C | 7.3718534  | 0.4149178  | -0.3529793 |
| C | 7.3222654  | 1.0199979  | 0.9800265  |
| C | -0.5095323 | -0.4514960 | -1.0752592 |
| C | 0.6823314  | -1.2230056 | -0.7133604 |
| H | -0.4050974 | 0.2589865  | -1.8909716 |
| H | 1.6050061  | -1.0854933 | -1.2680941 |
| H | 0.5632614  | -2.1728827 | -0.2015137 |
| H | 7.3829151  | 1.0918475  | -1.2030744 |
| H | 7.3172834  | 2.0999126  | 1.0809195  |
| H | 7.6855258  | 0.4549912  | 1.8326535  |
| C | 7.9306845  | -0.9568003 | -0.5928413 |
| H | 8.9795616  | -0.8777510 | -0.8920343 |
| H | 7.8692214  | -1.5639593 | 0.3123099  |
| H | 7.3856314  | -1.4590037 | -1.3961325 |
| C | -1.8992153 | -0.9365402 | -0.7829333 |
| H | -2.3016735 | -1.4469038 | -1.6623735 |
| H | -1.8990509 | -1.6336184 | 0.0574861  |
| H | -2.5593612 | -0.0974564 | -0.5479248 |
| H | 4.2037512  | 0.5979514  | -4.9105769 |
| C | 3.2164987  | 1.5845154  | -6.5648994 |
| H | 3.7671801  | 1.0541990  | -7.3455140 |
| H | 2.2015471  | 1.7714543  | -6.9245978 |
| H | 3.7104737  | 2.5414428  | -6.3840674 |
| C | 2.5013911  | -0.6005925 | -5.4770044 |
| H | 3.0401756  | -1.1957108 | -6.2187036 |
| H | 2.4894313  | -1.1532167 | -4.5360721 |
| H | 1.4744683  | -0.4601119 | -5.8240014 |
| C | 4.1947444  | 4.4247902  | 5.2394997  |
| S | 3.9073600  | 5.6908320  | 4.1983038  |
| O | 4.6018812  | 4.5051753  | 6.5026970  |
| C | 4.8833147  | 5.8177619  | 7.1367229  |
| H | 4.2316230  | 6.5421175  | 6.6479858  |
| C | 4.5175968  | 5.6445454  | 8.5974285  |
| H | 3.4660716  | 5.3729136  | 8.7064465  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| H | 5.1361637 | 4.8755051 | 9.0664147 |
| H | 4.6860955 | 6.5892929 | 9.1193082 |
| C | 6.3427268 | 6.1606067 | 6.8993265 |
| H | 6.5622560 | 7.1247619 | 7.3646333 |
| H | 6.9935883 | 5.4041543 | 7.3441101 |
| H | 6.5573519 | 6.2381772 | 5.8322274 |

I

45

Energy = -1615.652822022

|    |            |            |            |
|----|------------|------------|------------|
| O  | -3.5789945 | 3.1230762  | 1.1600624  |
| C  | -2.6866177 | 3.1540530  | 0.0781467  |
| S  | -3.5113438 | 4.3201940  | -1.1593726 |
| S  | -0.9651227 | 3.5782848  | 0.4638047  |
| Li | -0.6987789 | 1.5950041  | -0.9111703 |
| O  | 0.1546634  | -0.0301318 | -0.2437734 |
| C  | 0.5418681  | -1.3839362 | -0.6239233 |
| C  | -0.2347767 | -1.1467220 | 0.5966310  |
| H  | 1.6102107  | -1.5405206 | -0.5057916 |
| H  | 0.2543236  | -1.1619240 | 1.5644453  |
| H  | -1.2995168 | -1.3570491 | 0.5932026  |
| C  | -0.0740413 | -1.9341250 | -1.8758607 |
| H  | 0.0900799  | -3.0144433 | -1.9145443 |
| H  | -1.1495568 | -1.7463554 | -1.9006406 |
| H  | 0.3874851  | -1.4879707 | -2.7598658 |
| C  | -4.1282887 | 2.9265219  | -2.1858599 |
| H  | -3.5483125 | 2.8700004  | -3.1077383 |
| H  | -5.1811236 | 3.0727618  | -2.4242012 |
| C  | -3.9248169 | 1.6798727  | -1.3241269 |
| H  | -4.7244490 | 1.6184567  | -0.5822567 |
| O  | -2.6777570 | 1.8839158  | -0.6086764 |
| C  | -3.8272245 | 0.3911252  | -2.1136593 |
| H  | -3.6860433 | -0.4601365 | -1.4447938 |
| H  | -4.7527513 | 0.2354054  | -2.6720671 |
| H  | -2.9983506 | 0.4308102  | -2.8250507 |
| C  | -3.1924344 | 2.3220136  | 2.3250100  |
| O  | 0.0913305  | 2.0411350  | -2.6761342 |
| C  | 1.1438642  | 3.0463711  | -2.7315090 |
| C  | -0.1669010 | 3.3335610  | -3.3144445 |
| H  | 1.9689927  | 2.7756582  | -3.3816162 |
| H  | 1.4021643  | 3.4698348  | -1.7662987 |
| H  | -0.8398642 | 3.9458274  | -2.7182527 |
| C  | -0.4106126 | 3.2941842  | -4.7940452 |
| H  | -1.4206166 | 2.9383820  | -5.0130064 |
| H  | -0.3122130 | 4.3031567  | -5.2044576 |
| H  | 0.3102349  | 2.6422588  | -5.2911773 |
| H  | -2.1740550 | 1.9671183  | 2.1541430  |
| C  | -4.1565019 | 1.1510925  | 2.4491427  |
| H  | -3.9061484 | 0.5556129  | 3.3316521  |
| H  | -5.1848491 | 1.5076380  | 2.5571085  |
| H  | -4.0996854 | 0.5042953  | 1.5715855  |
| C  | -3.2181040 | 3.2422588  | 3.5345019  |
| H  | -2.9581278 | 2.6852408  | 4.4390297  |
| H  | -2.5003185 | 4.0549451  | 3.4055478  |
| H  | -4.2158407 | 3.6700521  | 3.6692818  |

T

60

Energy = -2651.696507876

|    |            |            |            |
|----|------------|------------|------------|
| O  | 3.3808271  | 2.2706410  | -3.6148409 |
| C  | 3.0281114  | 2.7277447  | -4.7995439 |
| S  | -1.2990651 | 3.3879654  | -4.2239321 |
| S  | 3.9929202  | 2.8946357  | -6.1507117 |
| Li | -1.7995316 | 1.1781101  | -3.4298948 |
| O  | -2.5894236 | -0.2700346 | -4.4913718 |
| C  | -2.6928367 | -1.6534646 | -4.0306658 |
| C  | -3.9002404 | -0.8744921 | -4.3137780 |
| H  | -2.4079664 | -1.7563911 | -2.9868732 |
| H  | -4.4789486 | -0.4576626 | -3.4960990 |
| H  | -4.4325570 | -1.0387408 | -5.2447937 |
| C  | -2.1691929 | -2.6973682 | -4.9709553 |
| H  | -2.5414314 | -3.6796053 | -4.6668788 |
| H  | -2.4965365 | -2.4992331 | -5.9934096 |
| H  | -1.0770958 | -2.7250810 | -4.9445946 |
| C  | -0.4063471 | 3.0287238  | -5.8115513 |
| H  | -0.9704515 | 3.4541138  | -6.6441475 |
| H  | -0.3517875 | 1.9496805  | -5.9658268 |
| C  | 0.9972294  | 3.6068417  | -5.8797722 |
| H  | 1.5089650  | 3.2313548  | -6.7667387 |
| O  | 1.7283273  | 3.0293003  | -4.7157392 |
| C  | 1.0856378  | 5.1168305  | -5.8057194 |
| H  | 2.1266841  | 5.4445422  | -5.8081293 |
| H  | 0.5920454  | 5.5396169  | -6.6844634 |
| H  | 0.5823536  | 5.4852383  | -4.9108763 |
| C  | 4.7781219  | 1.8512262  | -3.3410195 |
| H  | 5.1909155  | 1.5238926  | -4.2950580 |
| C  | 4.6715825  | 0.6981237  | -2.3641569 |
| H  | 4.0908231  | -0.1209957 | -2.7911162 |
| H  | 5.6768002  | 0.3331095  | -2.1417264 |
| H  | 4.2023966  | 1.0184238  | -1.4315324 |
| C  | 5.5389514  | 3.0516391  | -2.8086004 |
| H  | 6.5704679  | 2.7551696  | -2.6046141 |
| H  | 5.5546151  | 3.8614176  | -3.5405308 |
| H  | 5.0898031  | 3.4120236  | -1.8805428 |
| Li | 0.6652293  | 2.8407429  | -2.9016214 |
| O  | 1.2149085  | 4.0743590  | -1.4860821 |
| C  | 0.9982676  | 5.5200247  | -1.4615487 |
| C  | 0.3715496  | 4.6591472  | -0.4565911 |
| H  | 0.3671221  | 5.8501053  | -2.2826242 |
| H  | -0.6804988 | 4.4085706  | -0.5419881 |
| H  | 0.8015017  | 4.6064816  | 0.5380479  |
| C  | 2.2063397  | 6.3569973  | -1.1652602 |
| H  | 1.8902156  | 7.3682191  | -0.8952602 |
| H  | 2.7782266  | 5.9349070  | -0.3367181 |
| H  | 2.8516341  | 6.4273205  | -2.0444514 |
| S  | -2.3754155 | 1.0927904  | -1.0067699 |
| S  | 0.3170672  | 0.4023064  | -2.1949864 |
| C  | -0.7755228 | 0.5217082  | -0.8560659 |
| O  | -0.2542426 | 0.1000929  | 0.2932423  |
| C  | -1.0335889 | 0.0974684  | 1.5526738  |
| H  | -2.0806437 | -0.0261165 | 1.2739647  |
| C  | -0.5294694 | -1.0996127 | 2.3353805  |



|   |            |            |           |
|---|------------|------------|-----------|
| H | -0.6831187 | -2.0238076 | 1.7749176 |
| H | 0.5337157  | -0.9950337 | 2.5652490 |
| H | -1.0812857 | -1.1696398 | 3.2755146 |
| C | -0.8199364 | 1.4267105  | 2.2551273 |
| H | -1.3803882 | 1.4313303  | 3.1929544 |
| H | 0.2384915  | 1.5769118  | 2.4819950 |
| H | -1.1770873 | 2.2536745  | 1.6390422 |

TT  
58

Energy = -2643.433608955

|    |            |            |            |
|----|------------|------------|------------|
| O  | 0.0147660  | 8.3681392  | 0.4291320  |
| C  | -0.4314997 | 7.2286303  | 0.9295330  |
| S  | 1.2309572  | 2.3857370  | 0.8791102  |
| S  | -1.9857291 | 6.9058668  | 1.4594290  |
| Li | -2.0880548 | -0.2151685 | -1.7638007 |
| O  | -2.4262101 | -2.2066095 | -1.5447410 |
| C  | -1.4795233 | -3.2592096 | -1.1932645 |
| C  | -2.5918369 | -2.9316811 | -0.2978728 |
| H  | -0.5027876 | -2.8615623 | -0.9311346 |
| H  | -2.4106658 | -2.3399094 | 0.5936567  |
| H  | -3.4653658 | -3.5751788 | -0.2775049 |
| C  | -1.4858555 | -4.4732076 | -2.0742773 |
| H  | -0.9622005 | -5.2904879 | -1.5705297 |
| H  | -2.5073247 | -4.7917672 | -2.2905408 |
| H  | -0.9687723 | -4.2684719 | -3.0152223 |
| C  | 1.3692369  | 4.1824229  | 0.5547004  |
| H  | 1.1363547  | 4.3337666  | -0.5001750 |
| H  | 2.4121189  | 4.4385216  | 0.7492511  |
| C  | 0.4264658  | 5.0014016  | 1.4287666  |
| H  | -0.6084548 | 4.7132958  | 1.2456709  |
| O  | 0.5888082  | 6.3794520  | 0.9237488  |
| C  | 0.7588325  | 4.9894756  | 2.9086576  |
| H  | 0.0609476  | 5.6208092  | 3.4606570  |
| H  | 0.6755379  | 3.9700520  | 3.2916361  |
| H  | 1.7782936  | 5.3446250  | 3.0765225  |
| O  | -1.4614390 | -0.1707954 | -3.6429704 |
| C  | -1.2653683 | 0.9082843  | -4.6059553 |
| C  | -0.1168536 | 0.1700452  | -4.0766978 |
| H  | -1.4602484 | 1.8831900  | -4.1678394 |
| H  | 0.4970088  | 0.6178712  | -3.3026982 |
| H  | 0.3517479  | -0.5950633 | -4.6871159 |
| C  | -1.8147536 | 0.6645890  | -5.9798086 |
| H  | -1.3806462 | 1.3855940  | -6.6781108 |
| H  | -1.5735103 | -0.3436012 | -6.3219593 |
| H  | -2.8999530 | 0.7947464  | -5.9892145 |
| O  | -3.8943019 | 0.4879304  | -1.3511971 |
| C  | -4.5163525 | 1.7810281  | -1.5753199 |
| C  | -4.2547250 | 1.3245507  | -0.2090443 |
| H  | -5.5233923 | 1.7152270  | -1.9742515 |
| H  | -3.8602260 | 2.5169969  | -2.0268721 |
| H  | -3.3768000 | 1.7361091  | 0.2809985  |
| C  | -5.3339185 | 0.7866231  | 0.6827655  |
| H  | -4.9402985 | 0.0014233  | 1.3334313  |
| H  | -5.7159421 | 1.5910606  | 1.3174116  |
| H  | -6.1597354 | 0.3811795  | 0.0951169  |

|   |            |            |            |
|---|------------|------------|------------|
| C | -0.8698168 | 9.5523033  | 0.3205350  |
| H | -1.8845487 | 9.1713707  | 0.2059852  |
| C | -0.4132984 | 10.2822546 | -0.9269704 |
| H | -0.5025292 | 9.6425830  | -1.8068890 |
| H | -1.0447740 | 11.1614023 | -1.0732803 |
| H | 0.6233687  | 10.6132122 | -0.8286771 |
| C | -0.7411394 | 10.3646461 | 1.5962345  |
| H | -1.3903300 | 11.2407601 | 1.5277966  |
| H | -1.0473087 | 9.7783606  | 2.4645607  |
| H | 0.2878616  | 10.7043287 | 1.7353537  |
| C | -0.0600183 | 1.8019182  | -0.2162835 |
| S | -0.3330777 | 0.1221173  | 0.0037666  |
| S | -0.8593824 | 2.8033072  | -1.3065470 |

**S (S<sub>1</sub> = disulfide chain end)**

56

Energy = -2207.093911896

|    |            |            |            |
|----|------------|------------|------------|
| O  | 3.7554325  | 9.0292490  | 0.5379615  |
| C  | 3.0553434  | 8.1310679  | 1.2114785  |
| S  | 2.3915820  | 3.0667406  | 0.8645993  |
| S  | 1.7410583  | 8.4286738  | 2.2072258  |
| Li | -0.4509760 | 1.6211598  | -0.5473653 |
| O  | 0.1245809  | 1.7033739  | -2.4548618 |
| C  | 0.1716514  | 2.9772593  | -3.1733765 |
| C  | 1.4094786  | 2.2704790  | -2.8407480 |
| H  | -0.0970001 | 3.8118210  | -2.5309468 |
| H  | 2.0108508  | 2.6035141  | -2.0003848 |
| H  | 1.9193346  | 1.7030360  | -3.6124563 |
| C  | -0.4137615 | 2.9709211  | -4.5540983 |
| H  | -0.0860770 | 3.8649822  | -5.0920423 |
| H  | -0.0899992 | 2.0890450  | -5.1104111 |
| H  | -1.5056828 | 2.9834973  | -4.5099869 |
| C  | 3.2144516  | 4.6576064  | 0.4564790  |
| H  | 2.8080514  | 5.0207980  | -0.4881368 |
| H  | 4.2708830  | 4.4097969  | 0.3224474  |
| C  | 3.0355511  | 5.7097767  | 1.5413292  |
| H  | 1.9747738  | 5.8842111  | 1.7228091  |
| O  | 3.5850170  | 6.9471383  | 0.9427598  |
| C  | 3.7822195  | 5.4301791  | 2.8302779  |
| H  | 3.6098778  | 6.2275260  | 3.5550871  |
| H  | 3.4215384  | 4.4907683  | 3.2534575  |
| H  | 4.8548565  | 5.3396239  | 2.6414211  |
| O  | -2.4464521 | 1.6630452  | -0.5388008 |
| C  | -3.2746659 | 1.9720536  | 0.6248344  |
| C  | -3.2639957 | 2.8652664  | -0.5355617 |
| H  | -2.6773664 | 2.2719973  | 1.4820175  |
| H  | -2.6990648 | 3.7911224  | -0.5004208 |
| H  | -4.0905380 | 2.8323008  | -1.2377717 |
| C  | -4.4034496 | 1.0230049  | 0.8974312  |
| H  | -5.1074572 | 1.4866178  | 1.5940968  |
| H  | -4.9340521 | 0.7743848  | -0.0237188 |
| H  | -4.0303496 | 0.1031636  | 1.3543265  |
| O  | 0.0649099  | -0.1599454 | 0.1725512  |
| C  | 1.2243270  | -0.9772521 | -0.1378028 |
| C  | -0.1220962 | -1.4849096 | -0.4121353 |
| H  | 1.7567262  | -1.3306618 | 0.7390627  |

|   |            |            |            |
|---|------------|------------|------------|
| H | 1.8369676  | -0.6009772 | -0.9503590 |
| H | -0.4676662 | -1.4352489 | -1.4410776 |
| C | -0.7921082 | -2.4986867 | 0.4669534  |
| H | -1.8693540 | -2.3192800 | 0.5085098  |
| H | -0.6309791 | -3.4995531 | 0.0571696  |
| H | -0.3852459 | -2.4641500 | 1.4792490  |
| C | 3.4444691  | 10.4744908 | 0.6367450  |
| H | 2.3820364  | 10.5479650 | 0.8684479  |
| C | 3.7483122  | 11.0470299 | -0.7334857 |
| H | 3.1380926  | 10.5666925 | -1.5006430 |
| H | 3.5202072  | 12.1152379 | -0.7292543 |
| H | 4.8040537  | 10.9197881 | -0.9843645 |
| C | 4.2815604  | 11.0681821 | 1.7551649  |
| H | 4.0608328  | 12.1350909 | 1.8375111  |
| H | 4.0479885  | 10.5951152 | 2.7106535  |
| H | 5.3471775  | 10.9489295 | 1.5448922  |
| S | 0.3312174  | 3.5375705  | 0.7465350  |

**S (S<sub>2</sub> = trisulfide chain end)**

57

Energy = -2605.321444350

|    |            |            |            |
|----|------------|------------|------------|
| O  | 1.7202993  | 10.3235385 | 1.7799062  |
| C  | 0.7528848  | 9.7962349  | 1.0499611  |
| S  | -1.8197350 | 5.3745721  | 1.0475345  |
| S  | 0.2810258  | 10.2733567 | -0.4842611 |
| Li | -0.6994094 | 1.7137865  | -1.5885326 |
| O  | 0.5593161  | 0.6699613  | -2.7408777 |
| C  | 1.3570487  | 1.2669619  | -3.8108643 |
| C  | 2.0093960  | 0.6563499  | -2.6509103 |
| H  | 1.2828242  | 2.3513413  | -3.8140781 |
| H  | 2.4174645  | 1.2869414  | -1.8677499 |
| H  | 2.4427955  | -0.3339371 | -2.7445529 |
| C  | 1.2818321  | 0.5853224  | -5.1444233 |
| H  | 2.1058954  | 0.9300046  | -5.7753285 |
| H  | 1.3547698  | -0.4979159 | -5.0327151 |
| H  | 0.3439731  | 0.8296782  | -5.6498758 |
| C  | -0.6562897 | 6.6096608  | 1.7652329  |
| H  | 0.3586745  | 6.2837241  | 1.5375249  |
| H  | -0.8134196 | 6.5564648  | 2.8452154  |
| C  | -0.9041604 | 8.0157365  | 1.2379524  |
| H  | -0.8296560 | 8.0312758  | 0.1504386  |
| O  | 0.2290132  | 8.8054717  | 1.7609185  |
| C  | -2.1943055 | 8.6551293  | 1.7135709  |
| H  | -2.2932363 | 9.6628975  | 1.3070247  |
| H  | -3.0413218 | 8.0592791  | 1.3679505  |
| H  | -2.2200552 | 8.7015585  | 2.8046914  |
| O  | -2.3537843 | 1.8067182  | -2.6743913 |
| C  | -3.5933641 | 2.5677260  | -2.5428317 |
| C  | -2.7186499 | 2.7688146  | -3.7000278 |
| H  | -3.5322438 | 3.3104539  | -1.7522419 |
| H  | -2.0755267 | 3.6412721  | -3.7433552 |
| H  | -2.9820821 | 2.3153581  | -4.6500433 |
| C  | -4.8615893 | 1.7715187  | -2.6233108 |
| H  | -5.7040522 | 2.4473623  | -2.7941552 |
| H  | -4.8180837 | 1.0513882  | -3.4428760 |
| H  | -5.0404916 | 1.2364814  | -1.6873190 |

|   |            |            |            |
|---|------------|------------|------------|
| O | -1.1188231 | 0.6101710  | 0.0133436  |
| C | -1.4996474 | 1.1737661  | 1.2993122  |
| C | -0.2281096 | 0.4615858  | 1.1628177  |
| H | -2.3432943 | 0.6719389  | 1.7614787  |
| H | -1.5037316 | 2.2589755  | 1.3253870  |
| H | 0.6645045  | 1.0741763  | 1.0670761  |
| C | -0.0302270 | -0.9387866 | 1.6615943  |
| H | 0.6507767  | -1.4885101 | 1.0069025  |
| H | 0.4114625  | -0.9090962 | 2.6615277  |
| H | -0.9817553 | -1.4710214 | 1.7137396  |
| C | 2.5037696  | 11.4822599 | 1.2890122  |
| H | 2.5041925  | 11.4169315 | 0.2011749  |
| C | 3.8983259  | 11.2923171 | 1.8513055  |
| H | 4.3310475  | 10.3503435 | 1.5096401  |
| H | 4.5336768  | 12.1104203 | 1.5046025  |
| H | 3.8842044  | 11.3045012 | 2.9437522  |
| C | 1.8177129  | 12.7543611 | 1.7519402  |
| H | 2.3894519  | 13.6157996 | 1.3986052  |
| H | 0.8073020  | 12.8235872 | 1.3451112  |
| H | 1.7706701  | 12.7923192 | 2.8427508  |
| S | -1.1321685 | 5.1441040  | -0.9284170 |
| S | 0.4663440  | 3.7834684  | -0.9668063 |

**S (S<sub>3</sub> = tetrasulfide chain end)**

58

Energy = -3003.546605738

|    |            |            |            |
|----|------------|------------|------------|
| O  | 1.3543491  | 7.7549257  | -5.8625738 |
| C  | 0.5288152  | 7.0429152  | -5.1166527 |
| S  | 0.3983731  | 5.6014381  | -0.2101003 |
| S  | -0.6255815 | 5.9557413  | -5.6533281 |
| Li | 1.6247793  | -0.2552427 | 0.9188678  |
| O  | 2.7669622  | -1.4427942 | -0.1968462 |
| C  | 3.2199171  | -1.1202581 | -1.5482088 |
| C  | 4.1820277  | -1.2194979 | -0.4486915 |
| H  | 2.9206456  | -0.1200500 | -1.8501238 |
| H  | 4.5739091  | -0.3151796 | 0.0045781  |
| H  | 4.7874164  | -2.1148668 | -0.3533176 |
| C  | 3.0518934  | -2.2036974 | -2.5714138 |
| H  | 3.6621195  | -1.9729505 | -3.4490790 |
| H  | 3.3651463  | -3.1695278 | -2.1706208 |
| H  | 2.0093120  | -2.2711500 | -2.8922504 |
| C  | 1.0543984  | 6.5569315  | -1.6392461 |
| H  | 1.9446799  | 6.0472704  | -2.0067449 |
| H  | 1.3478060  | 7.5208430  | -1.2169845 |
| C  | 0.0279411  | 6.7290602  | -2.7513415 |
| H  | -0.3156468 | 5.7573209  | -3.1068765 |
| O  | 0.7935523  | 7.3461572  | -3.8507288 |
| C  | -1.1380330 | 7.6346965  | -2.4069829 |
| H  | -1.8162952 | 7.7218994  | -3.2572962 |
| H  | -1.6918749 | 7.2095906  | -1.5675215 |
| H  | -0.7819456 | 8.6282165  | -2.1255178 |
| O  | -0.1951008 | -0.4101692 | 0.1703831  |
| C  | -1.2560593 | -1.3599055 | 0.4923656  |
| C  | -1.4616649 | 0.0788283  | 0.6802715  |
| H  | -1.0271099 | -1.9459242 | 1.3783011  |
| H  | -1.4131468 | 0.5089105  | 1.6752437  |

|   |            |            |            |
|---|------------|------------|------------|
| H | -2.0424617 | 0.6318998  | -0.0504769 |
| C | -1.8380817 | -2.1098214 | -0.6686350 |
| H | -2.7864817 | -2.5646912 | -0.3695922 |
| H | -2.0203857 | -1.4402557 | -1.5112591 |
| H | -1.1637657 | -2.9090850 | -0.9865123 |
| O | 1.6009922  | -1.0415112 | 2.7537564  |
| C | 1.3298235  | -0.3396050 | 3.9972752  |
| C | 2.6380516  | -0.9603932 | 3.7789754  |
| H | 0.6045915  | -0.8394142 | 4.6307726  |
| H | 1.2165040  | 0.7340876  | 3.8891894  |
| H | 3.4527200  | -0.3025075 | 3.4879413  |
| C | 3.0288552  | -2.2587062 | 4.4201943  |
| H | 3.6723412  | -2.8386837 | 3.7539975  |
| H | 3.5859708  | -2.0566821 | 5.3391841  |
| H | 2.1458267  | -2.8509315 | 4.6681380  |
| C | 1.3108676  | 7.6732301  | -7.3425837 |
| H | 0.9454577  | 6.6760190  | -7.5865423 |
| C | 2.7442005  | 7.8592981  | -7.7985088 |
| H | 3.3899346  | 7.0852712  | -7.3797939 |
| H | 2.7804816  | 7.7874683  | -8.8879136 |
| H | 3.1237182  | 8.8404236  | -7.5035824 |
| C | 0.3557070  | 8.7366600  | -7.8524721 |
| H | 0.3160881  | 8.6852645  | -8.9431079 |
| H | -0.6519519 | 8.5753158  | -7.4651975 |
| H | 0.6977450  | 9.7331236  | -7.5634518 |
| S | 0.2968455  | 3.6324925  | -0.9486090 |
| S | 2.2076520  | 2.7456649  | -0.8315444 |
| S | 2.5623313  | 2.0111120  | 1.0867884  |

**S (S<sub>4</sub> = pentasulfide chain end)**

59

Energy = -3401.769873451

|    |            |            |            |
|----|------------|------------|------------|
| O  | -4.9515227 | 1.7739723  | -3.4911717 |
| C  | -3.6611921 | 2.0380670  | -3.3940889 |
| S  | 0.5232487  | 2.3881303  | -0.0163696 |
| S  | -2.8654895 | 3.3901783  | -3.9768395 |
| Li | 1.7451092  | 4.9745369  | 5.3421080  |
| O  | 1.7766060  | 4.2070388  | 7.1773683  |
| C  | 1.2023051  | 2.9108270  | 7.5309138  |
| C  | 2.6502308  | 3.1204991  | 7.5924345  |
| H  | 0.8200205  | 2.3835860  | 6.6606631  |
| H  | 3.2813098  | 2.7326122  | 6.7996256  |
| H  | 3.1224061  | 3.2856903  | 8.5553346  |
| C  | 0.3381957  | 2.8893863  | 8.7564902  |
| H  | 0.1969348  | 1.8555736  | 9.0835499  |
| H  | 0.8009029  | 3.4540857  | 9.5681073  |
| H  | -0.6456982 | 3.3138760  | 8.5410083  |
| C  | -1.5580150 | 0.3676236  | -1.0848982 |
| H  | -2.2044391 | 0.8804719  | -0.3733973 |
| H  | -1.8286718 | -0.6904603 | -1.1100967 |
| C  | -1.6608087 | 0.9986237  | -2.4674326 |
| H  | -1.3202709 | 2.0340905  | -2.4413480 |
| O  | -3.1095084 | 1.0248880  | -2.7341727 |
| C  | -0.9789407 | 0.2214671  | -3.5764569 |
| H  | -1.1206888 | 0.7246597  | -4.5341114 |
| H  | 0.0923016  | 0.1629461  | -3.3745743 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -1.3806927 | -0.7924128 | -3.6378352 |
| O | -0.0721774 | 5.6859795  | 5.0520736  |
| C | -0.6326427 | 6.9868005  | 5.4076662  |
| C | -0.5636316 | 6.5634730  | 4.0066658  |
| H | 0.1285895  | 7.6815294  | 5.7522631  |
| H | 0.2050835  | 6.9659844  | 3.3553933  |
| H | -1.4611037 | 6.1998287  | 3.5176773  |
| C | -1.9095131 | 6.9558777  | 6.1941928  |
| H | -2.3795325 | 7.9426940  | 6.1634415  |
| H | -2.6040204 | 6.2230864  | 5.7788785  |
| H | -1.7105112 | 6.7072316  | 7.2396344  |
| O | 3.0298785  | 6.4999566  | 5.3243832  |
| C | 3.6825692  | 7.0713614  | 4.1574174  |
| C | 4.4842724  | 6.4328728  | 5.2031673  |
| H | 3.6302307  | 8.1542305  | 4.1155290  |
| H | 3.4846920  | 6.5419001  | 3.2312100  |
| H | 4.8339152  | 5.4225539  | 5.0067779  |
| C | 5.2641191  | 7.2203185  | 6.2134908  |
| H | 5.2768664  | 6.7046273  | 7.1769479  |
| H | 6.2972472  | 7.3267259  | 5.8714670  |
| H | 4.8344165  | 8.2150500  | 6.3467074  |
| C | -5.8691420 | 2.6972799  | -4.2022358 |
| H | -5.4444765 | 3.6957395  | -4.0982524 |
| C | -7.1941563 | 2.5848426  | -3.4746894 |
| H | -7.0875574 | 2.8655839  | -2.4254332 |
| H | -7.9123695 | 3.2618617  | -3.9425764 |
| H | -7.5878249 | 1.5673356  | -3.5350998 |
| C | -5.9268592 | 2.2854337  | -5.6616294 |
| H | -6.6026385 | 2.9586392  | -6.1943784 |
| H | -4.9413728 | 2.3516253  | -6.1258569 |
| H | -6.3042316 | 1.2648734  | -5.7596525 |
| S | -0.3202397 | 2.8736970  | 1.8812600  |
| S | 0.8995062  | 2.1200099  | 3.4117931  |
| S | 2.5666554  | 3.3291145  | 3.7106323  |
| S | 0.1556668  | 0.3765159  | -0.4161509 |

**S (S<sub>5</sub> = hexasulfide chain end)**

60

Energy = -3799.992512349

|    |            |            |            |
|----|------------|------------|------------|
| O  | -3.4043795 | 0.6817352  | -6.0320696 |
| C  | -3.0366052 | 0.0726562  | -4.9197904 |
| S  | -1.5899499 | 0.8555829  | 0.2507731  |
| S  | -1.8305444 | -1.0755472 | -4.7540736 |
| Li | 1.7127925  | 5.1956935  | 5.5483218  |
| O  | 1.8391125  | 4.2054476  | 7.2702817  |
| C  | 1.1044521  | 2.9914017  | 7.6179047  |
| C  | 2.5595882  | 2.9560332  | 7.4567840  |
| H  | 0.5083169  | 2.6232008  | 6.7870414  |
| H  | 2.9900684  | 2.5534890  | 6.5458197  |
| H  | 3.1901823  | 2.9448494  | 8.3395904  |
| C  | 0.4432680  | 2.9878533  | 8.9640496  |
| H  | 0.1726632  | 1.9630841  | 9.2332191  |
| H  | 1.1140952  | 3.3855492  | 9.7278933  |
| H  | -0.4712317 | 3.5857351  | 8.9447878  |
| C  | -3.9430004 | 1.2764916  | -1.7059122 |
| H  | -3.3180424 | 2.1162352  | -2.0079029 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -4.9917147 | 1.5770583  | -1.7635487 |
| C | -3.6700638 | 0.0502191  | -2.5677615 |
| H | -2.6385948 | -0.2821935 | -2.4459430 |
| O | -3.8038457 | 0.5526473  | -3.9457173 |
| C | -4.6454855 | -1.0940358 | -2.3719424 |
| H | -4.4005101 | -1.9191248 | -3.0422909 |
| H | -4.5815609 | -1.4561496 | -1.3440115 |
| H | -5.6685561 | -0.7632496 | -2.5650037 |
| O | -0.0210124 | 6.1364051  | 5.5581464  |
| C | -0.3649660 | 7.4536609  | 6.0859661  |
| C | -0.5234386 | 7.1579311  | 4.6592987  |
| H | 0.5142230  | 8.0216389  | 6.3781417  |
| H | 0.2033711  | 7.5285884  | 3.9439914  |
| H | -1.5131576 | 6.9465925  | 4.2680331  |
| C | -1.5281403 | 7.4957615  | 7.0316241  |
| H | -1.8729456 | 8.5278771  | 7.1385512  |
| H | -2.3536957 | 6.8866739  | 6.6586236  |
| H | -1.2332613 | 7.1326244  | 8.0193503  |
| O | 3.1739140  | 6.5511104  | 5.5917516  |
| C | 3.7940171  | 7.2096268  | 4.4539369  |
| C | 4.5887271  | 6.3228392  | 5.3064086  |
| H | 3.8894172  | 8.2839897  | 4.5708448  |
| H | 3.4438367  | 6.8590191  | 3.4886232  |
| H | 4.7751022  | 5.3189139  | 4.9337595  |
| C | 5.5560633  | 6.8419569  | 6.3277317  |
| H | 5.5820010  | 6.1858490  | 7.2013371  |
| H | 6.5599191  | 6.8708098  | 5.8951520  |
| H | 5.2814930  | 7.8492778  | 6.6460229  |
| C | -2.7660429 | 0.3526497  | -7.3300861 |
| H | -1.7510703 | 0.0281236  | -7.1018337 |
| C | -2.7649821 | 1.6477354  | -8.1174061 |
| H | -2.2068344 | 2.4237239  | -7.5905313 |
| H | -2.2861954 | 1.4731677  | -9.0835891 |
| H | -3.7846907 | 1.9974931  | -8.2948222 |
| C | -3.5569348 | -0.7675424 | -7.9806365 |
| H | -3.0972162 | -1.0171155 | -8.9399529 |
| H | -3.5529495 | -1.6625327 | -7.3560523 |
| H | -4.5889182 | -0.4571163 | -8.1602522 |
| S | -0.8316770 | 2.8142981  | 0.4198825  |
| S | -1.1100417 | 3.4697877  | 2.4198473  |
| S | 0.3442504  | 2.6211288  | 3.6736692  |
| S | -3.6643282 | 0.9641830  | 0.0858261  |
| S | 2.1138093  | 3.7137175  | 3.6196737  |

**S (S<sub>6</sub> = heptasulfide chain end)**

61

Energy = -4198.214776288

|    |            |            |             |
|----|------------|------------|-------------|
| O  | -6.0811581 | -7.7223882 | -10.6942606 |
| C  | -6.3613832 | -6.8617613 | -9.7332748  |
| S  | -4.2258136 | -3.3451201 | -6.1962746  |
| S  | -7.3225038 | -7.1313701 | -8.3900954  |
| Li | 1.6215989  | -0.8635947 | 0.1881604   |
| O  | 1.6653901  | -1.9969053 | 1.8161768   |
| C  | 0.9218391  | -3.2350457 | 2.0397803   |
| C  | 2.3792335  | -3.2615323 | 1.9047430   |
| H  | 0.3442315  | -3.5266701 | 1.1667219   |

|   |            |             |             |
|---|------------|-------------|-------------|
| H | 2.8242236  | -3.5866810  | 0.9702349   |
| H | 2.9936523  | -3.3527242  | 2.7941274   |
| C | 0.2332595  | -3.3554959  | 3.3664255   |
| H | -0.0459034 | -4.3990077  | 3.5364046   |
| H | 0.8896917  | -3.0315850  | 4.1761648   |
| H | -0.6787420 | -2.7537069  | 3.3830717   |
| C | -4.4796124 | -3.8989894  | -9.2247462  |
| H | -3.6960732 | -4.6175404  | -8.9883763  |
| H | -4.2826365 | -3.4721336  | -10.2109734 |
| C | -5.8575071 | -4.5472320  | -9.1659879  |
| H | -6.0694986 | -4.9063505  | -8.1584565  |
| O | -5.7244051 | -5.7324335  | -10.0294643 |
| C | -6.9889146 | -3.6875450  | -9.6949193  |
| H | -7.9323786 | -4.2333871  | -9.6471859  |
| H | -7.0812317 | -2.7885336  | -9.0827881  |
| H | -6.7948376 | -3.3910816  | -10.7282016 |
| O | 0.1990310  | 0.4798256   | 0.4312732   |
| C | -0.5981806 | 1.1617491   | -0.5856213  |
| C | -1.2472975 | 0.3435029   | 0.4415577   |
| H | -0.4758391 | 0.7121128   | -1.5672941  |
| H | -1.6058574 | -0.6502268  | 0.1946146   |
| H | -1.7246355 | 0.8310939   | 1.2850692   |
| C | -0.5880353 | 2.6601674   | -0.5314375  |
| H | -1.4150702 | 3.0502186   | -1.1310036  |
| H | -0.7020143 | 3.0131490   | 0.4953000   |
| H | 0.3443162  | 3.0542009   | -0.9434501  |
| O | 3.3303627  | 0.1535572   | 0.1218054   |
| C | 3.7945802  | 0.9910197   | -0.9725101  |
| C | 4.5809164  | -0.1734511  | -0.5600018  |
| H | 4.1085678  | 1.9813370   | -0.6600377  |
| H | 3.1833706  | 0.9383385   | -1.8674149  |
| H | 4.4935614  | -1.0674215  | -1.1717381  |
| C | 5.8278910  | -0.0521837  | 0.2638781   |
| H | 5.9270065  | -0.9049106  | 0.9402653   |
| H | 6.6992659  | -0.0407514  | -0.3966657  |
| H | 5.8189197  | 0.8691146   | 0.8492814   |
| C | -6.6528072 | -9.0912860  | -10.6840857 |
| H | -6.8092180 | -9.3527559  | -9.6376451  |
| C | -5.5955380 | -9.9729231  | -11.3185016 |
| H | -4.6618397 | -9.9286015  | -10.7551352 |
| H | -5.9509374 | -11.0057472 | -11.3182154 |
| H | -5.4052069 | -9.6728579  | -12.3517268 |
| C | -7.9708727 | -9.0659399  | -11.4362325 |
| H | -8.3988256 | -10.0713377 | -11.4368420 |
| H | -8.6819375 | -8.3913954  | -10.9560816 |
| H | -7.8182109 | -8.7525852  | -12.4716418 |
| S | -2.2307937 | -3.9347117  | -5.8294215  |
| S | -1.1318492 | -2.2383915  | -5.2770133  |
| S | -1.5227243 | -1.7778251  | -3.2416625  |
| S | -4.3168198 | -2.4673757  | -8.0802583  |
| S | -0.3594773 | -2.9854568  | -1.9770453  |
| S | 1.5853582  | -2.2647182  | -1.8422535  |

**S (S<sub>7</sub> = octasulfide chain end)**

62

Energy = -4596.436880566



|    |             |            |            |
|----|-------------|------------|------------|
| O  | -12.9072117 | -4.8498484 | -4.9895225 |
| C  | -11.9494216 | -4.1572032 | -5.5774210 |
| S  | -6.6252449  | -3.2216355 | -5.5713598 |
| S  | -11.9222378 | -2.5060096 | -5.8470529 |
| Li | 1.6314005   | -0.7770884 | 0.4302528  |
| O  | 2.0974980   | -1.8926590 | 2.0013728  |
| C  | 1.3825955   | -3.0626243 | 2.5080534  |
| C  | 2.7075760   | -3.2107105 | 1.9042015  |
| H  | 0.5290346   | -3.3202068 | 1.8863324  |
| H  | 2.7945496   | -3.5853430 | 0.8896382  |
| H  | 3.5725354   | -3.3382339 | 2.5462340  |
| C  | 1.1631369   | -3.1065819 | 3.9907792  |
| H  | 0.8843525   | -4.1219821 | 4.2855755  |
| H  | 2.0706142   | -2.8221417 | 4.5267782  |
| H  | 0.3513229   | -2.4346887 | 4.2806388  |
| C  | -8.6869813  | -5.4676008 | -6.0391880 |
| H  | -8.6975263  | -5.4583762 | -4.9500009 |
| H  | -8.7962795  | -6.4980639 | -6.3849167 |
| C  | -9.7811517  | -4.5721642 | -6.6076849 |
| H  | -9.6142066  | -3.5332698 | -6.3216391 |
| O  | -10.9971615 | -5.0235718 | -5.9111084 |
| C  | -9.9980350  | -4.7051819 | -8.1022837 |
| H  | -10.8118449 | -4.0547038 | -8.4258140 |
| H  | -9.0900876  | -4.4073963 | -8.6305031 |
| H  | -10.2348577 | -5.7385331 | -8.3648732 |
| O  | 0.3931597   | 0.6481402  | 1.0108905  |
| C  | -0.6485098  | 1.2832424  | 0.2057111  |
| C  | -0.9982288  | 0.5407455  | 1.4189826  |
| H  | -0.7953379  | 0.7723163  | -0.7422929 |
| H  | -1.4119964  | -0.4590443 | 1.3392740  |
| H  | -1.2280233  | 1.0866550  | 2.3280202  |
| C  | -0.6203223  | 2.7816655  | 0.1595975  |
| H  | -1.5770176  | 3.1507021  | -0.2198464 |
| H  | -0.4529221  | 3.1983195  | 1.1546039  |
| H  | 0.1681121   | 3.1313046  | -0.5116484 |
| O  | 3.3108301   | 0.0903640  | -0.1866035 |
| C  | 3.5240469   | 0.7407990  | -1.4703105 |
| C  | 4.3254974   | -0.4279452 | -1.1019496 |
| H  | 3.9602370   | 1.7307496  | -1.3895401 |
| H  | 2.7010365   | 0.6309635  | -2.1687784 |
| H  | 4.0363952   | -1.3803145 | -1.5386017 |
| C  | 5.7467659   | -0.3156794 | -0.6372520 |
| H  | 5.9694651   | -1.0821417 | 0.1092263  |
| H  | 6.4185355   | -0.4644739 | -1.4871030 |
| H  | 5.9384072   | 0.6689444  | -0.2066324 |
| C  | -14.1468635 | -4.1890568 | -4.5133441 |
| H  | -13.8755346 | -3.1619276 | -4.2699373 |
| C  | -14.5607465 | -4.9565952 | -3.2736538 |
| H  | -13.7781115 | -4.9205980 | -2.5135973 |
| H  | -15.4638232 | -4.5009954 | -2.8618891 |
| H  | -14.7782677 | -5.9999331 | -3.5145342 |
| C  | -15.1686899 | -4.2256291 | -5.6347431 |
| H  | -16.0875326 | -3.7427509 | -5.2936072 |
| H  | -14.8048881 | -3.6889877 | -6.5127466 |
| H  | -15.4004076 | -5.2565173 | -5.9123801 |
| S  | -5.9628722  | -3.7202747 | -3.6313372 |

|   |            |            |            |
|---|------------|------------|------------|
| S | -3.9372446 | -4.2625814 | -3.7427791 |
| S | -2.7690171 | -2.5236523 | -3.8287698 |
| S | -7.0030230 | -4.9871519 | -6.6029084 |
| S | -2.5117033 | -1.7611261 | -1.8653581 |
| S | -1.0051065 | -2.8342932 | -0.8709539 |
| S | 0.8798536  | -2.1840826 | -1.4583073 |

**S (S<sub>8</sub> = nonasulfide chain end)**

63

Energy = -4994.659721357

|    |             |             |            |
|----|-------------|-------------|------------|
| O  | 4.5504802   | 0.3193450   | 1.8827632  |
| C  | 4.5717564   | -0.7230602  | 1.0727367  |
| S  | 0.8469055   | -2.1933929  | 0.3927178  |
| S  | 5.6490345   | -2.0034196  | 1.1088594  |
| Li | -6.6570497  | -12.8815947 | -0.8286830 |
| O  | -6.5525348  | -12.2073759 | -2.6847748 |
| C  | -7.5641558  | -12.1131356 | -3.7340076 |
| C  | -6.8504447  | -10.9173877 | -3.2783799 |
| H  | -8.5691839  | -12.2650620 | -3.3496803 |
| H  | -7.3398641  | -10.2153815 | -2.6116535 |
| H  | -6.0436321  | -10.5185931 | -3.8843728 |
| C  | -7.2341741  | -12.8008134 | -5.0248633 |
| H  | -7.9039425  | -12.4399976 | -5.8103707 |
| H  | -6.2036274  | -12.5959808 | -5.3206274 |
| H  | -7.3714258  | -13.8809531 | -4.9315957 |
| C  | 1.8164057   | -1.5693707  | -1.0453415 |
| H  | 1.4335010   | -0.5591069  | -1.2061614 |
| H  | 1.5637483   | -2.1758704  | -1.9146150 |
| C  | 3.3195537   | -1.5551284  | -0.8387734 |
| H  | 3.6787052   | -2.5200229  | -0.4798006 |
| O  | 3.5633713   | -0.5695384  | 0.2209087  |
| C  | 4.0680492   | -1.1330194  | -2.0925475 |
| H  | 5.1405202   | -1.0946721  | -1.8950712 |
| H  | 3.8897693   | -1.8644689  | -2.8835991 |
| H  | 3.7296303   | -0.1530606  | -2.4350331 |
| O  | -8.5091843  | -12.6118233 | -0.1642135 |
| C  | -8.9215381  | -12.4997855 | 1.2342431  |
| C  | -9.0847259  | -11.3673809 | 0.3211304  |
| H  | -8.0681351  | -12.4670345 | 1.9064246  |
| H  | -8.3866149  | -10.5377147 | 0.3625416  |
| H  | -10.0658983 | -11.1524379 | -0.0891297 |
| C  | -10.0711667 | -13.3683845 | 1.6498857  |
| H  | -10.4754100 | -13.0048022 | 2.5984713  |
| H  | -10.8643985 | -13.3499534 | 0.8999073  |
| H  | -9.7426198  | -14.4003969 | 1.7963607  |
| O  | -6.2699999  | -14.8294123 | -0.9532785 |
| C  | -7.0407060  | -16.0292076 | -0.6847974 |
| C  | -5.7908809  | -15.7846688 | 0.0403358  |
| H  | -7.0472964  | -16.7374875 | -1.5069623 |
| H  | -7.9946160  | -15.8534719 | -0.1986783 |
| H  | -5.8744435  | -15.4017247 | 1.0539784  |
| C  | -4.5138121  | -16.4954103 | -0.2967556 |
| H  | -3.6553775  | -15.8372370 | -0.1413629 |
| H  | -4.3979802  | -17.3648541 | 0.3560563  |
| H  | -4.5202170  | -16.8342126 | -1.3345648 |
| C  | 5.5700220   | 0.4816124   | 2.9477587  |

|   |            |             |            |
|---|------------|-------------|------------|
| H | 5.8997980  | -0.5219179  | 3.2156911  |
| C | 4.8458173  | 1.1477296   | 4.1005821  |
| H | 4.0125629  | 0.5322918   | 4.4449348  |
| H | 5.5453060  | 1.2772089   | 4.9293504  |
| H | 4.4687571  | 2.1308004   | 3.8091603  |
| C | 6.7212320  | 1.2949475   | 2.3846964  |
| H | 7.4800151  | 1.4220748   | 3.1606281  |
| H | 7.1810688  | 0.7852126   | 1.5362149  |
| H | 6.3779175  | 2.2829512   | 2.0691842  |
| S | 1.2439909  | -4.2320448  | 0.3915764  |
| S | 0.0085476  | -5.1478153  | -1.0566926 |
| S | -1.9146752 | -5.3851391  | -0.2565449 |
| S | -1.9495033 | -7.1033668  | 0.9531302  |
| S | -2.1184670 | -8.7937250  | -0.2761543 |
| S | -4.1408581 | -9.0264991  | -0.8830429 |
| S | -5.2755114 | -9.9064163  | 0.6492623  |
| S | -4.9750902 | -11.9600898 | 0.7200061  |

**Starting from here: Polymer chain end was modeled by simpler Me- to reduce noise in computations of large flexible transition state species, making also a new reference species necessary**

**T (new reference for all following transition states)**

36

Energy = -1025.370609522

|    |            |            |            |
|----|------------|------------|------------|
| S  | -2.6559031 | 2.5690310  | -2.3056193 |
| Li | -3.3789441 | 1.5750025  | -4.3611963 |
| O  | -3.4316218 | 2.8754751  | -5.8872765 |
| C  | -4.2193159 | 2.8786016  | -7.1159721 |
| C  | -4.3288155 | 3.9829647  | -6.1599709 |
| H  | -5.0091608 | 2.1319457  | -7.0999534 |
| H  | -5.1862347 | 4.0443711  | -5.4982604 |
| H  | -3.8191321 | 4.9180059  | -6.3687829 |
| C  | -3.4420288 | 2.9983736  | -8.3930554 |
| H  | -4.1192068 | 3.2690246  | -9.2077297 |
| H  | -2.6712934 | 3.7669846  | -8.3070935 |
| H  | -2.9690629 | 2.0465202  | -8.6474599 |
| C  | -1.9024021 | 1.1907966  | -1.3191361 |
| H  | -0.9769889 | 0.8419095  | -1.7815306 |
| H  | -2.5892155 | 0.3449992  | -1.2425131 |
| H  | -1.6718604 | 1.5350440  | -0.3088824 |
| O  | -5.2528082 | 0.8355854  | -4.2015002 |
| C  | -5.7650620 | 0.3207026  | -2.9335968 |
| C  | -6.2919372 | 1.5655550  | -3.4937322 |
| H  | -5.0365991 | 0.4254071  | -2.1337051 |
| H  | -5.9644153 | 2.5129767  | -3.0774880 |
| H  | -7.2518934 | 1.5595906  | -3.9996556 |
| C  | -6.5134885 | -0.9770799 | -3.0059317 |
| H  | -7.0852235 | -1.1194219 | -2.0847038 |
| H  | -7.2044089 | -0.9814942 | -3.8513523 |
| H  | -5.8218687 | -1.8173492 | -3.1076212 |
| O  | -2.2593477 | 0.0829466  | -5.0979752 |
| C  | -2.6553551 | -1.0585795 | -5.9034553 |
| C  | -2.0102965 | -1.2656971 | -4.6043312 |
| H  | -2.0712740 | -1.1789220 | -6.8098942 |
| H  | -3.7282327 | -1.1871455 | -6.0025164 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -2.6546653 | -1.5264341 | -3.7687777 |
| C | -0.5692741 | -1.6623767 | -4.4767786 |
| H | -0.1228963 | -1.2107629 | -3.5873348 |
| H | -0.4976081 | -2.7489687 | -4.3781070 |
| H | -0.0022984 | -1.3516324 | -5.3563504 |

**TS (TT into PO)**

49

Energy = -2053.119406520

|    |            |            |            |
|----|------------|------------|------------|
| S  | 3.6543864  | -5.2981647 | -1.0377337 |
| C  | 3.0121006  | -6.5493091 | -2.2001727 |
| H  | 1.9512711  | -6.7160581 | -2.0240930 |
| H  | 3.5816198  | -7.4540566 | -1.9841357 |
| H  | 3.1811209  | -6.2301598 | -3.2269160 |
| C  | 2.7421269  | -3.8171241 | -1.4041990 |
| S  | 3.2805074  | -2.5058572 | -0.4188446 |
| S  | 1.5267815  | -3.7715921 | -2.5683054 |
| Li | -1.7925829 | -0.0243157 | -0.6327283 |
| O  | -3.1088664 | 0.9023889  | 0.5768251  |
| C  | -3.8745943 | 0.2211816  | 1.6063710  |
| C  | -4.5647217 | 0.9026127  | 0.5087992  |
| H  | -3.8226017 | 0.6989946  | 2.5792504  |
| H  | -3.7774164 | -0.8590624 | 1.5921639  |
| H  | -4.9394915 | 0.2798046  | -0.2991632 |
| C  | -5.2299504 | 2.2358744  | 0.6823440  |
| H  | -5.1471523 | 2.8292908  | -0.2316116 |
| H  | -6.2922863 | 2.0887272  | 0.8956194  |
| H  | -4.7795492 | 2.7892778  | 1.5085986  |
| O  | -1.8984189 | 1.0162725  | -2.3422363 |
| C  | -0.8166335 | 1.1753450  | -3.2984562 |
| C  | -1.2635192 | 2.3219425  | -2.5053053 |
| H  | -1.1323136 | 1.0888236  | -4.3329233 |
| H  | 0.0994449  | 0.6603784  | -3.0295773 |
| H  | -0.6545152 | 2.5909073  | -1.6461997 |
| C  | -2.1297403 | 3.4054495  | -3.0751568 |
| H  | -2.8141377 | 3.7908102  | -2.3152400 |
| H  | -1.5013039 | 4.2330787  | -3.4156480 |
| H  | -2.7100809 | 3.0342131  | -3.9219974 |
| O  | -0.0610520 | 0.0428291  | 0.0907969  |
| C  | 1.4338067  | -0.9201856 | -0.4932180 |
| C  | 0.7266667  | -0.8911814 | 0.7937722  |
| H  | 2.1003919  | -0.1007943 | -0.7161970 |
| H  | 1.0165249  | -1.4882754 | -1.3118577 |
| H  | 0.1967521  | -1.8214987 | 1.0318773  |
| C  | 1.4470473  | -0.3404632 | 2.0066403  |
| H  | 0.7229675  | -0.0959438 | 2.7885294  |
| H  | 2.1496965  | -1.0771423 | 2.4067832  |
| H  | 1.9972433  | 0.5668002  | 1.7427715  |
| O  | -2.6588001 | -1.8091908 | -0.8922591 |
| C  | -2.1930081 | -3.1735160 | -1.0519217 |
| C  | -3.1404567 | -2.6033138 | -2.0138838 |
| H  | -2.5582283 | -3.8530575 | -0.2883359 |
| H  | -1.1437053 | -3.2658136 | -1.3159215 |
| H  | -2.7365109 | -2.2631837 | -2.9639773 |
| C  | -4.6009881 | -2.9458053 | -1.9997753 |
| H  | -5.2019223 | -2.0856503 | -2.3062792 |

H -4.7910988 -3.7597991 -2.7047728  
H -4.9146690 -3.2636980 -1.0036997

**TS (S into PO – S<sub>0</sub> = monosulfide chain end)**

46

Energy = -1218.547037461

|    |            |            |            |
|----|------------|------------|------------|
| C  | 0.5796694  | 2.4602675  | -1.9935667 |
| H  | 0.7654949  | 2.8953197  | -1.0079759 |
| H  | -0.5007049 | 2.4291020  | -2.1570451 |
| H  | 1.0197214  | 3.1194839  | -2.7448648 |
| S  | 1.3149681  | 0.7671273  | -2.1085432 |
| Li | -2.1863443 | -0.7856673 | 2.0681481  |
| O  | -3.2241656 | 0.5998224  | 1.0666933  |
| C  | -3.2884459 | 2.0294738  | 1.3128065  |
| C  | -4.5128381 | 1.2254134  | 1.3385185  |
| H  | -3.0725979 | 2.6352919  | 0.4385583  |
| H  | -2.8261006 | 2.3474563  | 2.2413370  |
| H  | -4.9068358 | 0.9543382  | 2.3144125  |
| C  | -5.4957495 | 1.2251988  | 0.2058187  |
| H  | -5.9581108 | 0.2410248  | 0.0968484  |
| H  | -6.2872771 | 1.9510298  | 0.4110640  |
| H  | -5.0067272 | 1.4946526  | -0.7320968 |
| O  | -3.3342611 | -2.4145546 | 2.1192771  |
| C  | -2.9274114 | -3.8073944 | 2.0876876  |
| C  | -3.8458994 | -3.2882667 | 1.0711563  |
| H  | -3.3230305 | -4.3979385 | 2.9077241  |
| H  | -1.8821543 | -3.9655851 | 1.8433546  |
| H  | -3.4243980 | -3.0570707 | 0.0964375  |
| C  | -5.3199817 | -3.5635341 | 1.1078951  |
| H  | -5.8813468 | -2.7116369 | 0.7157715  |
| H  | -5.5440154 | -4.4328920 | 0.4836214  |
| H  | -5.6501812 | -3.7684389 | 2.1279471  |
| O  | -0.4266107 | -1.0526549 | 1.4236846  |
| C  | 0.2511146  | -0.0373758 | 0.1470482  |
| C  | 0.0908139  | -1.4837325 | 0.1667310  |
| H  | 1.1131842  | 0.4057309  | 0.6155565  |
| H  | -0.5734429 | 0.5868597  | -0.1512678 |
| H  | -0.6768184 | -1.8760045 | -0.5069714 |
| C  | 1.3072160  | -2.3754770 | 0.2400520  |
| H  | 1.0306566  | -3.3610878 | 0.6249575  |
| H  | 1.7421533  | -2.5051745 | -0.7546780 |
| H  | 2.0606440  | -1.9391264 | 0.9005851  |
| O  | -2.0985791 | -0.1736508 | 3.9737475  |
| C  | -1.7238863 | -0.9739994 | 5.1255597  |
| C  | -3.0506542 | -0.3565190 | 5.0649815  |
| H  | -0.9545700 | -0.5203211 | 5.7418207  |
| H  | -1.6100312 | -2.0335684 | 4.9215868  |
| H  | -3.8795435 | -0.9995826 | 4.7813892  |
| C  | -3.3967806 | 0.8753436  | 5.8476027  |
| H  | -4.1026999 | 1.4998890  | 5.2945490  |
| H  | -3.8679084 | 0.5858234  | 6.7909712  |
| H  | -2.5013237 | 1.4597193  | 6.0675567  |

**TS (S into PO – S<sub>1</sub> = disulfide chain end)**

47

Energy = -1616.780358098

|    |            |            |            |
|----|------------|------------|------------|
| C  | -4.7160981 | 1.8085320  | -1.6041233 |
| H  | -5.4003644 | 2.2216180  | -0.8629644 |
| H  | -4.9911775 | 2.1646326  | -2.5994339 |
| H  | -3.6921471 | 2.1042025  | -1.3764987 |
| S  | -4.8520814 | -0.0208695 | -1.6404269 |
| S  | -4.2935155 | -0.5913577 | 0.3024139  |
| Li | 0.9345918  | -0.2978132 | -1.5851591 |
| O  | 0.2711876  | 1.1857480  | -2.7471164 |
| C  | -0.6711600 | 1.0853623  | -3.8478075 |
| C  | 0.6797035  | 1.5999279  | -4.0847321 |
| H  | -1.4980033 | 1.7848018  | -3.7808341 |
| H  | -0.9222906 | 0.0692409  | -4.1329798 |
| H  | 1.3991485  | 0.9161987  | -4.5277205 |
| C  | 0.9620516  | 3.0624385  | -4.2610191 |
| H  | 1.9361910  | 3.3198661  | -3.8380045 |
| H  | 0.9808151  | 3.3035711  | -5.3272966 |
| H  | 0.1924013  | 3.6669406  | -3.7772527 |
| O  | 2.8528834  | 0.0808945  | -1.1372312 |
| C  | 3.3802254  | -0.2594744 | 0.1756045  |
| C  | 3.2399945  | 1.1445779  | -0.2149860 |
| H  | 4.3605383  | -0.7235913 | 0.1440032  |
| H  | 2.6490699  | -0.7062197 | 0.8408876  |
| H  | 2.3800663  | 1.6803511  | 0.1785098  |
| C  | 4.4090225  | 1.9839486  | -0.6374292 |
| H  | 4.1105351  | 2.7008130  | -1.4065247 |
| H  | 4.7837494  | 2.5460028  | 0.2223844  |
| H  | 5.2152021  | 1.3591747  | -1.0265834 |
| O  | 0.0071849  | -0.5346066 | 0.0366506  |
| C  | -1.7735987 | -0.8465966 | -0.0406645 |
| C  | -1.0282560 | 0.1493844  | 0.7211554  |
| H  | -1.8358479 | -1.8521220 | 0.3425855  |
| H  | -2.0135551 | -0.6626577 | -1.0756698 |
| H  | -1.1649842 | 1.1816082  | 0.3820948  |
| C  | -0.9813997 | 0.0478914  | 2.2285958  |
| H  | -0.1342464 | 0.6196676  | 2.6171661  |
| H  | -1.8996173 | 0.4506561  | 2.6653324  |
| H  | -0.8700651 | -0.9950868 | 2.5362611  |
| O  | 0.9238931  | -1.9206640 | -2.7514378 |
| C  | 1.3439845  | -3.2629878 | -2.3915563 |
| C  | 2.0012385  | -2.5633314 | -3.4980644 |
| H  | 0.6047039  | -4.0262522 | -2.6109205 |
| H  | 1.8378803  | -3.3384156 | -1.4283917 |
| H  | 2.9685122  | -2.1128017 | -3.2916332 |
| C  | 1.7073655  | -2.8803119 | -4.9343219 |
| H  | 1.7726937  | -1.9798795 | -5.5501692 |
| H  | 2.4436215  | -3.5983711 | -5.3059801 |
| H  | 0.7108287  | -3.3131377 | -5.0402713 |

**TS (S into PO – S<sub>2</sub> = trisulfide chain end)**

48

Energy = -2015.008280296

|   |            |           |            |
|---|------------|-----------|------------|
| C | -3.8607328 | 4.2546798 | -0.3380574 |
| H | -4.8428300 | 4.3012412 | 0.1296513  |
| H | -3.9045402 | 3.7085620 | -1.2796003 |
| H | -3.4846759 | 5.2636370 | -0.5167162 |
| S | -2.6545472 | 3.4516205 | 0.7884559  |

|    |            |            |            |
|----|------------|------------|------------|
| S  | -3.4475898 | 1.5142594  | 1.0359992  |
| S  | -2.9195001 | 0.3233432  | -0.5921785 |
| Li | 1.2153103  | -2.1832931 | 2.3965437  |
| O  | 1.8732552  | -4.0608915 | 2.5890262  |
| C  | 1.1289674  | -5.2702880 | 2.8891530  |
| C  | 2.3006289  | -4.9113210 | 3.6924119  |
| H  | 1.2218966  | -6.0421381 | 2.1321242  |
| H  | 0.1304935  | -5.0998558 | 3.2785360  |
| H  | 2.1171138  | -4.4560651 | 4.6621594  |
| C  | 3.6275946  | -5.5898861 | 3.5228396  |
| H  | 4.4449573  | -4.8861904 | 3.6989864  |
| H  | 3.7171173  | -6.4020613 | 4.2494845  |
| H  | 3.7246796  | -6.0053928 | 2.5180653  |
| O  | 2.7938784  | -0.9959145 | 2.7357520  |
| C  | 3.1269842  | 0.1289601  | 1.8769034  |
| C  | 4.0481780  | -1.0035123 | 1.9908474  |
| H  | 3.3423092  | 1.0438059  | 2.4193678  |
| H  | 2.4929265  | 0.2215824  | 1.0019749  |
| H  | 4.0416898  | -1.7273795 | 1.1800188  |
| C  | 5.2991844  | -0.9410767 | 2.8158722  |
| H  | 5.5118496  | -1.9129028 | 3.2684067  |
| H  | 6.1448829  | -0.6726691 | 2.1768178  |
| H  | 5.2054242  | -0.1940569 | 3.6066422  |
| O  | 0.5480473  | -1.8677484 | 0.6612961  |
| C  | -0.7240153 | -0.6408445 | 0.2105411  |
| C  | -0.7233124 | -2.0951573 | 0.0780818  |
| H  | -0.1966512 | -0.0565699 | -0.5255708 |
| H  | -0.9668241 | -0.1909507 | 1.1597732  |
| H  | -1.4214918 | -2.6129365 | 0.7441631  |
| C  | -0.6996123 | -2.7083774 | -1.3043084 |
| H  | -0.3678691 | -3.7487612 | -1.2473469 |
| H  | -1.6989986 | -2.6909406 | -1.7487352 |
| H  | -0.0144021 | -2.1567643 | -1.9532000 |
| O  | -0.0743130 | -1.8469294 | 3.8860858  |
| C  | -0.4211533 | -0.5791982 | 4.5041247  |
| C  | 0.1372013  | -1.6611527 | 5.3180020  |
| H  | -1.4883983 | -0.3866046 | 4.5383576  |
| H  | 0.2088085  | 0.2535513  | 4.2093614  |
| H  | 1.1913376  | -1.5907855 | 5.5726546  |
| C  | -0.7131036 | -2.5053114 | 6.2207591  |
| H  | -0.3377370 | -3.5311305 | 6.2586458  |
| H  | -0.6836617 | -2.0970943 | 7.2346542  |
| H  | -1.7491571 | -2.5185453 | 5.8773513  |

**TS (S into PO – S<sub>3</sub> = tetrasulfide chain end)**

49

Energy = -2413.232535897

|    |            |            |            |
|----|------------|------------|------------|
| C  | 7.1789881  | -0.9387266 | -1.0020320 |
| H  | 8.0702934  | -1.5299818 | -0.7855954 |
| H  | 6.9471137  | -0.2999239 | -0.1515853 |
| H  | 7.3331785  | -0.3491401 | -1.9037322 |
| S  | 5.8296040  | -2.1540387 | -1.2613822 |
| S  | 4.1811324  | -0.9418862 | -1.7217671 |
| S  | 3.3247967  | -0.1997131 | 0.0719869  |
| S  | 1.9991372  | -1.5765519 | 0.8693891  |
| Li | -3.3928225 | -0.7189221 | -1.0660675 |

|   |            |            |            |
|---|------------|------------|------------|
| O | -4.0717817 | -2.4711110 | -0.4265690 |
| C | -5.4376206 | -2.9357229 | -0.2603349 |
| C | -4.5299362 | -2.9035473 | 0.8893905  |
| H | -5.6395156 | -3.8830779 | -0.7493107 |
| H | -6.1921478 | -2.1651096 | -0.3788175 |
| H | -4.6394612 | -2.0734816 | 1.5826772  |
| C | -3.8807609 | -4.1403496 | 1.4362835  |
| H | -2.8793796 | -3.9154879 | 1.8119460  |
| H | -4.4761888 | -4.5267294 | 2.2680476  |
| H | -3.8079585 | -4.9123573 | 0.6678624  |
| O | -4.8274439 | 0.6689566  | -0.7893802 |
| C | -4.4460982 | 2.0729838  | -0.8362828 |
| C | -4.9731257 | 1.4985044  | 0.4031303  |
| H | -5.0962768 | 2.6811934  | -1.4565211 |
| H | -3.3786276 | 2.2362839  | -0.9394871 |
| H | -4.2493106 | 1.2428071  | 1.1724627  |
| C | -6.3789933 | 1.7400417  | 0.8670939  |
| H | -6.7715879 | 0.8608241  | 1.3841921  |
| H | -6.3913260 | 2.5791167  | 1.5682264  |
| H | -7.0304392 | 1.9779386  | 0.0240620  |
| O | -1.7846571 | -0.0381166 | -0.4042056 |
| C | -0.1727229 | -0.8610263 | -0.1780131 |
| C | -0.9609137 | -0.0398619 | 0.7421601  |
| H | 0.4159602  | -0.3652809 | -0.9334738 |
| H | -0.4338027 | -1.8982944 | -0.3114506 |
| H | -1.3894007 | -0.5883626 | 1.5888397  |
| C | -0.4300918 | 1.3139058  | 1.1586524  |
| H | -1.2414528 | 1.9250145  | 1.5636708  |
| H | 0.3374091  | 1.2005412  | 1.9288100  |
| H | 0.0027597  | 1.8309486  | 0.2990834  |
| O | -3.2475042 | -0.8353341 | -3.0628902 |
| C | -2.1155814 | -1.4273115 | -3.7551732 |
| C | -2.3104154 | 0.0236024  | -3.7869215 |
| H | -2.3944890 | -2.0203775 | -4.6200095 |
| H | -1.3641253 | -1.8574850 | -3.1017002 |
| H | -1.7005744 | 0.6136143  | -3.1082350 |
| C | -2.8642275 | 0.7325331  | -4.9870594 |
| H | -3.4753383 | 1.5863495  | -4.6832527 |
| H | -2.0399768 | 1.1073548  | -5.6003024 |
| H | -3.4723474 | 0.0572678  | -5.5919520 |

**TS (S into PO – S<sub>4</sub> = pentasulfide chain end)**

50

Energy = -2811.456885453

|    |            |            |            |
|----|------------|------------|------------|
| C  | -1.0969333 | -6.1633119 | -6.3393177 |
| H  | -0.2404811 | -6.8382812 | -6.2985587 |
| H  | -1.2672480 | -5.8470633 | -7.3668756 |
| H  | -1.9770678 | -6.6517065 | -5.9262013 |
| S  | -0.6275966 | -4.7224656 | -5.3064422 |
| S  | -2.3227334 | -3.5168947 | -5.3520877 |
| S  | -2.3058918 | -2.3845406 | -7.1518943 |
| S  | -1.0566226 | -0.6968849 | -6.9263839 |
| S  | -2.0730944 | 0.8577371  | -6.0151931 |
| Li | -0.9093339 | 1.6352412  | -0.5981775 |
| O  | -0.5467858 | 3.4654794  | -1.3113854 |
| C  | -0.2371317 | 4.6737915  | -0.5669532 |



|   |            |            |            |
|---|------------|------------|------------|
| C | -1.4012360 | 4.6392441  | -1.4556226 |
| H | 0.6675823  | 5.1720886  | -0.8990608 |
| H | -0.3715651 | 4.5866192  | 0.5060387  |
| H | -2.3740704 | 4.5024506  | -0.9903886 |
| C | -1.4008211 | 5.2901501  | -2.8072387 |
| H | -2.0065428 | 4.7154172  | -3.5123848 |
| H | -1.8322421 | 6.2917511  | -2.7287694 |
| H | -0.3845088 | 5.3748149  | -3.1966039 |
| O | -1.8512458 | 1.8659530  | 1.1595000  |
| C | -2.4885555 | 0.7723194  | 1.8746287  |
| C | -3.3001118 | 1.8692048  | 1.3440787  |
| H | -2.2556603 | 0.7477755  | 2.9340000  |
| H | -2.4644173 | -0.1790250 | 1.3531842  |
| H | -3.8318905 | 1.6801340  | 0.4153330  |
| C | -3.8498653 | 2.9582259  | 2.2161272  |
| H | -3.8862269 | 3.9063979  | 1.6736434  |
| H | -4.8692209 | 2.7021366  | 2.5178373  |
| H | -3.2391436 | 3.0834548  | 3.1120494  |
| O | -1.8841188 | 0.5076676  | -1.7524687 |
| C | -1.6015150 | 0.5724062  | -3.5598620 |
| C | -2.8141846 | 0.8115014  | -2.7772841 |
| H | -1.3156136 | -0.4468803 | -3.7656266 |
| H | -0.8614211 | 1.3512408  | -3.6385243 |
| H | -3.1517469 | 1.8539588  | -2.7640680 |
| C | -3.9723810 | -0.1519779 | -2.9045766 |
| H | -4.6429063 | -0.0454556 | -2.0475258 |
| H | -4.5388140 | 0.0526593  | -3.8167436 |
| H | -3.6074716 | -1.1813321 | -2.9407502 |
| O | 0.8948054  | 0.9071126  | -0.1392659 |
| C | 1.6453014  | -0.0482467 | -0.9366845 |
| C | 1.2424576  | -0.3917425 | 0.4287932  |
| H | 2.6702075  | 0.2523043  | -1.1276475 |
| H | 1.0966545  | -0.4549694 | -1.7792084 |
| H | 0.3765677  | -1.0398228 | 0.5374192  |
| C | 2.2027085  | -0.3667446 | 1.5806097  |
| H | 1.6971564  | -0.0522240 | 2.4970993  |
| H | 2.6040311  | -1.3709436 | 1.7419985  |
| H | 3.0315282  | 0.3147444  | 1.3795509  |

**TS (S into PO – S<sub>5</sub> = hexasulfide chain end)**

51

Energy = -3209.678849470

|    |            |            |            |
|----|------------|------------|------------|
| C  | 4.1491430  | -5.4256723 | 0.3813415  |
| H  | 5.0499700  | -5.3701123 | 0.9888255  |
| H  | 4.0509823  | -6.4214753 | -0.0538528 |
| H  | 3.2620195  | -5.1911734 | 0.9666283  |
| S  | 4.2778478  | -4.2861716 | -1.0500951 |
| S  | 4.5265247  | -2.4222531 | -0.1607142 |
| S  | 2.6366039  | -1.6874001 | 0.4252695  |
| S  | 1.6714689  | -0.8242007 | -1.2448643 |
| S  | 2.4747290  | 1.0906830  | -1.6254839 |
| S  | 1.7327852  | 2.4762952  | -0.2878908 |
| Li | -2.9957138 | 3.6503010  | -3.2640161 |
| O  | -1.9507538 | 3.5673681  | -4.9567280 |
| C  | -1.0571584 | 4.5699497  | -5.5118442 |
| C  | -2.2666587 | 4.1835587  | -6.2421520 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -0.0977591 | 4.1727846  | -5.8265507 |
| H | -1.0324251 | 5.5053038  | -4.9627560 |
| H | -3.1177538 | 4.8561514  | -6.1770800 |
| C | -2.2286911 | 3.2715754  | -7.4319319 |
| H | -3.1191290 | 2.6384154  | -7.4598521 |
| H | -2.2089259 | 3.8683665  | -8.3479708 |
| H | -1.3404697 | 2.6372524  | -7.4072387 |
| O | -4.7518961 | 2.7642407  | -3.6702744 |
| C | -5.5379249 | 2.1173702  | -2.6327673 |
| C | -4.9409418 | 1.3168739  | -3.7039189 |
| H | -6.5960860 | 2.3535801  | -2.6741046 |
| H | -5.0756123 | 2.1347088  | -1.6514170 |
| H | -4.0278822 | 0.7772934  | -3.4655962 |
| C | -5.7432702 | 0.7861079  | -4.8543136 |
| H | -5.1420326 | 0.7679948  | -5.7668413 |
| H | -6.0588606 | -0.2379139 | -4.6364350 |
| H | -6.6308761 | 1.3985181  | -5.0239954 |
| O | -2.2864081 | 3.0167901  | -1.6628631 |
| C | -0.5088601 | 3.1008218  | -1.2228659 |
| C | -1.4935996 | 2.0351368  | -1.0317837 |
| H | -0.5183283 | 3.9337067  | -0.5370925 |
| H | -0.0422780 | 3.2219237  | -2.1867007 |
| H | -1.3254149 | 1.1463350  | -1.6494325 |
| C | -1.9106560 | 1.6723522  | 0.3758825  |
| H | -2.8523348 | 1.1169477  | 0.3567831  |
| H | -1.1477224 | 1.0470882  | 0.8466505  |
| H | -2.0485792 | 2.5760507  | 0.9750632  |
| O | -3.4543878 | 5.5871091  | -2.9502678 |
| C | -2.7207049 | 6.4759087  | -2.0652168 |
| C | -4.0295409 | 5.9622580  | -1.6586666 |
| H | -2.6404787 | 7.4920793  | -2.4374276 |
| H | -1.8199481 | 6.0436864  | -1.6440971 |
| H | -4.0266282 | 5.1294910  | -0.9604438 |
| C | -5.2736707 | 6.7977745  | -1.7112109 |
| H | -6.1408361 | 6.1837156  | -1.9671808 |
| H | -5.4532437 | 7.2448966  | -0.7295623 |
| H | -5.1742479 | 7.5978740  | -2.4474962 |

**TS (S into PO – S<sub>6</sub> = heptasulfide chain end)**

52

Energy = -3607.902225273

|    |            |            |            |
|----|------------|------------|------------|
| C  | 4.9531747  | -2.1072574 | -5.6314437 |
| H  | 4.5288528  | -1.5714940 | -4.7845156 |
| H  | 5.3483444  | -1.4207622 | -6.3770981 |
| H  | 5.7397135  | -2.7799895 | -5.2862266 |
| S  | 3.6868578  | -3.1986497 | -6.3844383 |
| S  | 2.2752827  | -1.8617656 | -7.1125418 |
| S  | 1.0103427  | -1.2824324 | -5.5217500 |
| S  | -0.4390095 | -2.7667095 | -5.2288583 |
| S  | -1.9668238 | -2.5289911 | -6.6730511 |
| S  | -3.2394405 | -0.9466395 | -6.0976456 |
| S  | -4.5767993 | -1.5761806 | -4.6550117 |
| Li | -1.4551476 | 1.0465426  | -0.6946410 |
| O  | -0.8339494 | 2.2119410  | -2.1872859 |
| C  | 0.1904554  | 2.0568062  | -3.2022963 |
| C  | 0.2491332  | 3.1857559  | -2.2707467 |

|   |            |            |            |
|---|------------|------------|------------|
| H | -0.1663947 | 2.2213791  | -4.2138407 |
| H | 0.8457666  | 1.2044562  | -3.0565180 |
| H | 0.9428277  | 3.1025656  | -1.4385439 |
| C | -0.1478099 | 4.5754413  | -2.6714130 |
| H | -0.6066932 | 5.1023968  | -1.8310978 |
| H | 0.7410055  | 5.1342259  | -2.9771644 |
| H | -0.8518408 | 4.5528222  | -3.5054108 |
| O | -1.7797252 | 2.2895848  | 0.8509349  |
| C | -2.7653617 | 1.9583549  | 1.8685909  |
| C | -2.9617923 | 3.1295937  | 1.0121085  |
| H | -2.4085956 | 2.0977222  | 2.8838338  |
| H | -3.3190514 | 1.0471256  | 1.6690159  |
| H | -3.6582477 | 3.0238934  | 0.1843364  |
| C | -2.7129089 | 4.5283178  | 1.4934802  |
| H | -2.3320064 | 5.1533282  | 0.6817277  |
| H | -3.6518280 | 4.9646984  | 1.8450544  |
| H | -1.9940656 | 4.5343103  | 2.3151126  |
| O | -2.9913345 | 0.0076058  | -1.0119969 |
| C | -3.3841383 | -0.8962443 | -2.5650973 |
| C | -4.1116232 | 0.1605905  | -1.8622433 |
| H | -3.4547677 | -1.9044257 | -2.1892303 |
| H | -2.5489654 | -0.6327794 | -3.1941716 |
| H | -4.1308881 | 1.1208260  | -2.3890759 |
| C | -5.4488340 | -0.1641915 | -1.2330948 |
| H | -5.7088307 | 0.5969982  | -0.4924791 |
| H | -6.2352275 | -0.1858445 | -1.9931242 |
| H | -5.4094761 | -1.1369840 | -0.7360855 |
| O | 0.0666224  | -0.1031202 | -0.0894037 |
| C | 0.4900390  | -1.3743253 | -0.6493634 |
| C | -0.0706888 | -1.3233729 | 0.7022982  |
| H | 1.5641215  | -1.4604998 | -0.7771872 |
| H | -0.1234157 | -1.7316297 | -1.4703695 |
| H | -1.1094873 | -1.6222512 | 0.8129477  |
| C | 0.7853346  | -1.4079893 | 1.9310337  |
| H | 0.3697205  | -0.7924158 | 2.7328423  |
| H | 0.8182412  | -2.4435122 | 2.2806553  |
| H | 1.8036880  | -1.0767527 | 1.7187711  |

**TS (S into PO – S<sub>7</sub> = octasulfide chain end)**

53

Energy = -4006.123817040

|    |            |            |            |
|----|------------|------------|------------|
| C  | 6.7838832  | -3.2060646 | -6.2883145 |
| H  | 6.0384385  | -2.6012328 | -6.8008616 |
| H  | 7.1068239  | -4.0433114 | -6.9031865 |
| H  | 7.6401979  | -2.5861502 | -6.0182737 |
| S  | 6.1135627  | -3.8135895 | -4.6934167 |
| S  | 4.5751144  | -5.0824796 | -5.2705411 |
| S  | 2.8663438  | -3.9238437 | -5.7087403 |
| S  | 1.8861236  | -3.4565653 | -3.9118055 |
| S  | 0.7496157  | -5.1122075 | -3.3072455 |
| S  | -1.0324548 | -5.1703010 | -4.4481495 |
| S  | -2.4346148 | -3.7898673 | -3.6912893 |
| S  | -3.4394835 | -4.5745479 | -2.0671889 |
| Li | -0.6765252 | -1.0861382 | 1.5342986  |
| O  | 0.2643280  | -0.2753651 | -0.0338941 |
| C  | 1.4621080  | -0.7836416 | -0.6783218 |

|   |            |            |            |
|---|------------|------------|------------|
| C | 1.4804920  | 0.5307908  | -0.0323527 |
| H | 1.3859271  | -0.8386967 | -1.7594533 |
| H | 1.9107609  | -1.6360478 | -0.1796988 |
| H | 1.9356835  | 0.5897797  | 0.9525646  |
| C | 1.4197915  | 1.8103278  | -0.8128870 |
| H | 0.8686797  | 2.5736636  | -0.2578559 |
| H | 2.4340481  | 2.1812292  | -0.9837866 |
| H | 0.9359369  | 1.6533282  | -1.7788644 |
| O | -1.1929486 | 0.4616446  | 2.7133735  |
| C | -2.3624219 | 0.4172921  | 3.5764198  |
| C | -2.3009689 | 1.3805047  | 2.4753067  |
| H | -2.1717429 | 0.7572489  | 4.5891195  |
| H | -2.9562229 | -0.4845505 | 3.4721218  |
| H | -2.8541852 | 1.1344445  | 1.5727403  |
| C | -2.0057380 | 2.8345541  | 2.6958640  |
| H | -1.4353380 | 3.2433014  | 1.8580225  |
| H | -2.9447085 | 3.3900022  | 2.7691446  |
| H | -1.4385775 | 2.9797516  | 3.6172489  |
| O | -2.1711614 | -2.1732712 | 1.2236506  |
| C | -2.3953416 | -3.4029437 | -0.1224402 |
| C | -3.2089211 | -2.2514045 | 0.2686473  |
| H | -2.4747064 | -4.3081254 | 0.4589319  |
| H | -1.5139957 | -3.2465048 | -0.7234165 |
| H | -3.2018109 | -1.4282200 | -0.4547386 |
| C | -4.5910156 | -2.4909928 | 0.8356798  |
| H | -4.9367286 | -1.6006249 | 1.3681219  |
| H | -5.3012354 | -2.7104176 | 0.0338206  |
| H | -4.5743897 | -3.3317519 | 1.5342295  |
| O | 0.7641861  | -2.0700068 | 2.5137225  |
| C | 0.5846797  | -3.1136420 | 3.5060030  |
| C | 1.3215421  | -1.8947136 | 3.8497279  |
| H | 1.1360722  | -4.0231236 | 3.2901226  |
| H | -0.4390731 | -3.2431305 | 3.8409056  |
| H | 0.7892148  | -1.1394195 | 4.4215431  |
| C | 2.8185608  | -1.8591794 | 3.9368887  |
| H | 3.2002880  | -0.8896678 | 3.6072985  |
| H | 3.1265607  | -2.0103059 | 4.9751682  |
| H | 3.2617662  | -2.6445364 | 3.3217371  |

**TS (S into PO – S<sub>8</sub> = nonasulfide chain end)**

54

Energy = -4404.344859987

|    |            |            |            |
|----|------------|------------|------------|
| S  | -2.3021791 | -1.0201909 | -6.8941114 |
| C  | -2.2977641 | -0.0020784 | -8.4187631 |
| H  | -2.4940059 | -0.7058434 | -9.2290576 |
| H  | -1.3212823 | 0.4575600  | -8.5585724 |
| H  | -3.0861458 | 0.7461290  | -8.3733486 |
| S  | -2.0405130 | 0.3720522  | -5.3791719 |
| S  | 0.0160478  | 0.8288780  | -5.2248591 |
| S  | 0.9663972  | -0.7104082 | -4.1663468 |
| S  | 0.6075927  | -0.4437220 | -2.1126058 |
| S  | 1.9024260  | 1.0349476  | -1.3834939 |
| S  | 3.8098857  | 0.1848120  | -1.0441036 |
| S  | 3.7965675  | -0.8874826 | 0.7731296  |
| S  | 3.9860675  | 0.3976248  | 2.3768661  |
| Li | -1.4978357 | -0.0037478 | 3.3915124  |

|   |            |            |           |
|---|------------|------------|-----------|
| O | -1.2411543 | -1.7278782 | 2.4560523 |
| C | -2.1481005 | -2.7308298 | 1.9339202 |
| C | -1.1012427 | -3.1118579 | 2.8864980 |
| H | -2.0070132 | -2.9423717 | 0.8788649 |
| H | -3.1752532 | -2.6308519 | 2.2690290 |
| H | -1.4049068 | -3.2578873 | 3.9201780 |
| C | 0.1590048  | -3.8067646 | 2.4633332 |
| H | 1.0003823  | -3.4882697 | 3.0837226 |
| H | 0.0381457  | -4.8868948 | 2.5828793 |
| H | 0.3871015  | -3.5909446 | 1.4181587 |
| O | -2.7852436 | -0.1849011 | 4.9251612 |
| C | -2.7393845 | 0.8026231  | 5.9926610 |
| C | -2.4149090 | -0.5968712 | 6.2755648 |
| H | -3.7141782 | 1.1875453  | 6.2736412 |
| H | -1.9394798 | 1.5281071  | 5.8879563 |
| H | -1.3608826 | -0.8503443 | 6.3533201 |
| C | -3.3737293 | -1.5211905 | 6.9658403 |
| H | -3.2720763 | -2.5396817 | 6.5825885 |
| H | -3.1546795 | -1.5387759 | 8.0369925 |
| H | -4.4036846 | -1.1885340 | 6.8237133 |
| O | 0.0513558  | 0.8637868  | 3.9903764 |
| C | 1.5987049  | 0.7809308  | 2.9847147 |
| C | 1.3508478  | 0.5028063  | 4.4009814 |
| H | 1.6764272  | 1.8109708  | 2.6760829 |
| H | 1.3411208  | 0.0325363  | 2.2519466 |
| H | 1.4482190  | -0.5542517 | 4.6745010 |
| C | 1.9706738  | 1.4094047  | 5.4426637 |
| H | 1.4563963  | 1.2844141  | 6.3994127 |
| H | 3.0274680  | 1.1658526  | 5.5862747 |
| H | 1.8847790  | 2.4542606  | 5.1339091 |
| O | -2.4616349 | 1.2061026  | 2.1101481 |
| C | -1.8193031 | 1.8678674  | 0.9892598 |
| C | -2.2414181 | 2.6515174  | 2.1520571 |
| H | -2.4230512 | 1.8858702  | 0.0877709 |
| H | -0.7710212 | 1.6189816  | 0.8609094 |
| H | -1.4684266 | 2.9184382  | 2.8674779 |
| C | -3.4755177 | 3.5039463  | 2.1391827 |
| H | -3.9503598 | 3.5104872  | 3.1236396 |
| H | -3.2040346 | 4.5329060  | 1.8872034 |
| H | -4.1921919 | 3.1399868  | 1.4004451 |

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How to cite: *Angew. Chem. Int. Ed.* **2025**, 64, e202501337  
doi.org/10.1002/anie.202501337

**Dynamic Polyester**

# Kinetically Enhanced Access to a Dynamic Polyester Platform via Sequence Selective Terpolymerisation of Elemental Sulphur

Cesare Gallizioli, Peter Deglmann, and Alex J. Plajer\*

**Abstract:** Elemental sulphur, a waste product of the oil refinement process, contains preformed dynamic sulphur–sulphur bonds promising to impart dynamicity onto polymers obtained from this monomer. Yet robust methodologies to access linear polymers with tuneable properties and functionality are rare. Addressing these problems, we here report a rare sequence selective terpolymerisation of elemental sulphur with aromatic thioanhydrides and epoxides under simple lithium alkoxide catalysis yields semi-aromatic poly(ester-alt-S<sub>x</sub>). This enables access to terpolymers from a greatly improved range of epoxide comonomers compared to previous methodologies, including industrially relevant, flexible, rigid, functional and natural product-derived variants, allowing tuning of glass transition temperatures across a  $T_g$  range of >150 °C. Mechanistic investigations reveal that the insertion of S<sub>8</sub> leads to an unusual rate acceleration via coordinative participation of the polyester links sitting adjacent to the propagating chain end. The thermal stability of the polymers allows for post polymerisation backbone modification via –S–S– bond metathesis. After crosslinking, these can be applied as thermally reprocessable and acid degradable adhesives. Our contribution paves the way for the rational buildup of diverse and functional polymer structures from elemental sulphur waste.

## Introduction

Covalent bonds between sulphur atoms exhibit lower bond dissociation energy than those between atoms of the second period, bonds that current commodity polymers are typically constructed of.<sup>[1]</sup> Hereby, such –S–S– bond containing polymers address current sustainability challenges plastics face, as they can exhibit enhanced degradability as well as chemical and mechanical recyclability.<sup>[2–4]</sup> Furthermore, the reversible opening and closing of the sulphur–sulphur bond introduces the potential for self-healing or stimuli responsive behaviour, while the electronic nature of the sulphur centres bestows these materials with unique properties such as the ability for transition metal coordination and increased refractive indices.<sup>[5–11]</sup> The controlled incorporation of sulphur–sulphur

moieties remains, however, challenging, particularly when it comes to linear polymers, and often involves the employment of synthetically non-trivial building blocks that require elaborate synthesis.<sup>[12,13]</sup>

In this regard, elemental sulphur (S<sub>8</sub>) represents a promising starting material, as the desired –S–S– bonds are already preformed. Utilisation is furthermore attractive, as S<sub>8</sub> constitutes a major scale waste product of the petrochemical industry, which is produced as part of the desulphurisation process of crude oil. As S<sub>8</sub> cannot be polymerised by itself into thermodynamically stable macromolecules, many recent efforts have focused on developing copolymerisation strategies forming polymers with oligosulphur S<sub>x</sub> links. Typically, this relies on thermally activated radical pathways enabling copolymerisation with (multifunctional) alkenes via so-called inverse vulcanisation, giving access to a wide range of crosslinked materials.<sup>[14–23]</sup> In contrast, the synthesis of linear chains from S<sub>8</sub> in a controlled fashion is more challenging, in particular regarding chains exceeding the oligomer regime.<sup>[24–27]</sup> In this context the anionic copolymerisation of sulphur relies on the formation of thiolate intermediates that then achieve S<sub>8</sub> ring opening. Unfortunately, although this mechanistic necessity enables copolymerisation of expensive sulphurated heterocycles, it excludes many commonly applied oxygenated comonomers, generating alkoxide intermediates upon insertion.<sup>[28,29]</sup> Here epoxides would not only be attractive comonomers due to the industrial relevance of propylene oxide (PO) but also because of the commercial availability of many others that potentially allows for a facile tuning of the material properties.<sup>[30]</sup> In this regard we recently found that thiolate intermediates can also be formed during the copolymerisation of CS<sub>2</sub> with epoxides and thereby enable incorporation of S<sub>8</sub> and effectively make epoxides compatible

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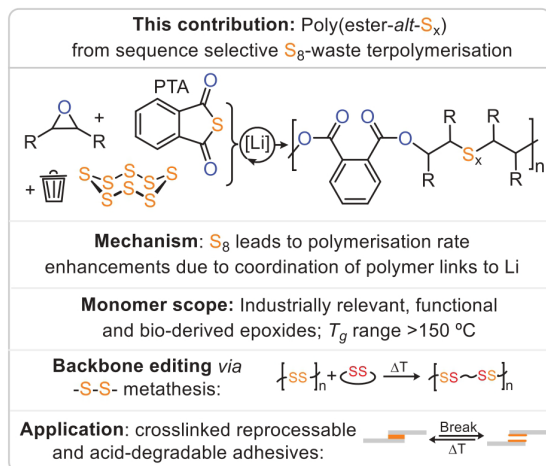


Figure 1. Outline of the current study.

monomers for elemental sulphur.<sup>[31]</sup> The ring-opening terpolymerisation (ROTERP) derives from anionic ring-opening copolymerisation (ROCOP), in which two monomers are combined in a strictly alternating fashion, and sulphurated variants have recently been in increased focus due to the property and chemical recyclability benefits of sulphur containing polymers.<sup>[32–53]</sup> In ROTERP, however, three rather than two monomers are terpolymerised in a sequence selective fashion, and the reasons how and when to achieve this recently developed concept are largely unanswered. Unfortunately, though the S<sub>8</sub> ROTERP depended on an excess of highly toxic carbon disulphide, it exhibited limited epoxide scope and produced thionocarbonate  $\text{--O--(C=S)--O--}$  links, which have poor thermal stability, decomposing into carbonyl sulphide. This hindered processing and hence any applications as well as other controlled utilisation of the  $\text{--S--S--}$  bond. Addressing these problems, we here report the incorporation of elemental sulphur into polyesters (Figure 1) via ROTERP with epoxides and thioanhydrides (Figure 2).

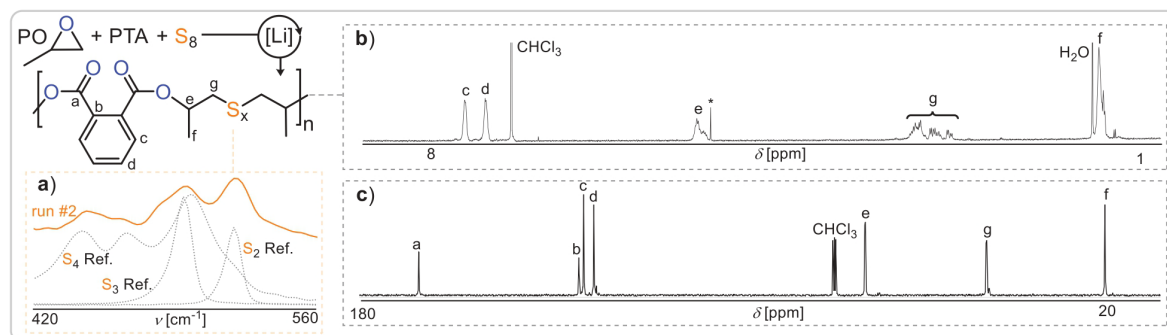
## Results and Discussion

Investigating whether phthalic thioanhydride (PTA) can compatibilise epoxides with elemental sulphur (Figure 1), we attempted ROTERP employing 1 eq. Lithiumbenzyloxide (LiOBn, generated in situ from  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  and BnOH), 500 eq. PO, 50 eq. PTA and 100 eq. S (i.e., 1/8 eq. S<sub>8</sub>) at room temperature for 24 h, resulting in full PTA conversion (Table 1 run #1). <sup>1</sup>H NMR analysis of the product mixture reveals the formation of broad indicative polymer resonances in 97% selectivity alongside some sharp resonances for small molecule byproducts. The polymer could be easily isolated by precipitation in methanol and centrifugation. Gel permeation chromatography (GPC) shows an apparent weight averaged molecular weight of 22 kg mol<sup>−1</sup> with a polydispersity of 1.5, which confirms the macromolecular nature of the product. NMR analysis reveals the aromatic region of the spectrum

to feature two dominant CH resonances at 7.4 and 7.6 ppm, which correlate by HSQC to aryl esters at 166 ppm (see ESI Figure S1), and this is indicative of a symmetrically substituted aryl diester unit. Accordingly, the tertiary CH proton from PO ring-opening likewise correlates to the quaternary carbon resonance at 166 ppm, implying that these so-called head-positions sit adjacent to the phthalate core. The CH<sub>2</sub> tail position of the ring-opened PO appear between 3.5 and 2.6 ppm which in comparison to literature known polymers can be tentatively assigned to be connected to oligosulphide  $\text{--S}_x\text{--}$  links.<sup>[29,31]</sup> The formation of these is confirmed by Raman spectroscopy showing indicative absorbances between 560 and 420 cm<sup>−1</sup>. Close comparison of these regions to small molecule di- RSSR, tri- RSSSR and tetra- RSSSSR standards indicates that while some disulphide links appear to have formed, a substantial proportion of the  $\text{--S}_x\text{--}$  links comprise tri- and tetrasulphides (ESI Figure S10). Taken together, the spectroscopic data suggest the selective formation of a poly(ester-*alt*-S<sub>x</sub>) sequence in which the  $\text{--S}_x\text{--}$  are flanked by CH<sub>2</sub> tail-groups while the phthalate esters sit next to CH head groups of the ring opened epoxides. To investigate if the oligosulphide linkage distribution is affected by the amount of elemental sulphur supplied in the starting monomer feed, we halved the amount of supplied sulphur (run #2). Here the reaction rate slowed down substantially, necessitating longer reaction times to reach high monomer conversion with polymer formation in 93% selectivity. Raman spectroscopy now reveals a more prominent formation of disulphide links, suggesting tunability of the  $\text{--S}_x\text{--}$  linkage distribution with the supplied initial sulphur feed.

Close inspection of the NMR spectrum reveals minor aryl CH resonances at 7.5 and 7.7 ppm alongside the major set of resonances corresponding to the main poly(ester-*alt*-S<sub>x</sub>) sequence. These can be assigned to arylthioesters connected to ring-opened PO tail positions.<sup>[54,55]</sup> Integration shows that 9% of polymer linkages are thioesters compared to 4% at higher sulphur loading. Formation of thioester links can be ascribed to co-occurring PTA/PO ROCOP (vide infra). As doubling the sulphur loading (compared to run #1) again decreases thioester errors (run #3), sulphur loading also appears to not only enhance reaction rate but also linkage selectivity. Increasing the reaction temperature (run #4 to #6) to 100 °C results in a substantial improvement of reaction rate so that full conversion is achieved within minutes, albeit somewhat at the expense of molecular weight. Increasing the PTA to LiOBn loading (run #8 and #9) increases the final obtained molecular weights to a maximum of  $M_w = 43 \text{ kg mol}^{-1}$  at a linkage selectivity of 97%. Conversely, at higher catalyst loadings (run #10 and #11), decreased molecular weights of  $M_w = 6 \text{ kg mol}^{-1}$  are observed, demonstrating some level of control over the obtained degree of polymerisation with our methodology. From the combined results it appears that sequence selectivity positively correlates to higher S<sub>8</sub> loading relative to PTA and an increase in reaction temperature. Confirming that lithium acts as a true catalyst, we performed runs with NaOBn and KOBn in place of LiOBn (runs #12 and #13), resulting in slower rates and low elemental sulphur incorporation.





**Figure 2.**  $S_8$ /PTA/PO ROTERP. a) Raman spectrum of the  $S_x$  region with  $S_2$ – $S_4$  reference spectrum. b)  $^1\text{H}$  NMR and c)  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) corresponding to Table 1 run #3. \*Residual  $\text{CH}_2\text{Cl}_2$ .

**Table 1:** PTA/ $S_8$ /PO ROTERP.

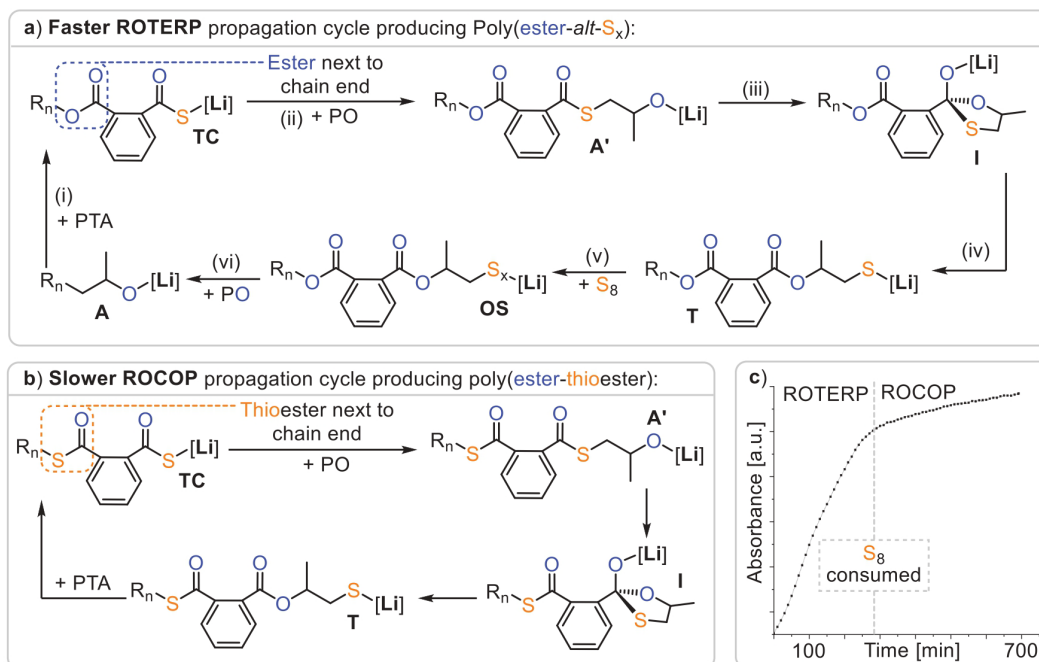
| Run               | LiOBn:PO:PTA:1/4 $S_8$ | $T$ (°C) | Time   | Conversion <sup>a)</sup> (%) | Polym. <sup>b)</sup> (%) | Linkage selectivity <sup>c)</sup> (%) | $M_w$ <sup>d)</sup> (kDa) | $\bar{D}$ <sup>d)</sup> |
|-------------------|------------------------|----------|--------|------------------------------|--------------------------|---------------------------------------|---------------------------|-------------------------|
| #1                | 1:500:50:100           | 30       | 2 h    | 99                           | 93                       | 96                                    | 22                        | 1.5                     |
| #2                | 1:500:50:50            | 30       | 24 h   | 87                           | 97                       | 91                                    | 18                        | 1.7                     |
| #3                | 1:500:50:200           | 30       | 2 h    | 99                           | 93                       | 97                                    | 18                        | 1.5                     |
| #4                | 1:500:50:50            | 100      | 5 min  | 93                           | 99                       | 93                                    | 17                        | 1.6                     |
| #5                | 1:500:50:100           | 100      | 2 min  | 99                           | 96                       | 99                                    | 11                        | 1.5                     |
| #6                | 1:500:50:200           | 100      | 2 min  | 99                           | 96                       | 98                                    | 8                         | 1.3                     |
| #7                | 1:500:200:200          | 30       | 72 h   | 90                           | 99                       | 75                                    | 43                        | 1.6                     |
| #8                | 1:500:200:200          | 100      | 5 min  | 85                           | 99                       | 88                                    | 35                        | 1.7                     |
| #9                | 1:5000:1000:1000       | 100      | 24 h   | 99                           | 99                       | 97                                    | 28                        | 1.6                     |
| #10               | 1:250:25:25            | 100      | 2 min  | 99                           | 99                       | 99                                    | 6                         | 1.5                     |
| #11               | 1:250:10:10            | 100      | 2 min  | 99                           | 99                       | 99                                    | 6                         | 1.1                     |
| #12 <sup>e)</sup> | 1:500:50:50            | 30       | 7 days | 70                           | 99                       | 20                                    | 4                         | 1.2                     |
| #13 <sup>f)</sup> | 1:500:50:50            | 30       | 6 days | 70                           | 99                       | 16                                    | 6                         | 1.3                     |

<sup>a)</sup> Relative peak integrals in the normalised  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of the crude reaction mixture of aromatic polymer resonances versus unconsumed PTA. <sup>b)</sup> Relative peak integrals in the normalised  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of the crude reaction mixture of polymer resonances versus small molecule byproducts. <sup>c)</sup> Relative peak integrals in the normalised  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of polymer resonances corresponding to ester and polysulphide linkages relative to all linkages formed. <sup>d)</sup> Determined by GPC measurements conducted in THF with a narrow polystyrene standard. <sup>e)</sup> NaOBn was employed. <sup>f)</sup> KOBn was employed.

The structure of the terpolymers let us suggest a propagation mechanism as depicted in Figure 3a. Starting from a lithium alkoxide **A**, such as LiOBn or an intermediate resulting from PO ring opening, propagation occurs in (i) by PTA insertion to form a lithium thiocarboxylate **TC**, which regenerates a lithium alkoxide **A'** via PO insertion in (ii). From here the alkoxide chain end intramolecularly attacks the adjacent thioester group, forming a tetrahedral intermediate **I** that collapses in (iii) and (iv) into a lithium thiolate intermediate **T**. This exchanges the position of an oxygen and sulphur centre in a so-called O/S exchange reaction. Thereafter  $S_8$  insertion and equilibration of the  $S_x$  chain lead to a distribution of lithium oligosulphide intermediates **OS** in (v). Finally, PO insertion leads to (vi), which closes the catalytic cycle and generates the poly(ester-*alt*- $S_x$ ) sequence. Alternatively, as shown in Figure 3b, lithium thiolates **T** can insert PTA to close a PTA/PO ROCOP cycle, forming thioester errors. Hence, to achieve high sequence selectivity, thiolates **T** need to selectively insert  $S_8$  over PTA. Comparing ROTERP and ROCOP, we performed a polymerisation (see Figure 3c) with excess PTA and epoxide compared to  $S_8$  in the

initial monomer feed so that elemental sulphur would deplete over the course of the reaction and monitored the reaction via in situ IR at  $1127\text{ cm}^{-1}$  at which both ROTERP and ROCOP could be monitored in separated experiments. Interestingly, we observe a sudden eight fold decrease in reaction rate upon sulphur consumption. This indicates that the polymerisation is accelerated by elemental sulphur, which indeed could be confirmed in separate ROCOP and ROTERP runs under analogous conditions, and this observation is in line with the results of Table 1 (and Table 2, vide infra), in which higher sulphur loading positively correlates with polymerisation rate. Although no clear reaction order in  $S_8$  could be determined, performing an in situ IR experiment with excess  $S_8$  and epoxide with respect to PTA reveals an approximately linear correlation of polymer production with time, indicating a 0<sup>th</sup> order dependence on PTA concentration in line with related terpolymerisations (see ESI Figure S21).<sup>[56]</sup>

To investigate the origin of rate enhancement and sequence selectivity, we turned to density functional theory (DFT, Figure 4) at a meta-hybrid DFT level.<sup>[57–64]</sup> This involved conformational searches and structure optimisations

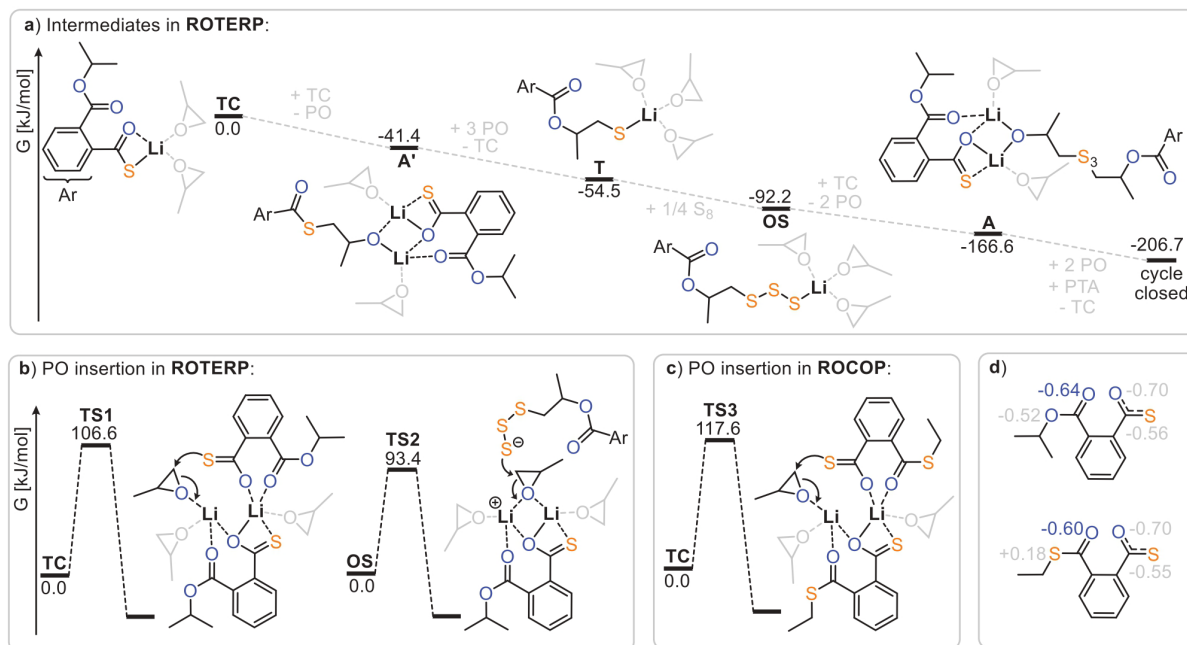


**Figure 3.** Mechanistic hypothesis for a) S<sub>8</sub>/PTA/PO ROTERP and b) co-occurring PTA/PO ROCOP. c) Polymerisation performed at 1 eq. LiOBn: 100 eq. S: 200 eq. PTA: 1000 eq. epoxide and 80 °C showing a sudden decrease in polymerisation rate upon elemental sulphur consumption. Note that ethyl glycidyl ether (EGE) was employed in place of PO due to its increased boiling point facilitating analysis by in situ IR spectroscopy.

**Table 2:** Monomer scope of the new methodology.

| Run <sup>a)</sup> | Epoxide            | LiOBn:Epox.:PTA:1/4S <sub>8</sub> | Time   | Conversion <sup>b)</sup> | Polym. <sup>c)</sup> | Linkage select.<br>(%) <sup>d)</sup> | M <sub>w</sub> (kDa) <sup>d)</sup> | Đ <sup>d)</sup> | T <sub>g</sub> (°C) <sup>e)</sup> | T <sub>d</sub> (5%) (°C) <sup>f)</sup> |
|-------------------|--------------------|-----------------------------------|--------|--------------------------|----------------------|--------------------------------------|------------------------------------|-----------------|-----------------------------------|----------------------------------------|
| #0                | PO                 | 1:500:200:200                     | 5 min  | 85%                      | 99%                  | 88%                                  | 35                                 | 1.7             | 30                                | 265                                    |
| #1                | BO                 | 1:500:200:200                     | 1 h    | 88%                      | 98%                  | 91%                                  | 56                                 | 1.7             | 26                                | 276                                    |
| #2                | DO                 | 1:500:200:200                     | 16 h   | 72%                      | 97%                  | 92%                                  | 26                                 | 1.5             | −23                               | 282                                    |
| #3                | DO                 | 1:500:200:400                     | 16 h   | 99%                      | 97%                  | 97%                                  | 19                                 | 1.6             | −25                               | 270                                    |
| #4                | CHO                | 1:500:200:200                     | 16 h   | 76%                      | 95%                  | 76%                                  | 23                                 | 1.6             | 85                                | 270                                    |
| #5                | CHO                | 1:500:200:400                     | 1 h    | 90%                      | 99%                  | 98%                                  | 16                                 | 1.6             | 61                                | 269 <sup>k)</sup>                      |
| #6                | DMO                | 1:500:200:200                     | 40 h   | 66%                      | 99%                  | 94%                                  | 12                                 | 1.5             | 30                                | 261                                    |
| #7                | IBO <sup>g)</sup>  | 1:500:200:200                     | 1 h    | 72%                      | n.d.                 | 94%                                  | 40                                 | 1.6             | 18                                | 190                                    |
| #8                | IBO <sup>g)</sup>  | 1:500:200:400                     | 1 h    | 70%                      | n.d.                 | 96%                                  | 27                                 | 1.6             | 13                                | 218                                    |
| #9                | SO <sup>h)</sup>   | 1:500:200:200                     | 40 h   | 70%                      | 99%                  | n.d.                                 | 7                                  | 1.4             | 40                                | 250                                    |
| #10               | SO <sup>h)</sup>   | 1:500:200:400                     | 44 h   | 86%                      | 99%                  | n.d.                                 | 8                                  | 1.6             | 53                                | 258                                    |
| #11               | PO <sup>i)</sup>   | 1:500:200:200                     | 2 h    | 95%                      | 99%                  | 98%                                  | 10                                 | 1.8             | 61                                | 279                                    |
| #12               | CHO <sup>i)</sup>  | 1:500:200:200                     | 65 h   | 70%                      | 99%                  | 82%                                  | 11                                 | 1.6             | 128                               | 270 <sup>k)</sup>                      |
| #13               | EGE                | 1:500:200:200                     | 10 min | 99%                      | 98%                  | 88%                                  | 24                                 | 1.7             | 8                                 | 274                                    |
| #14               | PGE                | 1:500:200:200                     | 16 h   | 99%                      | 95%                  | 96%                                  | 25                                 | 1.7             | 47                                | 289                                    |
| #15               | VGE                | 1:500:200:200                     | 2 h    | 90%                      | 99%                  | 88%                                  | 26                                 | 1.7             | 66                                | 265                                    |
| #16               | VGE <sup>i)</sup>  | 1:500:200:200                     | 1.5 h  | 80%                      | 99%                  | 92%                                  | 9                                  | 1.5             | 85                                | 273                                    |
| #17               | CE <sup>h)</sup>   | 1:500:200:200                     | 16 h   | 66%                      | 99%                  | n.d.                                 | 12                                 | 1.6             | 129                               | 279                                    |
| #18               | ECH                | 1:500:200:200                     | 5 min  | 98%                      | 93%                  | 93%                                  | 10                                 | 2.6             | 39                                | 256                                    |
| #19               | DEO <sup>i)</sup>  | 1:500:200:200                     | 1 h    | n.d.                     | n.d.                 | n.d.                                 | n.d.                               | n.d.            | 13                                | 264                                    |
| #20               | ESBO <sup>i)</sup> | 1:500:200:200                     | 72 h   | n.d.                     | n.d.                 | n.d.                                 | n.d.                               | n.d.            | −40                               | 238                                    |

<sup>a)</sup> ROTERP conducted at 100 °C. <sup>b)</sup> Relative peak integrals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of the crude reaction mixture of aromatic polymer resonances versus unconsumed PTA. <sup>c)</sup> Relative peak integrals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of the crude reaction mixture of polymer resonances versus small molecule byproducts. <sup>d)</sup> Relative peak integrals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of polymer resonances corresponding to ester and polysulphide linkages relative to all linkages formed. <sup>e)</sup> Determined by GPC measurements conducted in THF with a narrow polystyrene standard. <sup>f)</sup> Determined by DSC from the second heating curve at 10 K min<sup>−1</sup>. <sup>g)</sup> Determined by thermogravimetric analysis (TGA). <sup>h)</sup> Complete determination of selectivity not possible due to overlapping signals. <sup>i)</sup> NTA was employed in place of PTA. <sup>j)</sup> Cross-linked network is obtained, preventing solution characterisation. <sup>k)</sup> minor degradation step observed at lower temperatures.



**Figure 4.** a) Intermediate speciation as well as PO insertion barriers for b)  $S_8$ /PTA/PO ROTERP and c) PTA/PO ROCOP. d) NBO population analysis of thiocarbonylates modelled as monoanionic species produced by (top) ROTERP and (bottom) ROCOP. Isopropyl and ethyl groups at the chain ends were employed for computational simplicity.  $S_3$  groups were exemplarily employed for oligosulphide groups  $S_x$ . For computational details see ESI Section S6.

at the TPSSH/def-TZVP level (using the solvation model COSMO and assuming a dielectric constant of infinity), followed by M06-2X/def2-TZVPD single-point calculations. For the final Gibbs free energies, the solvation model COSMO-RS was employed, assuming a solvent mixture of 5:1 PO and PTA at 30 °C. Statistical thermodynamic contributions to Gibbs free energies were also taken into account. The most favoured structures were identified by assessing a multitude of species as exhaustively as possible, while also considering dimerisation equilibria at catalyst concentrations during ROTERP. The reader is referred to the supporting information (ESI Section S6) for a summary of these species and their associated Gibbs free energies.

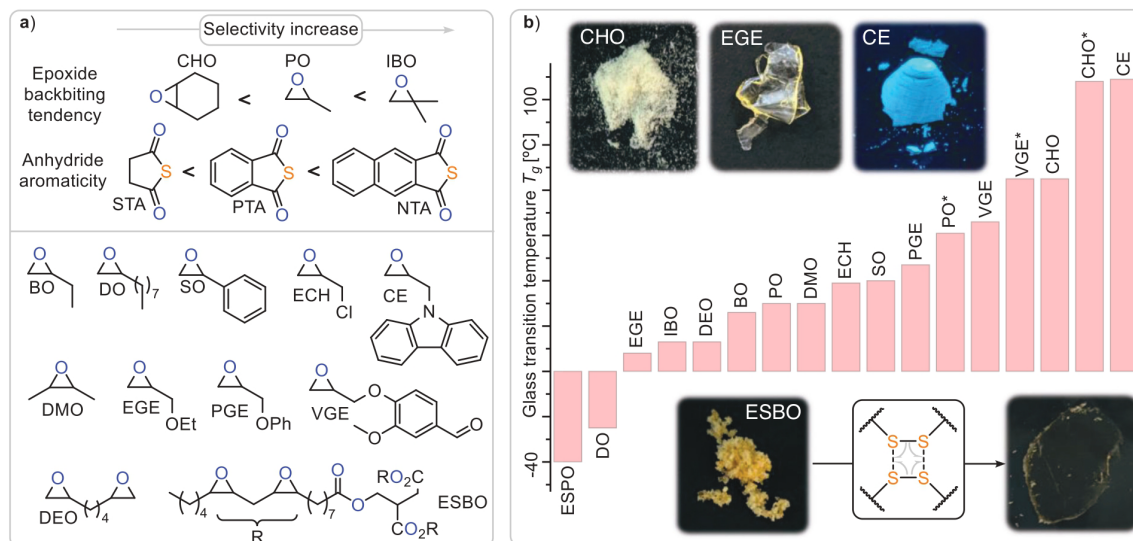
Figure 4a shows the intermediate speciation and propagation energetics modelled according to the mechanistic hypothesis of Figure 3a, confirming its thermodynamic viability, as Gibbs free energy decreases along any polymer growth step. Based on previous work on related polymerisations, it can be assumed that propagation steps involving the insertion of these monomers, as well as O/S exchange, are faster than the PO insertion steps.<sup>[31,56]</sup> Here, PO ring-opening by either the lithium thiocarboxylate TC (TS1,  $\Delta G^\ddagger = 106.6$  kJ mol<sup>-1</sup>) or the lithium oligosulphide OS (TS2,  $\Delta G^\ddagger = 94.4$  kJ mol<sup>-1</sup>), modelled exemplarily for a trisulphide) occurs fastest in a dinuclear fashion, clearly revealing a lithium thiocarboxylate resting state (Figure 4b). While in TS1 the propagating chain end remains coordinated, TS2 occurs in a zwitterionic fashion in which the oligosulphide chain end is decoordinated by an equivalent of PO at the dimeric Li<sub>2</sub> core. We infer that this decoordination is enabled by the high oxophilicity of lithium,

which at least partially explains its increased catalytic activity compared to other alkali metals.

Interestingly, the rate-determining transition state is lowest in energy when the ester group adjacent to the chain end participates in the coordination of the lithium dimer. For PTA/PO ROCOP, the analogous rate-determining transition state (TS3 in Figure 4c) likewise involves a dimeric structure. However, in contrast to ROTERP, a thioester group rather than an ester coordinates the lithium, which is associated with a higher insertion barrier of  $\Delta G^\ddagger = 117.6$  kJ mol<sup>-1</sup>. Thus, we attribute the rate enhancement observed when moving from ROCOP to ROTERP to the presence of an ester, rather than a thioester, adjacent to the chain end. In fact, natural bond orbital (NBO) analysis of thioester and ester appended thiocarbonylates (Figure 4d) reveals the carbonyl oxygen of the latter to feature less accumulation of negative partial charge on the carbonyl oxygen than for the former. This renders esters a better neutral ligand for lithium than thioesters, which we infer to be responsible for the observed rate-enhancement.

Regarding selectivity, i.e., the seemingly preferential  $S_8$  over PTA insertion by the lithium thiolate intermediate T (Figure 3), we found that PTA insertion is practically as exergonic as  $S_8$  insertion, with a  $\Delta\Delta G = 2.6$  kJ mol<sup>-1</sup> in favour of PTA incorporation. However, propagation via PO insertion thereafter is more favoured from oligosulphides OS by  $\Delta\Delta G^\ddagger = 24.2$  kJ mol<sup>-1</sup>. This implies that PTA insertion by T must be reversible to allow for the correction of erroneous insertions during ROTERP, which we confirmed experimentally (see ESI Figure S17). Here, a model lithium thiolate (<sup>t</sup>BuSLi) was





**Figure 5.** a) Monomer scope of the methodology elucidating selectivity governing factors. b)  $T_g$  range and optical photographs of obtained polymers for Table 2 run at 1 eq. LiOBn: 500 eq. epoxide: 200 eq. thioanhydride: 200 eq. S.

first reacted with PTA, and subsequently elemental sulphur was added. Indeed,  $^1\text{H}$  NMR analysis of the reaction mixture revealed initial consumption of PTA, which reformed after the addition of  $\text{S}_8$ .

Importantly the crude reaction mixture also shows the presence of some minor resonances (1%–7% by integration) corresponding to small molecule byproducts which can be easily separated during work-up (see ESI Figures S3 and S4; Scheme S1). GPC analysis shows these to be primarily species in the small molecule regime  $>1\text{ kg mol}^{-1}$ , as for example, cyclised repeat units (or doubles and triples of these). This suggests the presence of some backbiting reactions as competitive depolymerisation pathways alongside propagation. In these **T** reacts with an oligosulphide link near the chain end within the same polymer chain instead of with  $\text{S}_8$  thereby leading to the formation of macrocycles. This pathway could be tentatively confirmed via exposure of a terpolymer to in situ generated thiolates that, upon thermal activation, lead to some depolymerisation as seen by  $^1\text{H}$  NMR. Furthermore, obtained weights are lower than theoretical molecular weights. We previously observed in terpolymerisations of  $\text{S}_8$  that sulphur–sulphur polymer linkages act as chain-transfer sites, decreasing molecular weights and broadening polydispersities.<sup>[31]</sup> Here thiolate **T** attacks more oligosulphide links or links of other polymers effectively catalysing sulphur–sulphur bond metathesis which can lead to the formation of multiple cyclic polymers instead of a single polymer chain and thereby reduce the obtained molecular weight. In fact, following the  $\text{CH}_2$  region of the crude  $^1\text{H}$  NMR spectrum reveals that longer  $\text{S}_x$  links decrease in proportion in favour of shorter  $\text{S}_x$  links as elemental sulphur is consumed, confirming that  $\text{S}_x$  undergoes metathesis during ROTERP. Furthermore, such a methathesis can also occur spontaneously, as very recently demonstrated.<sup>[65]</sup> In fact, prolonged reaction of a terpolymer with dimethyltrisulphide  $\text{MeS}_3\text{Me}$  in PO at 100 °C leads to a reduction of molecular

weight by cleaving polymer chains and end-capping these with a Me group (see ESI Figure, Scheme S1 and Figure S94). This suggests that sulphur–sulphur bond metathesis can also occur spontaneously under reaction conditions.

Next, we turned to exploring the monomer scope of our methodology (Figure 5). We decided to survey our methodology at an initial loading of 1 eq. LiOBn: 500 eq. epoxide: 200 eq. PTA: 200 eq. S at 100 °C which for PO (Table 2 run #0) delivers a linkage selectivity of 87%, hence allowing us to study how monomer choice affects selectivity, shedding further mechanistic light on our methodology.

Moving from PO to its longer chain variants BO (run #1) and DO (run #2) results in a slight improvement of linkage selectivity, while as expected lowering the glass transition temperature from 30 °C for the PO terpolymer to –23 °C for the DO terpolymer. As for PO, the addition of more sulphur to the initial monomer feed ratio (run #3) results in an increase to 97% selectivity. Moving to bicyclic CHO (run #4) results in 76% linkage selectivity and an increased  $T_g$  of 85 °C, and both can be attributed to the rigidity of the cyclohexyl backbone. Mechanistically this leads to a strained bicyclic intermediate upon backbiting, thereby disfavoured O/S exchange and  $\text{S}_8$  incorporation.<sup>[66]</sup> Nevertheless, an increase in sulphur loading achieves near perfect linkage selectivity (run #5), which has been challenging to achieve in related sulphurated polymerisations.<sup>[67,68]</sup> In line with this interpretation, the geminally disubstituted epoxide IBO (run #7), that favours backbiting due to the Thorpe–Ingold effect, leads to an increase in sequence selectivity compared to monosubstituted PO.<sup>[65,66]</sup> Notably, IBO does not contain diastereotopic protons, simplifying  $^1\text{H}$  NMR analysis that again supports an increase in longer oligosulphide links with sulphur loading (run #8, see ESI Figure S89) by this complementary technique. Moving to SO (run #9 and #10), an intrinsically challenging monomer in this class of polymerisation also results in successful polymer formation,

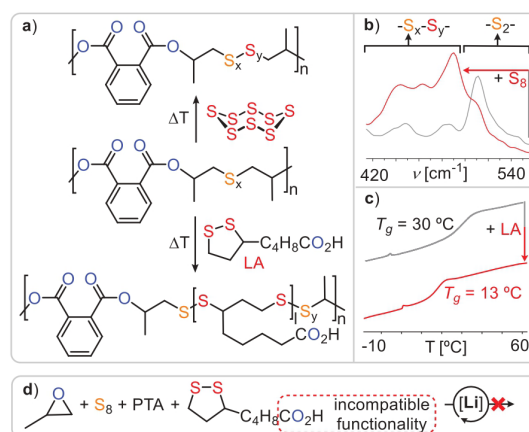
albeit with no head-to-head or tail-to-tail regioselectivity. As it has been previously reported that SO ring opening occurs both at the head CHPh and tail CH<sub>2</sub> positions of the epoxide, this demonstrates that the regioselectivity of the initial epoxide ring opening explains the head-to-head-*alt*-tail-to-tail regioselectivity observed for PO and others epoxides, thus further supporting the mechanistic hypothesis.<sup>[69]</sup>

Employing naphthalic thioanhydride (NTA), featuring a larger aromatic system compared to PTA, improves sequence selectivity both in combination with PO (run #11) and CHO (run #12). We attribute this to the larger aromatic system favouring O/S exchange by stabilisation of the accumulating negative charge on the carbonyl centre during backbiting. Furthermore, polymers derived from NTA exhibit increased glass transition temperatures compared to those from PTA and thereby result in a maximum  $T_g$  of 128 °C. Conversely, moving to electron richer aliphatic thioanhydrides, such as stearic thioanhydride (STA), does not result in any reactivity at all, completing the mechanistic picture that ROTERP is best and most selectively achieved for monomers that favour the backbiting step for either steric or electronic reasons. Epoxides bearing heteroatom containing and functional substituents are likewise tolerated, such as glycidyl ethers bearing an ethyl (EGE, run #13) and phenylether (PGE, run #14) substituent. Glycidyl ethers are particularly attractive as they allow for the use of natural product derived epoxides such as vanillin glycidyl ether (VGE, run #15), which likewise undergo ROTERP, producing a terpolymer with functional pending aldehyde substituents useful in, e.g., postfunctionalisation reactions (vide infra). Also, in this case NTA (run #16) increases glass transition temperatures and sequence selectivity compared to PTA.

Demonstrating the high functional group tolerance of the methodology, we employed a carbazole functionalised epoxide (run #17), producing a high  $T_g$  polymer, which, due to the intrinsic luminescence of carbazole, fluoresces under UV light. As for SO, regio unselective epoxide ring-opening renders the polymer regio-random. Even epichlorohydrin bearing electrophilic CH<sub>2</sub>Cl groups is tolerated, albeit with decreased molecular weight and broadened polydispersities (run #18), indicating some branching due to co-occurring nucleophilic substitution with the side chains.<sup>[70]</sup> Motivated by this circumstance, we employed a bifunctional epoxide DEO (run #19), which indeed yields an insoluble network with PTA and S<sub>8</sub>. We could even extend this to epoxidised soybean oil, yielding a crosslinked network with a very low  $T_g$  of −40 °C. Despite the insolubility of these networks in good solvents for linear terpolymers (THF, CHCl<sub>3</sub>) they can be compression moulded into brittle films at 80 °C due to the dynamics of the incorporated -S<sub>x</sub>- bonds.

Considering the combined monomer scope, our methodology can yield polymers with -S<sub>x</sub>- functionalities across an impressive  $T_g$  range of ca. 170 °C. Particularly high  $T_g$  polymers exceeding 100 °C have been challenging to obtain from elemental sulphur, as, e.g., inverse vulcanisation techniques typically yield low  $T_g$  materials.<sup>[71,72]</sup>

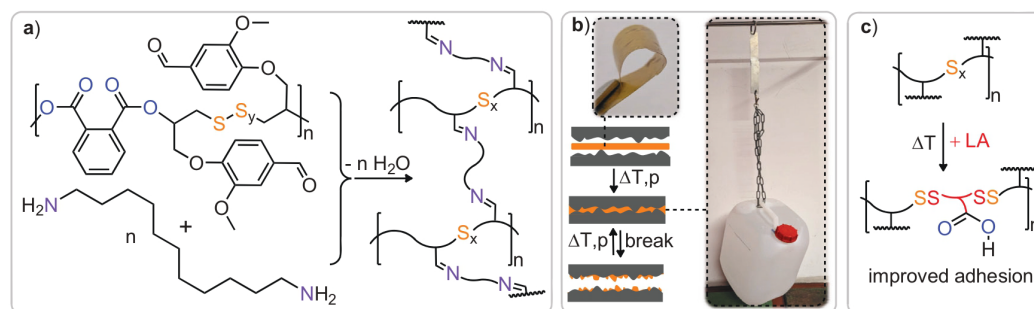
In terms of thermal stability, the vast majority of materials are stable to above 250 °C which represents an approximate 100 °C improvement over previous ROTERP polymers from



**Figure 6.** a) Thermal backbone editing of S<sub>8</sub>/PTA/PO terpolymer with S<sub>8</sub> or lipoic acid (LA). b) Zoom into the S<sub>x</sub>- region of the Raman spectrum (black) before and (red) after thermal S<sub>8</sub> insertion (10 w%). c) DSC data (black) before and (red) after lipoic acid insertion (50 w% feed ratio). d) Attempted polymerisation of LA during ROTERP fails.

elemental sulphur, which were prone to decomposition via loss of COS as soon as sulphur–sulphur bonds opened.<sup>[31]</sup> In contrast, the polymers reported in this contribution are stable at temperatures where sulphur–sulphur bonds can be thermally activated. Hereby the polymer backbone becomes amenable to modifications, a concept which recently attracted attention under the term “skeletal or backbone editing”.<sup>[73–75]</sup> In order to modify the polymer backbone, we heated a finely ground mixture of a PO terpolymer (Table 1 run #9) and 5 or 10 w% elemental sulphur at 140° for 120 min in an attempt to incorporate further sulphur into the polymer. Assessing the <sup>1</sup>H NMR spectrum indeed shows diagnostic changes of the CH<sub>2</sub>-S<sub>x</sub>- region with signals increasing in relative intensity that correspond to longer oligosulphide chains (Figure 6b). This observation could be more clearly observed in the <sup>1</sup>H NMR spectrum of the IBO terpolymer, which does not feature diastereotopic protons (see ESI, Figure S136). Raman spectroscopy confirms this observation. As shown in Figure 6, while the Raman band at 510 cm<sup>-1</sup> corresponding to disulphide links is most intense in the starting polymer, this decreases in intensity upon reaction with elemental sulphur with bands below 490 cm<sup>-1</sup> corresponding to higher order oligosulphides increasing in intensity; these observations are more pronounced at 10 w% than at 5 w% elemental sulphur in the starting mixture. GPC analysis confirms that the polymer remains intact upon sulphur insertion with  $M_w$  shifting from 28 kDa ( $\bar{D} = 1.6$ ) to 29 kDa ( $\bar{D} = 1.6$ ) with 5 w% S<sub>8</sub> and 23 kDa ( $\bar{D} = 1.7$ ) with 10 w% S<sub>8</sub>, indicating some chain cleavage or rearrangement via sulphur bond metathesis in the process. Backbone editing could also be expanded to cyclic disulphide, such as lipoic acid. Hence, we heated a 1:1 mixture in w% of lipoic acid with an S<sub>8</sub>/PTA/PO terpolymer at 140 °C for 240 min followed by precipitation of the product mixture to remove unconsumed lipoic acid. The so-formed polymer exhibits additional resonances in its <sup>1</sup>H NMR spectrum in the aliphatic region between 1.8 and 3.6 ppm (see ESI Figure S138). These correspond to ring-opened lipoic





**Figure 7.** a) Crosslinking of  $S_8$ /PTA/PO terpolymer via imine condensation with 1,12-dodecylamine. b) Application of compression mouldable polymer films as adhesives on steel with photographs of bonded steel plates holding a filled water canister. c) Schematic representation of backbone edited material obtained from lipoic acid insertion, which improves adhesion on aluminium.

acid and are broadened and shifted relative to the starting lipoic acid reactant in 47% of the repeat units by integration. Editing of the polymer backbone is also supported by a redistribution of the Raman  $S_x$  bands (see ESI Figure S139). GPC analysis shows slightly broadened molecular weight distribution (see ESI Figure S141), which we again attribute to chain cleavage and rearrangement via sulphur–sulphur bond metathesis. As can be seen in Figure 6c, insertion of lipoic acid does decrease the glass transition temperature from 30° to 17 °C. Hence, backbone editing provides a means to alter the thermal properties after synthesis. Notably this also allows the incorporation of functional groups which are intrinsically incompatible with the polymerisation methodology, as attempting to perform ROTERP in the presence of lipoic acid (Figure 6d) results in no reaction at all (Figure 7).

The large monomer scope of the ROTERP methodology enables the incorporation of functional groups into the polymer side chains that also allow for post polymerisation modification of these. In this regard the  $S_8$ /PTA/VGE terpolymer (Table 1 run #15) features aldehyde functionalities that can undergo imine condensation, offering an opportunity for the incorporation of degradable crosslinks to enhance mechanical properties.<sup>[76–78]</sup> The reaction of the VGE terpolymer (Table 2 run #14) with (see ESI Methods section) leads to gelation of the reaction mixture. Removal of the solvent yields a solid that is entirely insoluble (> 99% gel fraction) in common organic solvents which the starting linear polymer is soluble in (DCM, THF, DMF), clearly substantiating crosslinking (see ESI Figure S146). However, due to the dynamicity of sulphur–sulphur and imine bonds, this network can be processed by compression moulding into flexible films that exhibit a maximum stress of  $49.9 \pm 4.6$  MPa at  $2.7\% \pm 0.3\%$  elongation at break (see ESI Table S3). The thermally reprocessed material recovers 88% and 77% of maximum stress and strain resistance respectively. The potential for thermal reprocessing of these networks enables their application as reusable adhesives as has been for example demonstrated for polymers from inverse vulcanisation.<sup>[18,21,79]</sup> In contrast to other approaches to such networks, our stepwise access allows to combine polymer links during synthesis to rationally impart functionality onto the material. Accordingly, to evaluate the adhesion performance of the imine crosslinked polysulphide, it was tested on wood as well as abraded steel

and aluminium sheets ( $100 \times 25$  mm) with the polymer applied to an overlapping area of  $25 \times 16$  mm, and the two sheets were bonded together by compression moulding (see ESI methods section). Lap shear experiments were subsequently performed at a pull rate of  $5 \text{ mm min}^{-1}$  showing a typical maximum stress of  $5.4 \pm 1.2$  MPa on steel (three run average, both adhesive and cohesive type failure). These performance properties are competitive, when compared to other sulphur based adhesives reported previously and, for example, exceed the performance of commercial glues such as epoxy glue reference (see ESI Table S3).<sup>[18,21,79–82]</sup> Importantly, after material failure, the respective parts can be rebound by compression moulding under restoration of the adhesion performance, achieving  $6.6 \pm 1.1$  MPa. We attribute the slight increase in performance to some curing occurring via completion of imine condensation during reprocessing. Adhesive testing on wood reveals that material failure of the wood specimen occurs before failure of the adhesive. On aluminium, however, a lower maximum stress of  $2.8 \pm 0.8$  MPa (adhesive type failure) was achieved. We opted to improve performances by the introduction of polar groups which are expected to aid interaction with the substrate surface and applied the above established backbone editing protocol, as lipoic acid features polar carboxylic acid groups. Gratifyingly, heating a finely ground mixture of the crosslinked material with 20 w% lipoic acid at 140 °C results in the formation of a homogenous material. Only trace amounts of lipoic acid could be identified in the sol-fraction of a sol-gel test supporting incorporation into the network. Although Raman spectroscopy was prevented by the high absorbance of the material, differential scanning calorimetry (DSC) shows a decrease in  $T_g$  from 53° to 36 °C further substantiating incorporation (see ESI Figure S152). Testing the modified material as an adhesive on aluminium gratifyingly reveals a more than threefold improvement of adhesion performances with a stress at break of  $5.6 \pm 0.3$  MPa (cohesive type failure). Hence, the backbone modifiability can be used to improve material performance.

Yet not only the  $S_x$  bonds but also the imine crosslinks provide additional functionality to the material: they impart acid degradability. As can be seen in the supplementary video, exposing the adhesive to hydrochloric acid results in the debonding of the sheets within 30 min. Hence, the stepwise

synthetic approach allows tailoring adhesives with respect to several target properties.

## Conclusions

In conclusion, we have reported a new sequence selective terpolymerisation of elemental sulphur delivering polyester featuring dynamic oligosulphide units. Sequence selectivity is achieved on kinetic grounds in which coordinative participation of polyester links adjacent to the chain end leads to a rate increase, as they represent better donors. The exceptionally broad monomer scope gives straightforward access to a wide glass transition temperature range as well as functional side chains. The improved thermal stability renders the backbone editable via insertion into the —S—S— bonds. Crosslinking of aldehyde functionalised polymer via imine condensation yields thermally reprocessable adhesive in which backbone editing can be used to enhance adhesive performance while the imine bond grants acid degradability. Our contribution demonstrates how mechanistic understanding achieves to impart the dynamicity of elemental sulphur into a popular class of polymers, namely polyester, with tuneable properties and functionality.

## Supporting Information

Additional references cited within the Supporting Information.<sup>[83–88]</sup>

## Acknowledgements

The authors thank the “Verband der chemischen Industrie” and the “Daimler and Benz Foundation” (personal scholarships for A. J. P) as well as the “Deutsche Forschungsgemeinschaft” (project number 542928411) for financial support.

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Polymerisation catalysis • Ring-opening (co/ter)polymerisation • Sulphur waste utilisation • Sulphur-containing polymers

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Manuscript received: January 16, 2025

Revised manuscript received: March 28, 2025

Accepted manuscript online: April 10, 2025

Version of record online: June 04, 2025



Supporting information for  
**Kinetically Enhanced Access to a Dynamic Polyester Platform  
via Sequence Selective Terpolymerisation of Elemental Sulfur**

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## Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are referenced to the residual proton resonance of the deuterated solvents. Epoxides were dried over calcium hydride at room temperature for 2 days followed by distillation under argon atmosphere. BnOH was dried over 4Å molecular sieves and degassed. Elemental sulfur (99.99% purity) was sublimed under dynamic vacuum at 100°C. Phthalic thioanhydride (PTA) was synthesized according to the literature procedure and then purified by recrystallisation from  $t\text{BuOMe}$  followed by recrystallisation from  $\text{CHCl}_3$  and two sublimations under dynamic vacuum at 90°C and was stored inside an argon filled glovebox prior to use.<sup>[1]</sup> VGE (vanillin monoglycidyl ether) and 9-(Oxiran-2-ylmethyl)-9H-carbazole (CE) were prepared following previously reported procedures.<sup>[2],[3]</sup> Naphthalic thioanhydride (NTA) was prepared following the synthetic procedure used for Phthalic anhydride (PTA) with the difference that the product precipitates from the solution. It was isolated via filtration and washed with boiling  $\text{H}_2\text{O}$ . Characterisation agreed with the literature.<sup>[4]</sup> The obtained crystals were sublimed under vacuum at 120°C and stored in the glove box. All other reagents were used as received if not stated otherwise. All reagents were stored and used inside an Ar filled glovebox.

A confocal WITec Alpha 300 RA + Raman imaging system equipped with a UHTS 300 spectrometer and a back-illuminated Andor Newton 970 EMCCD camera together with the WITec Suite SIX 6.1 software package were employed for Raman measurements. All spectra were acquired with an excitation wavelength of  $\lambda = 532 \text{ nm}$ , using integration times of 0.3–0.35 s and a laser intensity of 20 mW for Raman imaging. For large area Raman imaging (typically  $180 \times 150 \mu\text{m}^2$ ) a 50× long working distance objective (Zeiss LD EC Epiplan-Neofluar Dic 50×, numerical aperture  $\text{NA} = 0.55$ ) and a step size of  $0.5 \mu\text{m pixel}^{-1}$  were used. Raman imaging with a 100× objective (Zeiss EC Epiplan-Neofluar Dic 100×,  $\text{NA} = 0.9$ , typically  $50 \times 50 \mu\text{m}^2$ ) was conducted with a step size of  $0.2 \mu\text{m pixel}^{-1}$ . All spectra were corrected for cosmic ray spikes and subjected to a background removal routine.

TGA data was measured using a Netzsch TG 209. DSC was measured on a Netzsch 204 F1 “Phoenix” at 10 K/min heating rate.

Size exclusion chromatography (SEC) was performed using a Waters 515 HPLC pump and THF as eluent at a flow rate of 0.5 mL/min. A volume of 100  $\mu\text{L}$  of polymer solution (1-2 mg/mL) was injected with a 707 Waters autosampler into a column setup comprising a guard column (MesoPore Guard 5 x 0.75 cm, particle size 3  $\mu\text{m}$ ). Polymer size distribution was monitored with a Waters 414 refractive index detector. Narrow distributed polystyrene standards were used for calibration and 1,2-dichlorobenzene as internal reference. Each polymer sample was dissolved in HPLC-grade THF (2 mg/mL) and filtered through a 0.45  $\mu\text{m}$  porous filter frit prior to analysis. Elmann’s reagent was added to the mixture before filtration, this was done to end cap the polymer chains and prevent depolymerization in THF.

Polymer films were made using a Weber Hot press at 130°C and 5 metric tons for 30 min, after that the plates were left to cool down slowly while keeping the pressure, that way we assured to have flat films and avoid any bending or cracking due to inhomogeneous cooling.

Tensile tests were performed on an Instron 5565 universal tester using a 1 kN load cell and pneumatic clamps. The thickness of the specimens was measured with a digital micrometre (Mitutoyo 293–831, digimatic MDC Lite) in the range of 600 to 650  $\mu\text{m}$ . The E-Moduli of all specimens were investigated at a strain rate of  $0.2 \text{ mm min}^{-1}$  and calculated between 0.1% and 0.3% strain. To ensure a better evaluation of the properties, the measure was conducted on 3 dog bones cut from the same film.

Lap shear test was run on a universal testing machine Zwick 1485 with a pull rate of 5 mm/min. Samples of 100x25 mm with an overlay of 25x16 mm were tested.

In situ IR measurements were done with a ReactIR 15 from Mettler Toledo equipped with a DST Series AgX Fiber Conduit probe. All monomers were dissolved in an excess of epoxide and preheated at  $80^{\circ}\text{C}$  to ensure dissolution. Once the mixture was at the required temperature, the baseline was set and after that a solution containing the catalyst was injected and the evaluation started. Due to the necessity of running this reaction at  $80^{\circ}\text{C}$ , Ethyl glycidyl ether (EGE) was chosen as the epoxide due to its' increased boiling point compared to propylene oxide.

## Section S2: Polymerisation and post functionalization procedure

**General Polymerization Protocol:** Inside an argon-filled glovebox, LiHMDS and BnOH were dissolved in the epoxide, and the mixture was transferred to an oven-dried vial equipped with an oven-dried stirrer bar. S<sub>8</sub> and PTA were then added, and the vial was sealed with a melamine cap containing a Teflon inlay. The vial was then brought outside the glovebox, placed in a pre-heated aluminum block at the specified temperature, and maintained for the specified time. To ensure reproducibility, the polymerization was conducted at 30°C, representing "room temperature" during summer.

At the end of the reaction, the polymer was isolated by dilution in DCM (5 mL), filtered through a 0.5 µm syringe filter to remove traces of unreacted solids, such as elemental sulfur, and then the mixture was successively added to 40 mL of MeOH. This caused the polymer to precipitate making it possible to isolate it through centrifugation.

To ensure the stability of the samples during GPC measurements, Ellman's reagent (ca. 10 mg/mL) was added to the THF solutions for analysis to quench reactive thiol chain ends. <sup>[5][6]</sup> Note that if this step is omitted, slow depolymerization occurs during GPC measurements.

**Metathesis experiment:** An isolated polymer obtained from isobutylene oxide (IBO, due to more facile NMR analysis of the S<sub>x</sub> region) was dissolved in PO (to model the medium during polymerization), subsequently an excess (0.2 mL) of dimethyl trisulfide was added to the solution and the mixture was heated to 100° for 3h before precipitation with MeOH. Both the crude mixture and the precipitated polymer were analyzed with GPC to evaluate the changes in the molecular weight. Note that recently spontaneous trisulfide metathesis has been reported.<sup>[7]</sup>

**Insertion protocol:** The terpolymer was frozen in liquid nitrogen and manually grinded to a powder, after that it was left in a drying oven to remove any water that condensed on it during the cooling process. Once the powder was dried, it was mixed with different amount of sulfur or lipoic acid and the whole mixture was heated to 140°C to melt the components and enable polysulfide activation. After 2h for sulfur and 4h for lipoic acid, the mixture was cooled to room temperature, dissolved in DCM and precipitated with MeOH followed by isolation via centrifugation.

**Cross linking protocol:** The VGE terpolymer was dissolved in DCM and 1,12-dodecandiamine was added. Knowing that for each repeating unit of polymer there are 2 aldehyde groups stemming from VGE, we added 0.9 eq. of diamine per repeat unit to avoid partially reaction of diamines. The mixture was left stirring at room temperature overnight and afterwards opened to the atmosphere. Once DCM was completely evaporated, the network was dried at 80°C overnight under vacuum to further promote imine condensation through the removal of water.

**Lipoic acid insertion into cross linked material:** The network was grinded with the aid of a cryo-ball mill (-195.8°C, 25 mm diameter sphere, frequency of 30 oscillation per second). The resulting powder was then mixed with lipoic acid, and the mixture was heated at 80°C for 30 minutes to melt lipoic acid and allow the liquid to swell into the network powder. After that, the mixture was heated at 140°C for 2h to promote disulfide activation allowing the insertion lipoic acid in the network. The resulting material was then hot pressed at 130°C to promote further curing.

**Adhesion test:** 3 different substrates were tested: Steel S235, aluminium and oak wood (total area 100×25 mm with an overlapping area of 25×16 mm). For metals, the plates were first abraded with sandpaper to remove any oxidized layer and promote interaction with the surface. This was followed by cleaning with acetone. After that the polymer film was placed in between the two plates that were then hot pressed under 2 metric tons at 130°C for 30 min. After that, the temperature was switched off and the plates were left to cool down slowly to room temperature. Since the wood plates were too fragile to be hot pressed under the same condition, adhesion was achieved by clamping the two plates together and then the whole setup was left inside an oven at 125°C. After 30 min clamps were readjusted and then the setup was left in the oven overnight. Excess polymer that squeezed out was removed with a scalpel. The materials were also compared with a commercial epoxy glue: WEICON – epoxy minute adhesive. In this case the sealant was also applied after abrading and cleaning, the bicomponent epoxy glue was put on one side of the plate and then the other side was pressed under 2 metric tons at room temperature for 30 minutes. In each case the performance and associated errors were calculated from 3 distinct samples.

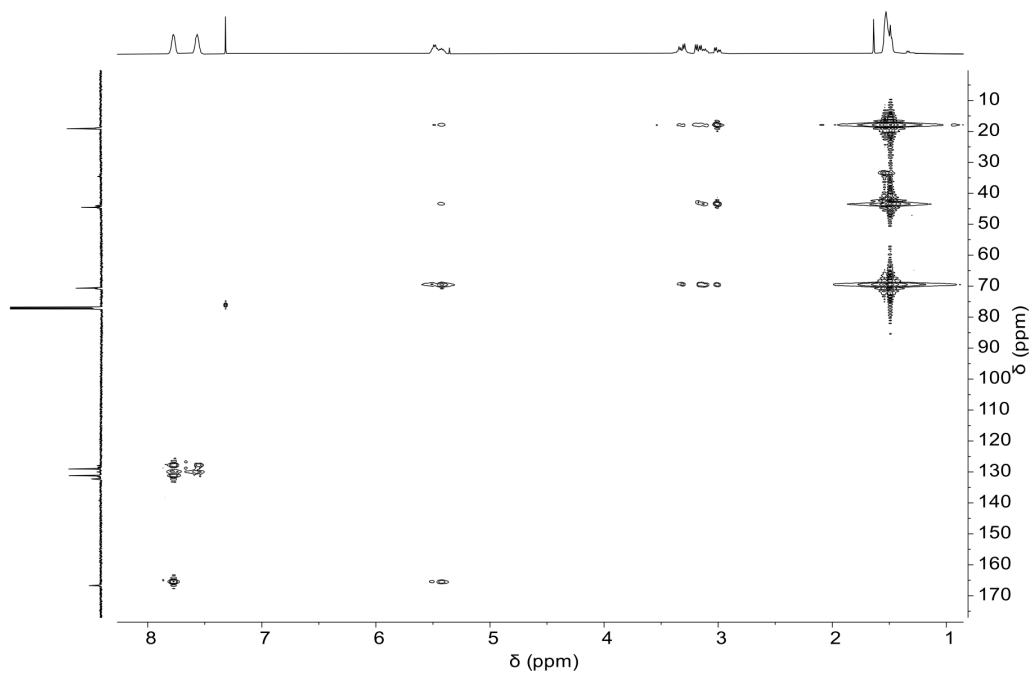
Section S3: S<sub>8</sub>/PTA/PO ROTERP

Figure S1: <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #5.

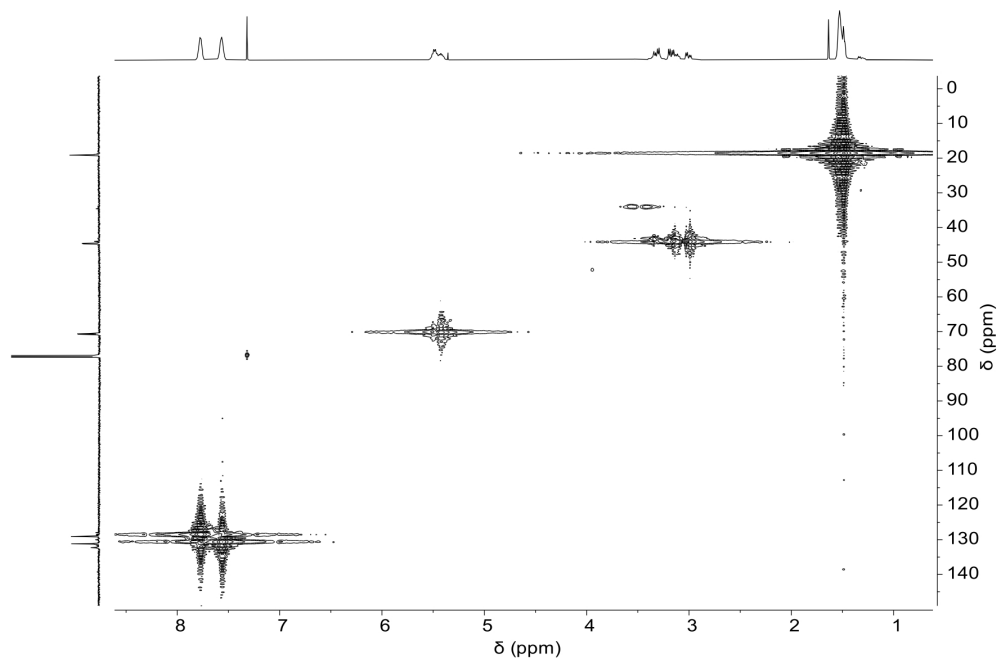


Figure S2: <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #5.

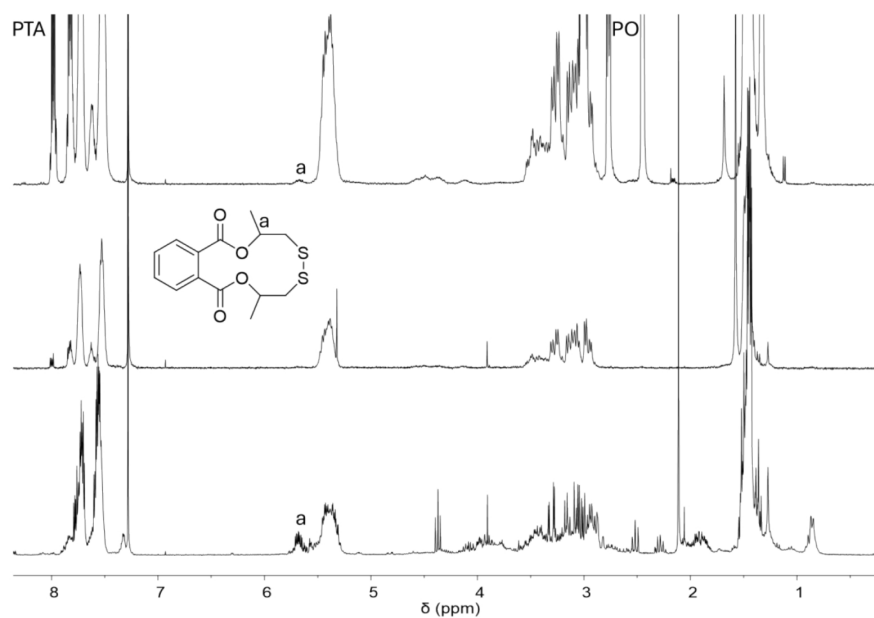
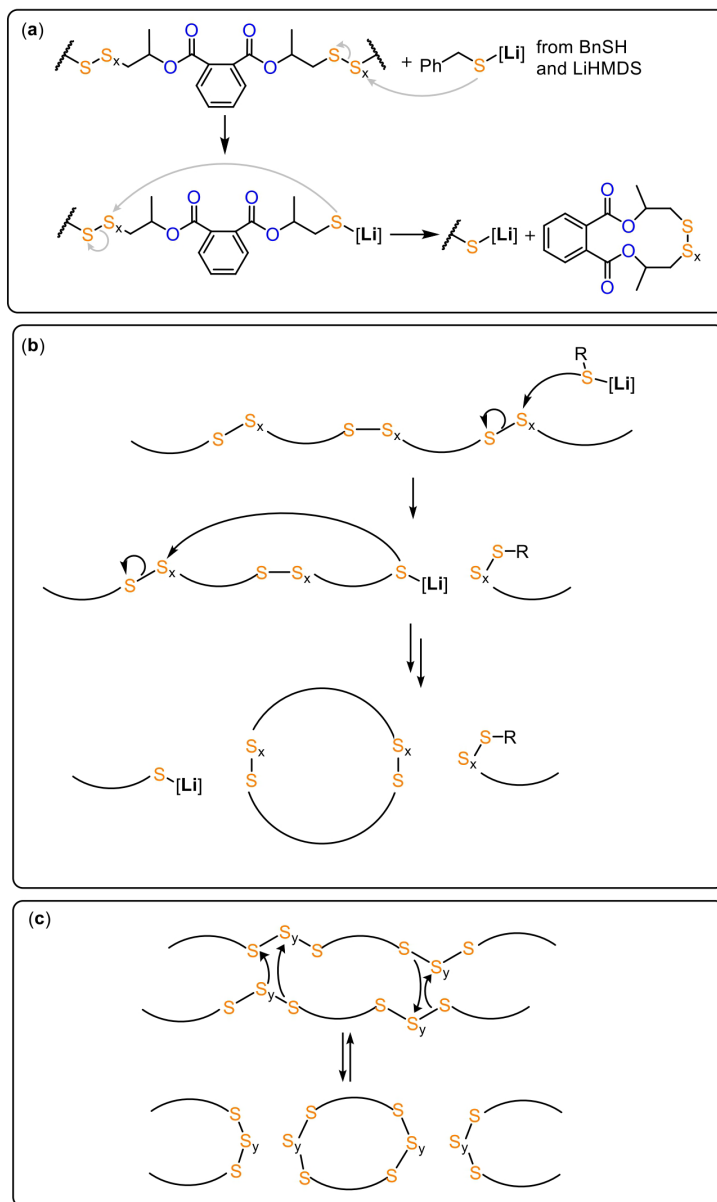


Figure S3: <sup>1</sup>H-NMR spectra of (top) crude mixture (b) isolated terpolymer and (c) depolymerization attempt. For the depolymerization experiment thiolate species (5 mol% per repeat unit of polymer) were prepared from benzyl mercaptan and LiHMDS following by prolonged heating (reflux overnight) of an isolated terpolymer with the so generated thiolate species in THF producing resonances that correspond to macrocyclic species in line with depolymerisation hypothesis.



Scheme S1: Mechanistic hypothesis for (a) backbiting/depolymerisation reaction evoked by  $\text{LiSBn}$ ; note that this can likewise occur from thiolates intermediates during the ROTERP cycle. (b) Formation of larger macrocycles following the same mechanism; note that these can be in principle any size including macrocyclic polymers when the attack of the thiolate occurs to very distant  $\text{S}_x$  units. (c) Macrocyclisation following the recently discovered spontaneous metathesis mechanism.<sup>[7]</sup>



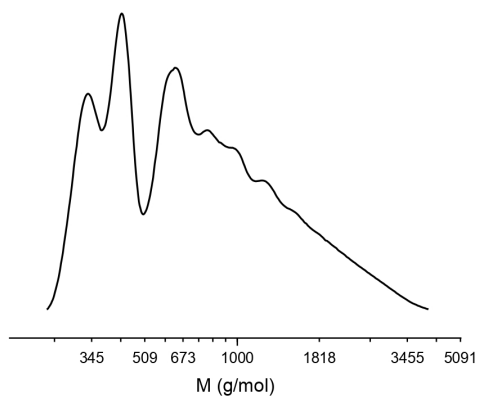


Figure S4: GPC analysis of the dried liquid phase obtained after the precipitation of terpolymer from DCM/MeOH. Molecular weight of one repeat unit  $S_x = S_2$  is 312 g/mol (344 g/mol for  $S_3$ , 376 g/mol for  $S_4$ , 408 g/mol for  $S_5$ ). Macrocycles comprising 2 or 3 repeat units tentatively correspond peaks around 600 and 900 g/mol.

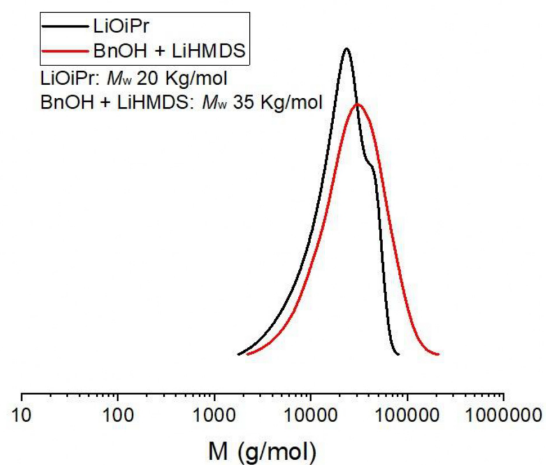


Figure S5: Comparison of the GPC signals obtained from two terpolymerisation having same loading and conditions (1 eq. LiOR: 500 eq. PO: 200 eq. PTA: 200 eq. S at 100°C) indicating that *in situ* produced  $\text{HN}(\text{SiMe}_3)_2$  does not have negative effects on the polymerisation outcome.

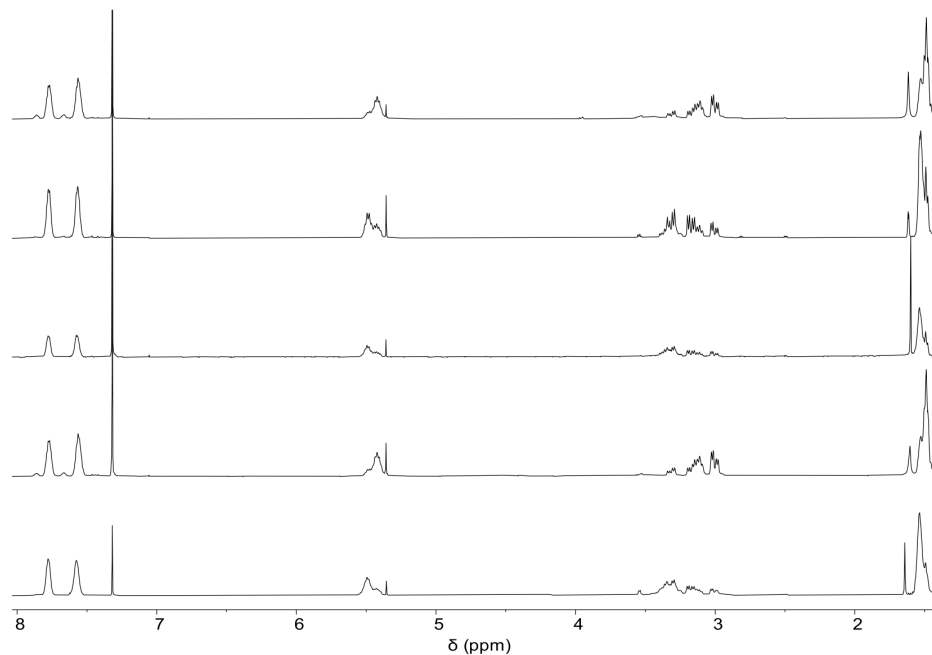


Figure S6: Overlaid <sup>1</sup>H-NMR spectra (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymers corresponding to table 1 run #1,2,3,4,6.

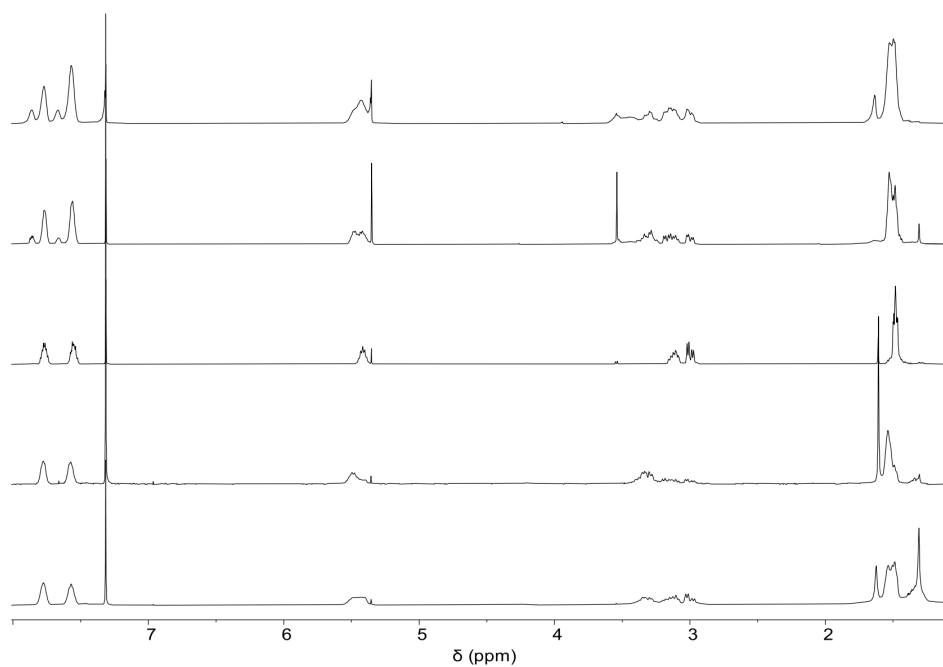


Figure S7: Overlaid <sup>1</sup>H-NMR spectra (400 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymers corresponding to table 1 run #7,8,9,10,11.

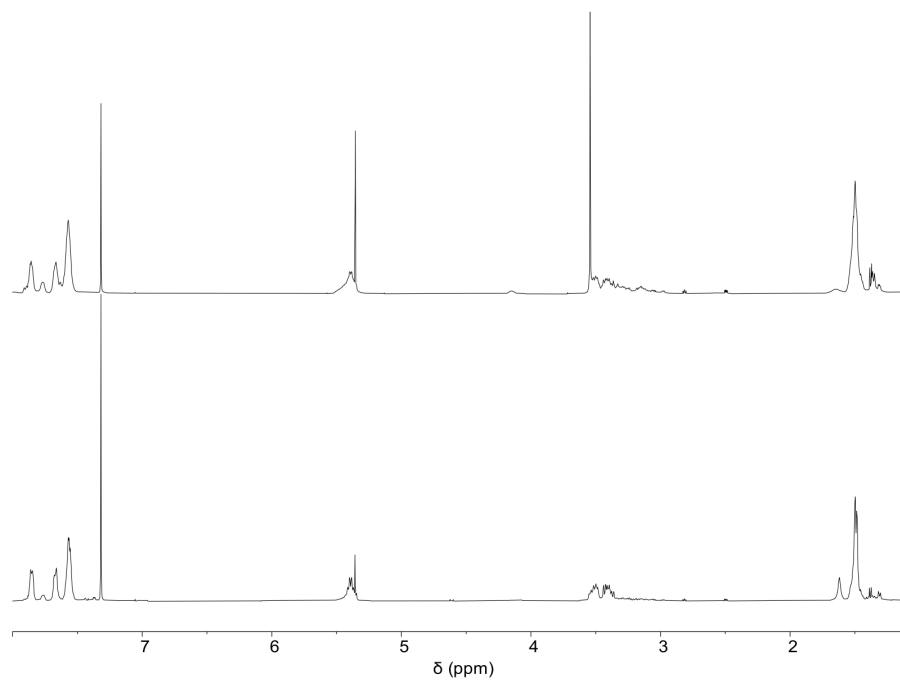


Figure S8: Overlaid  $^1\text{H}$ -NMR spectra (400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to table 1 run #12,13.

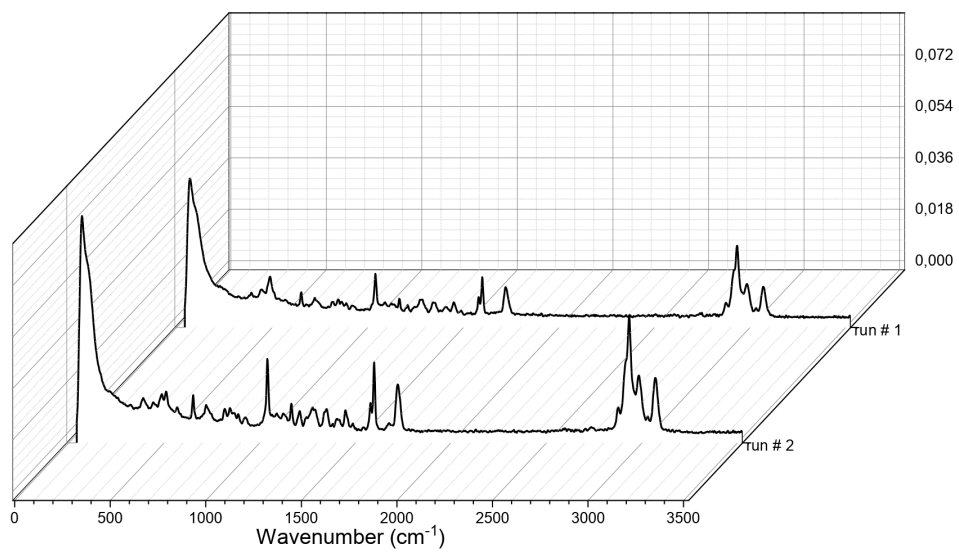


Figure S9: Overlaid Raman spectra of the polymers corresponding to table 1 run #1 and #2.

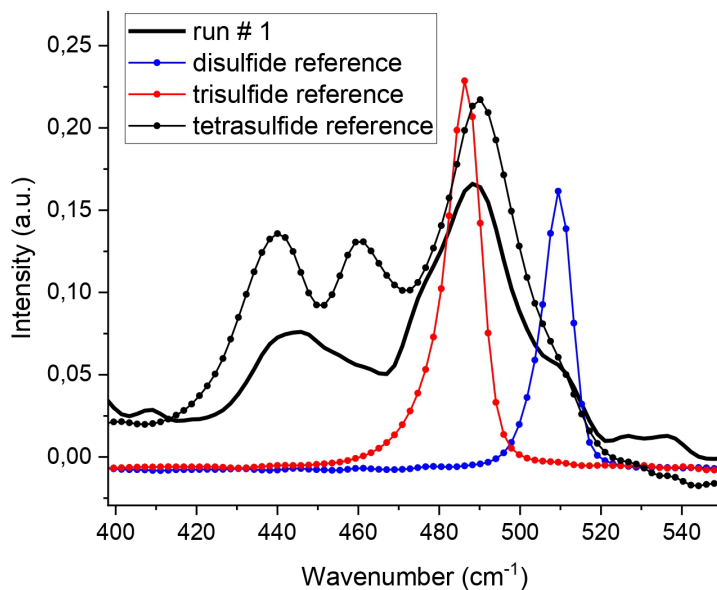


Figure S10: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectra of the polymer corresponding to table 1 run # 1, compared with dimethyl disulfide, dimethyl trisulfide, and  $R_2$ -tetrasulfide [ $R = -\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ] reference compounds.

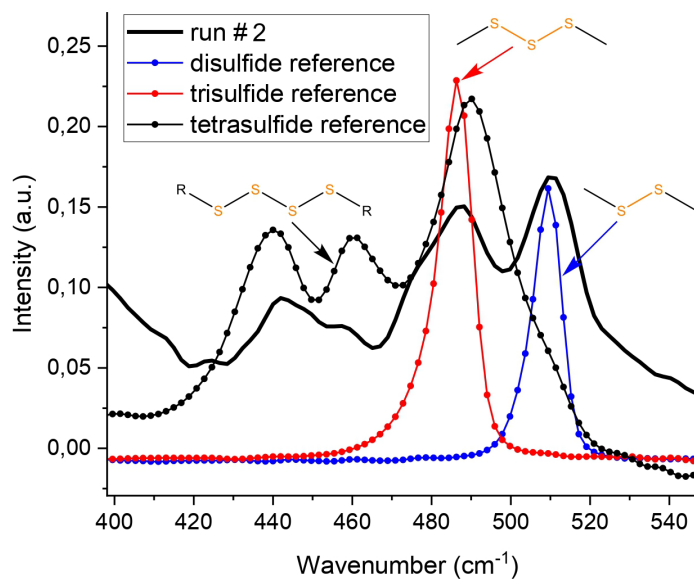


Figure S11: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectra of the polymer corresponding to table 1 run # 2, compared with dimethyl disulfide, dimethyl trisulfide, and  $R_2$ -tetrasulfide [ $R = -\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ] reference compounds.

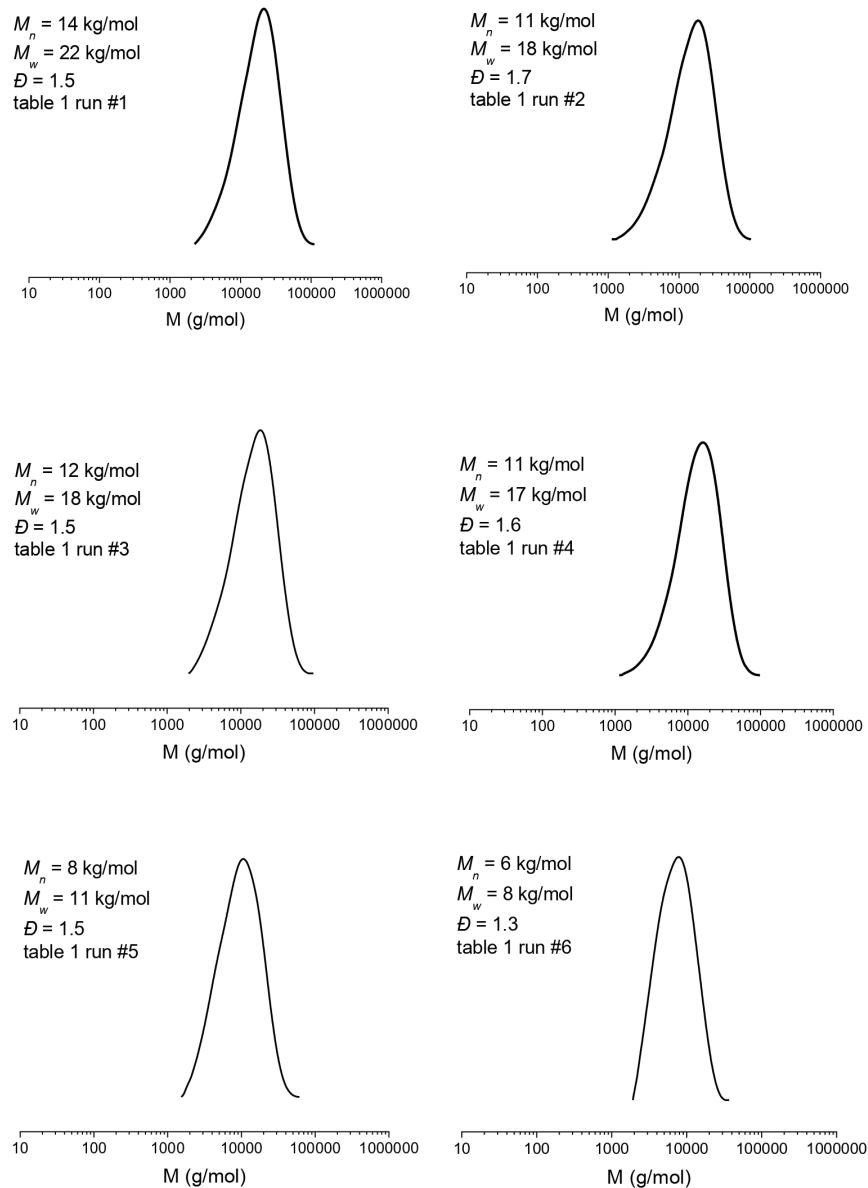


Figure S12: GPC curves corresponding to table 1 run #1,2,3,4,5,6.

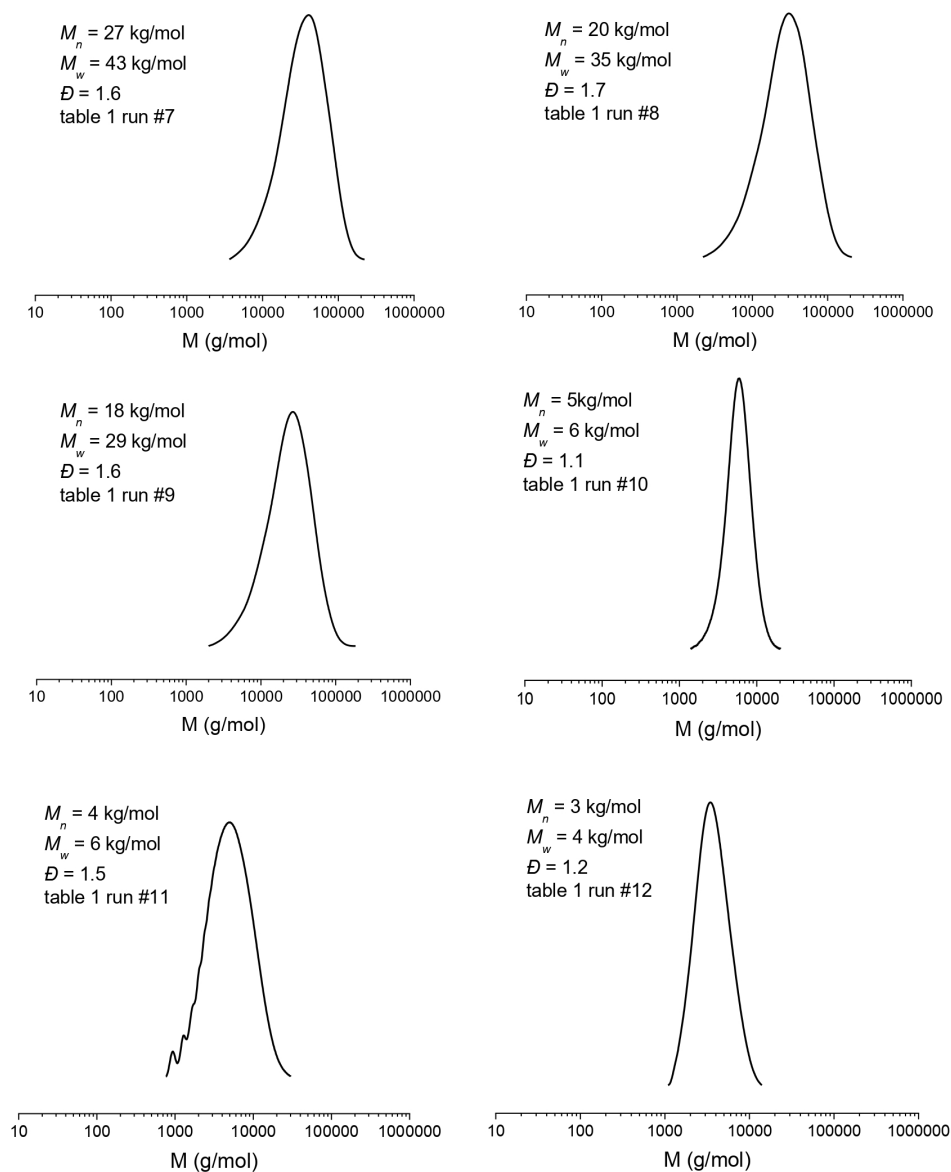


Figure S13: GPC curves corresponding to table 1 run #7,8,9,10,11,12.

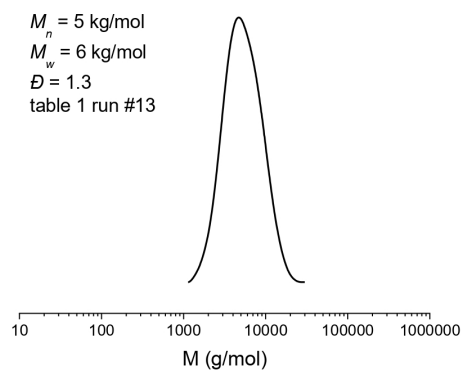
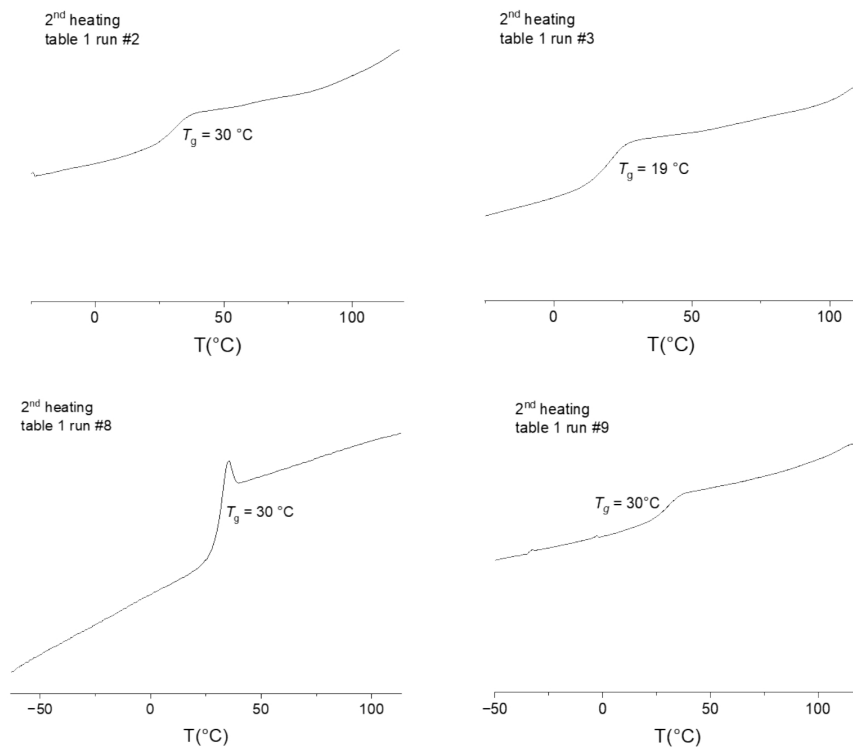


Figure S14: GPC curve corresponding to table 1 run #13.

Figure S15: DSC 2<sup>nd</sup> heating curves of the polymers corresponding to table 1 run #2,3,8,9.

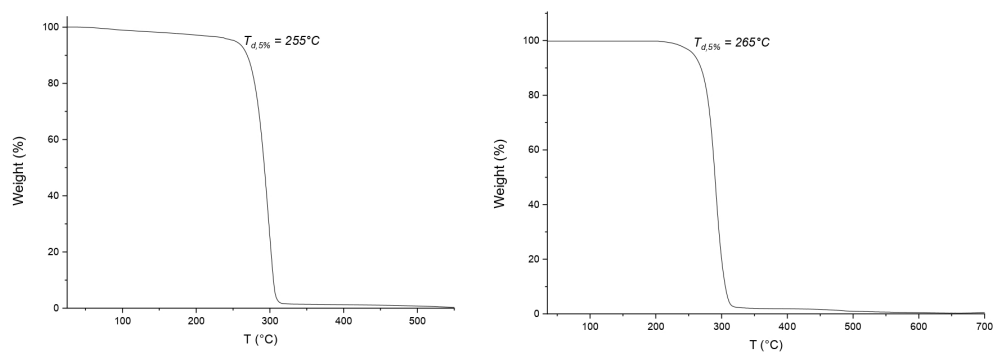


Figure S16: TGA data of the polymers corresponding to table 1 run # 1 (left) and #8 (right).

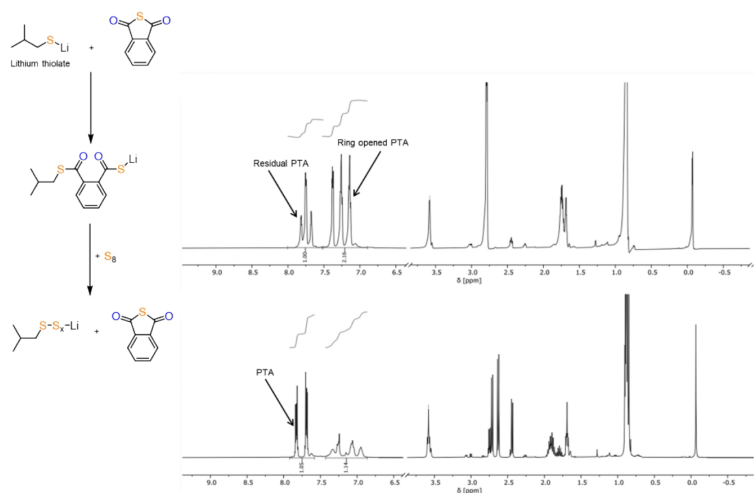


Figure S17: Zoom into the  $^1\text{H}$ -NMR (400 MHz,  $d_8$ -THF,  $25^\circ\text{C}$ ) of the model reaction between lithium thiolate, PTA and  $\text{S}_8$ .

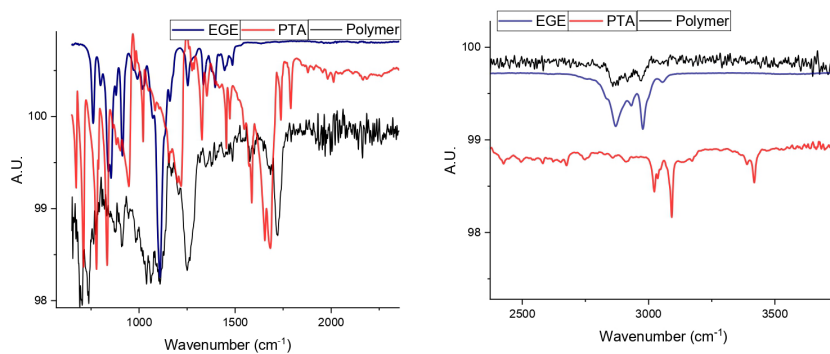


Figure S18: Overlaid IR spectra of ethyl glycidyl ether (EGE), phthalic thioanhydride (PTA) and the polymer obtained from these two monomers and elemental sulfur.



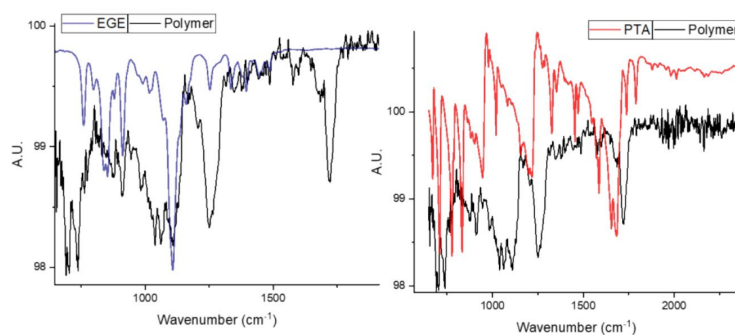


Figure S19: Overlaid IR spectra of the polymer and parent monomers. Left: polymer and EGE. Right: polymer and PTA.

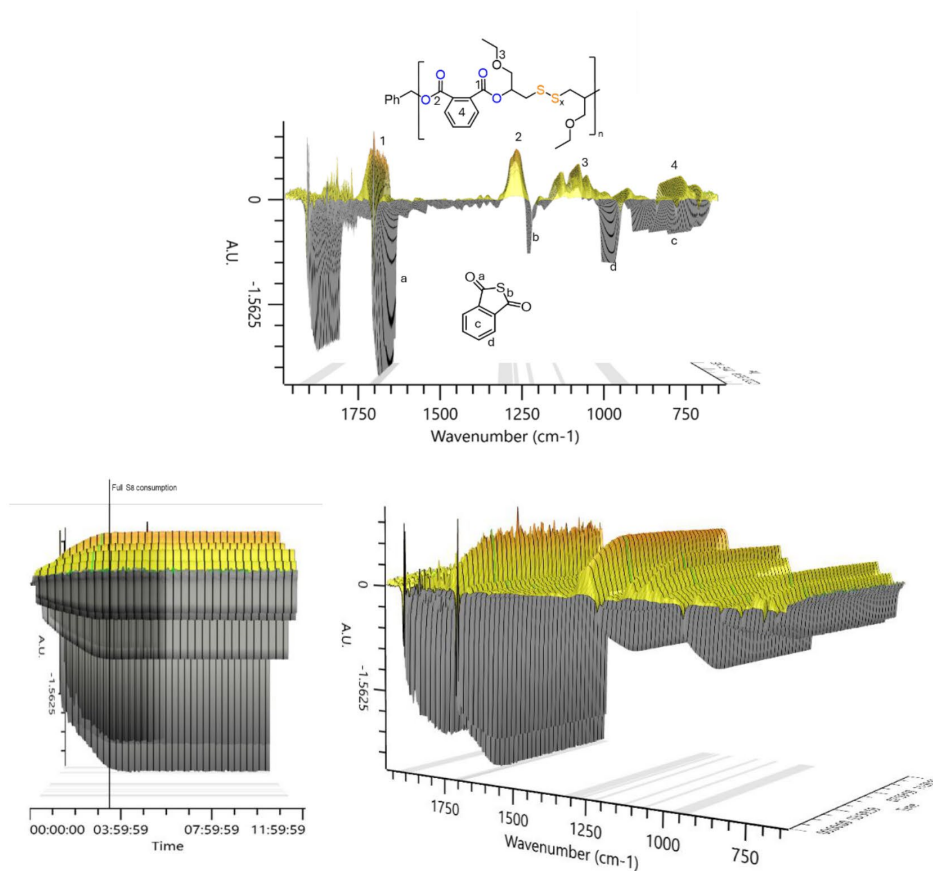


Figure S20: Different views on the overlaid *In situ* IR measurements of epoxide(EGE)-PTA-S<sub>8</sub> terpolymerisation at 1 eq. LiOBn: 1000 eq. EGE: 200 eq. PTA : 100 eq. S and 80°C. Note that the baseline was set before polymerisation so that the consumption of monomers results in negative intensity. Assignment according to reference spectra.

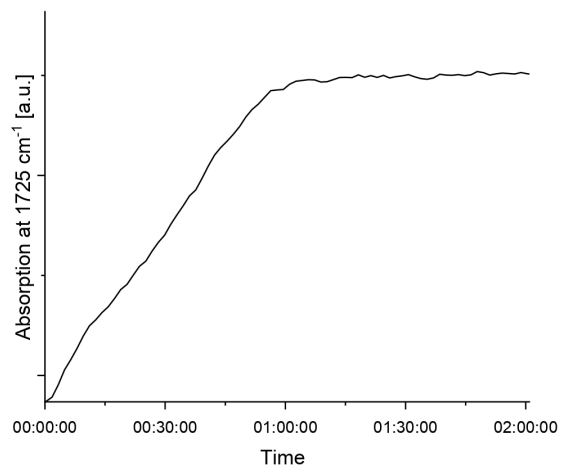


Figure S21: Increase of the polymer IR signal at 1725 cm<sup>-1</sup> over time at 1 eq. LiOBn: 1000 eq. epoxide (EGE): 100 eq. PTA : 500 eq. S and 80°C.

## Section S4: Monomer scope

Monomer scoping was conducted with the same polymerisation methodology described in **Section S2**; all the reactions were run at 100°C.

Table S1: list of epoxides deployed in the monomer scope.

| Run | Epoxide       | Run | Epoxide       |
|-----|---------------|-----|---------------|
| #1  | BO            | #11 | DMO           |
| #2  | DO            | #12 | IBO           |
| #3  | DO 400 eq. S  | #13 | IBO 400 eq. S |
| #4  | CHO           | #14 | VGE           |
| #5  | CHO 400 eq. S | #15 | ECH           |
| #6  | CE            | #16 | DEO           |
| #7  | EGE           | #17 | ESBO          |
| #8  | PGE           | #18 | PO-NTA        |
| #9  | SO            | #19 | VGE-NTA       |
| #10 | SO 400 eq. S  | #20 | CHO-NTA       |

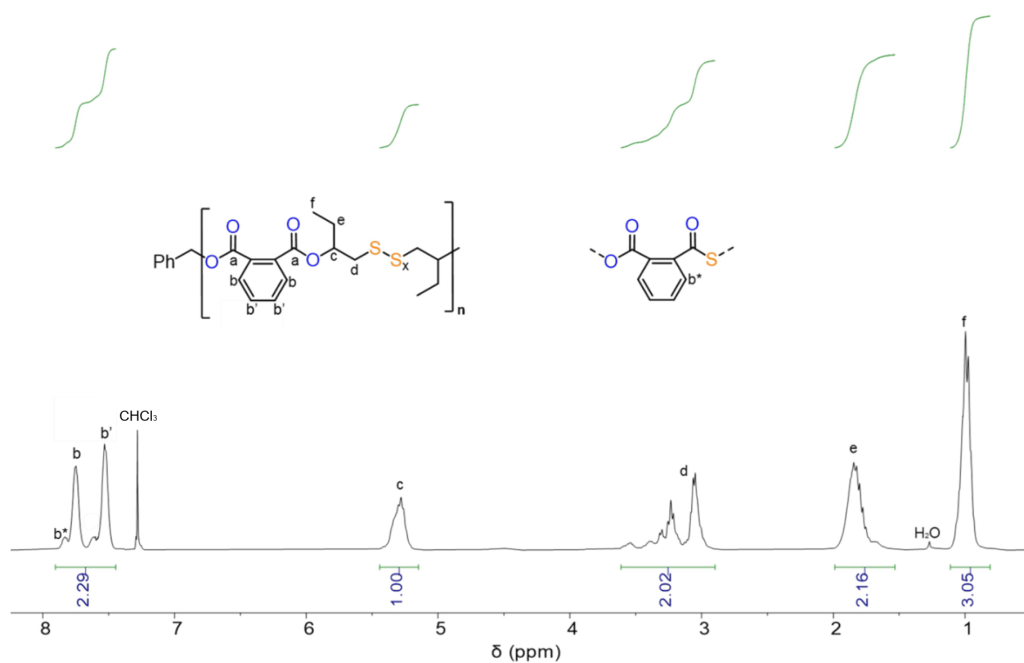


Figure S22: <sup>1</sup>H-NMR spectrum (600 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #1.

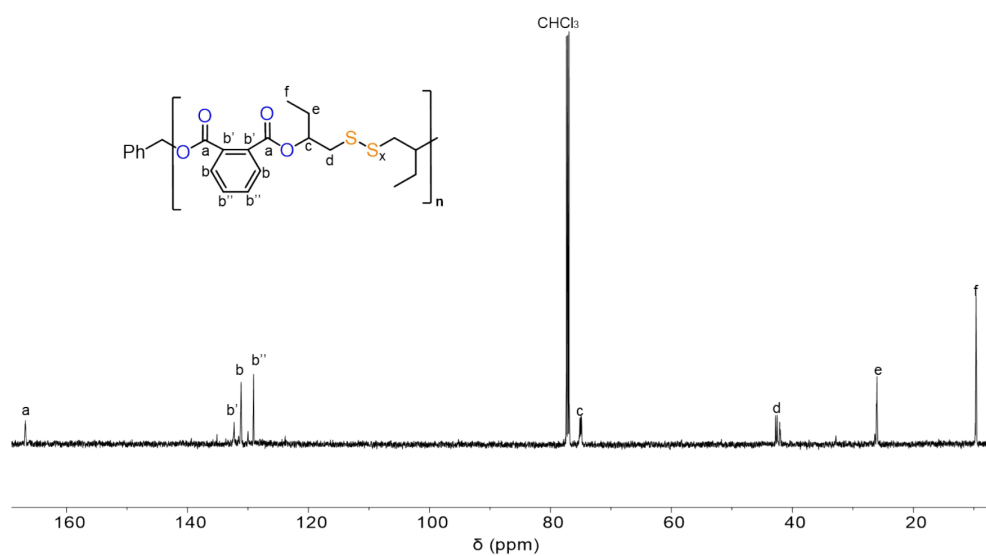


Figure S23:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #1.

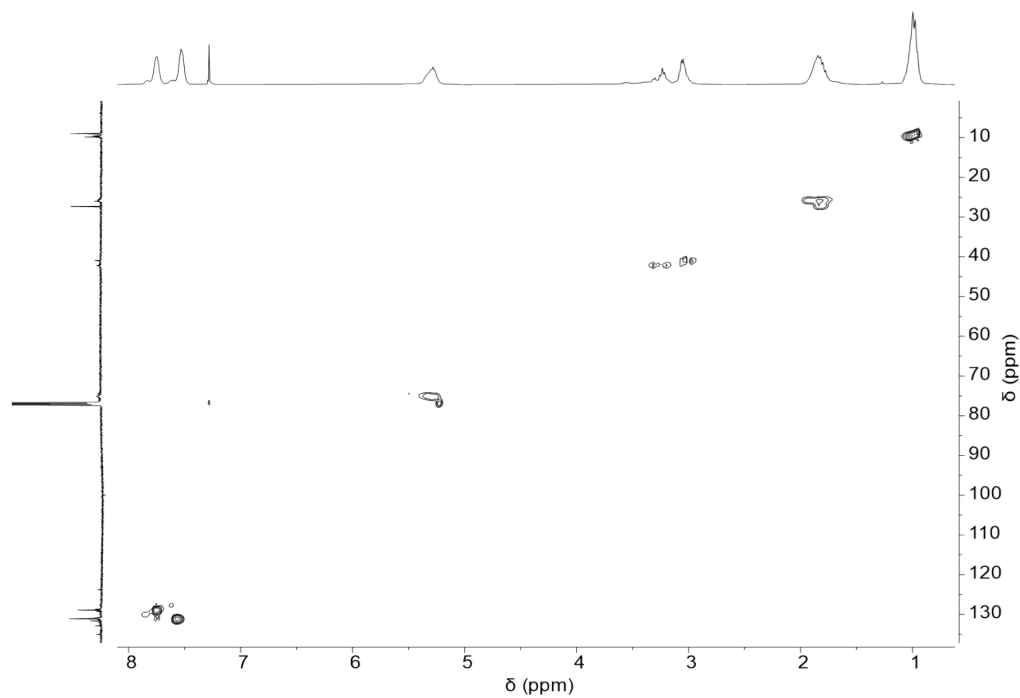


Figure S24:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #1.

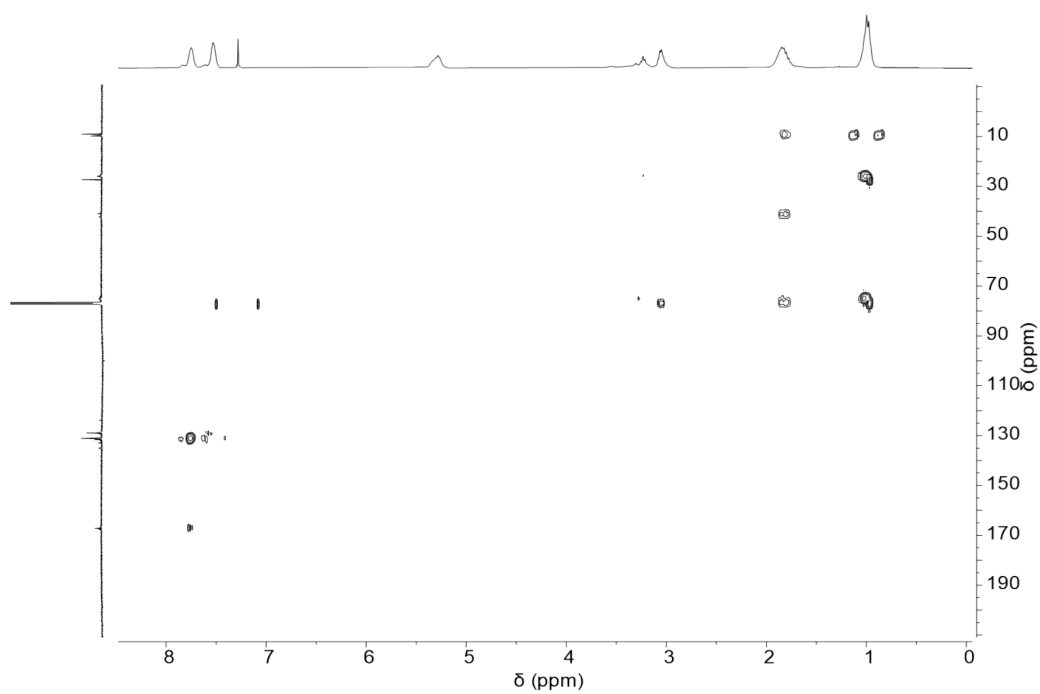


Figure S25:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table run #1.

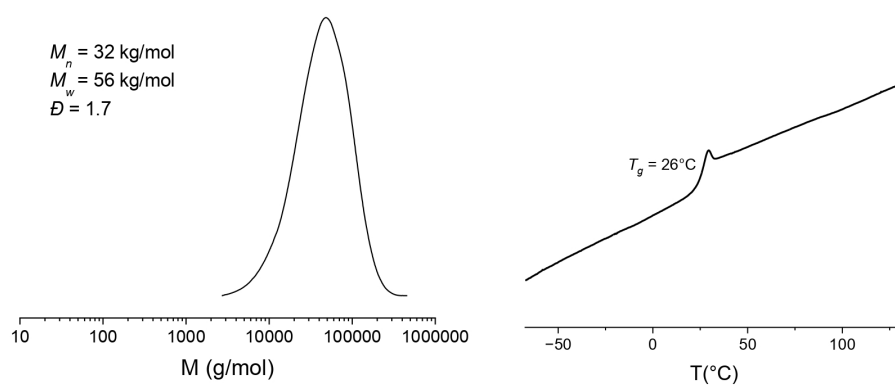


Figure S26: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #1.

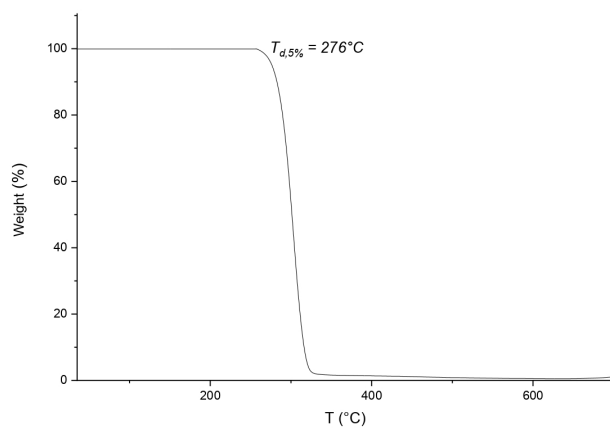


Figure S27: TGA data of the polymer corresponding to ESI table 1 run # 1.

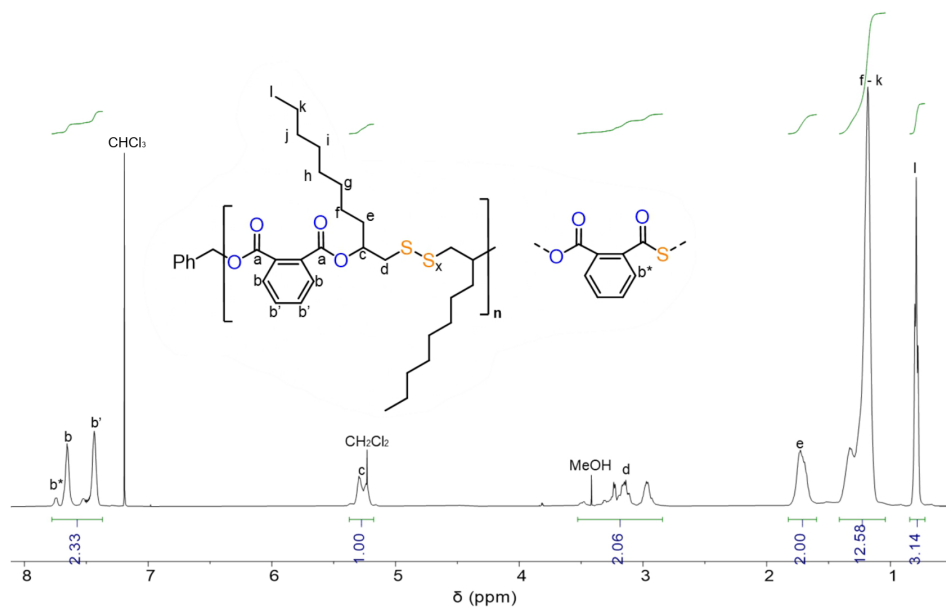


Figure S28:  $^1\text{H-NMR}$  spectrum (600 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #2.

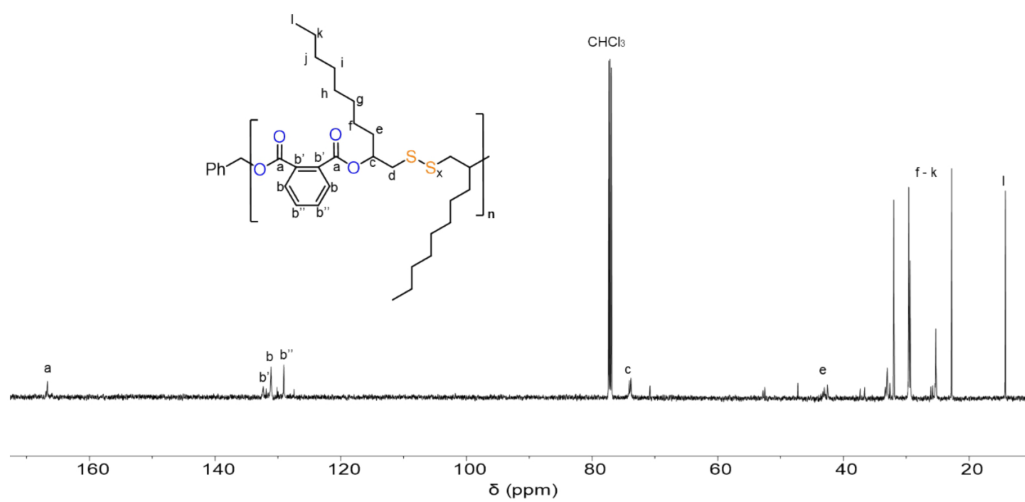


Figure S29:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #2.

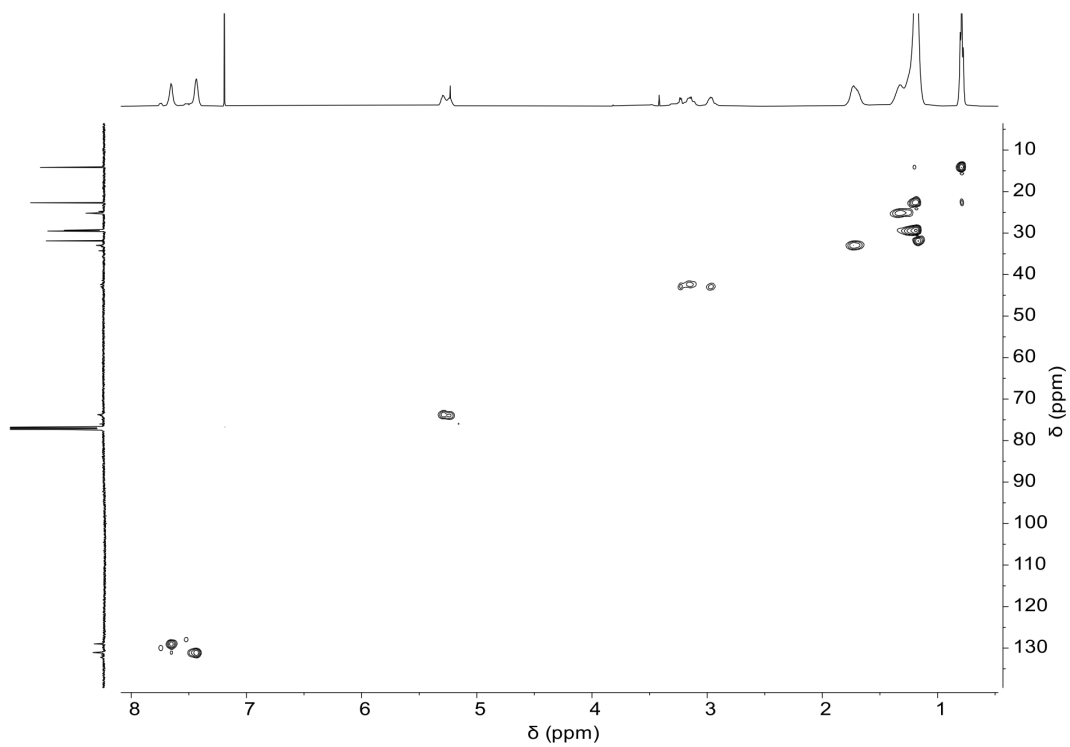


Figure S30:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #2.

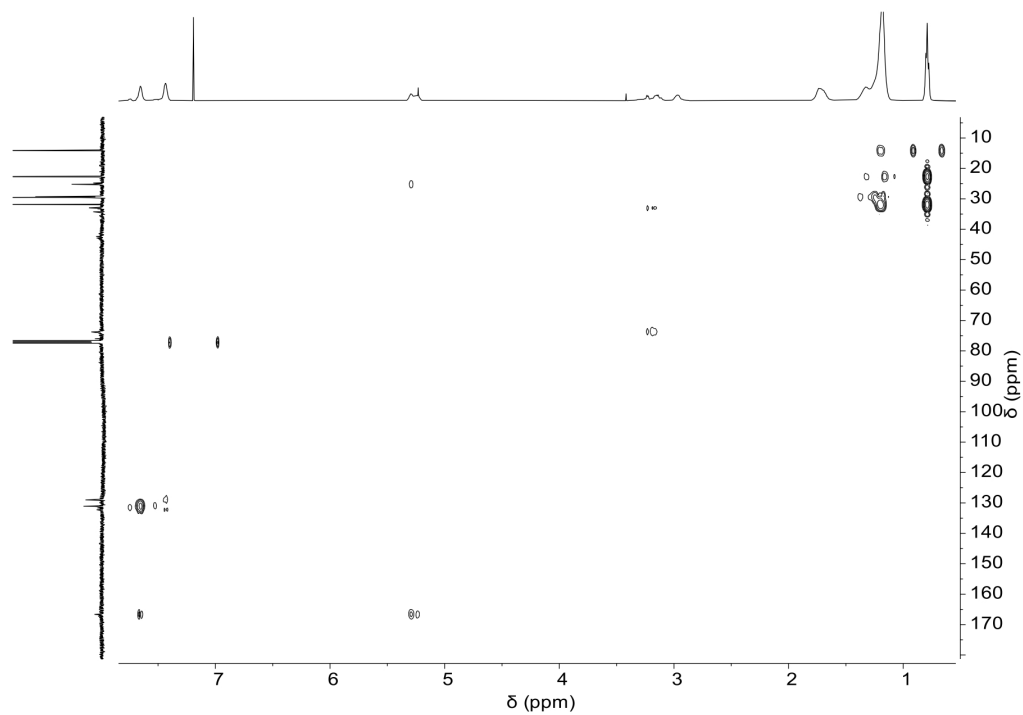


Figure S31:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #2.

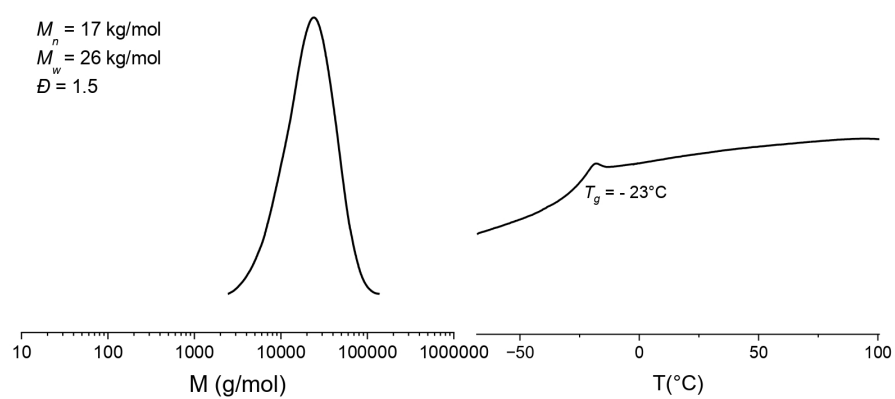


Figure S32: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #2.



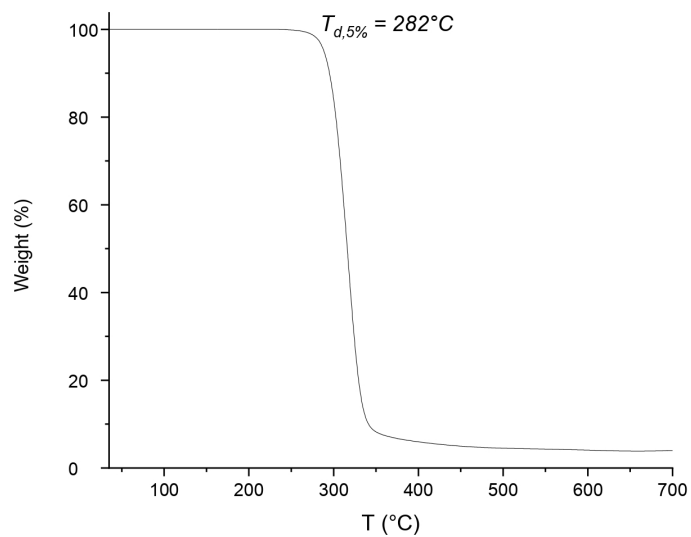


Figure S33: TGA data of the polymer corresponding to ESI table 1 run #2.

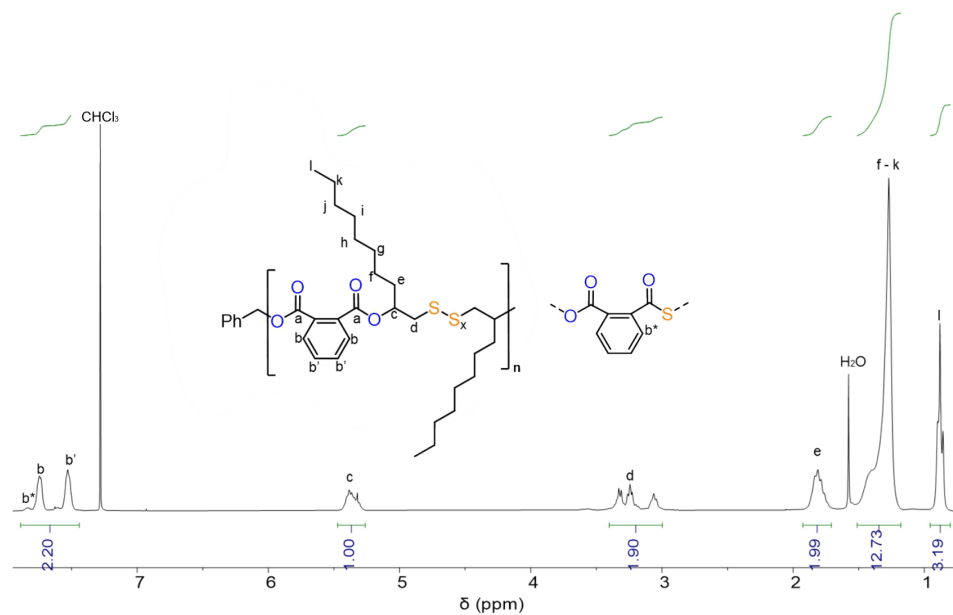


Figure S34:  $^1\text{H-NMR}$  spectrum (600 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #3.

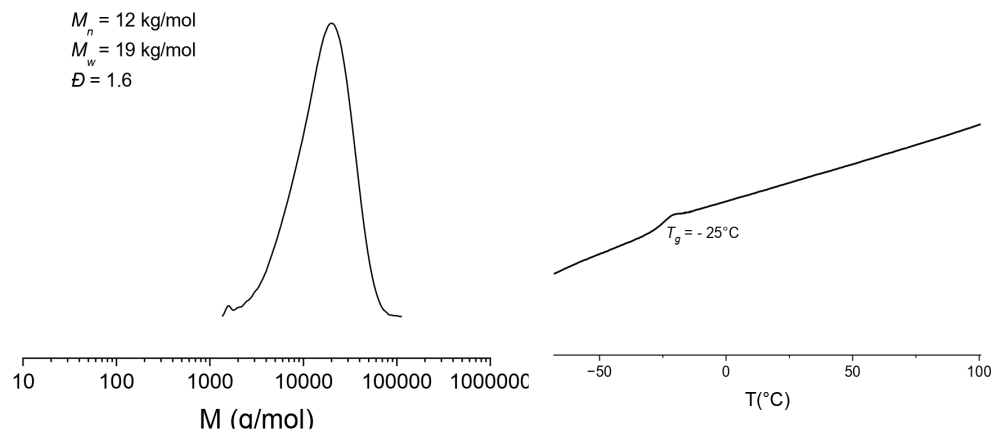


Figure S35: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #3.

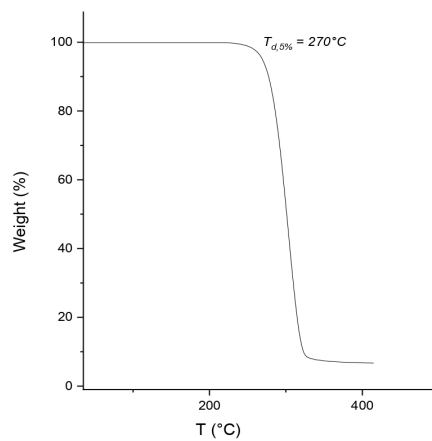


Figure S36: TGA data of the polymer corresponding to ESI table 1 run #3.

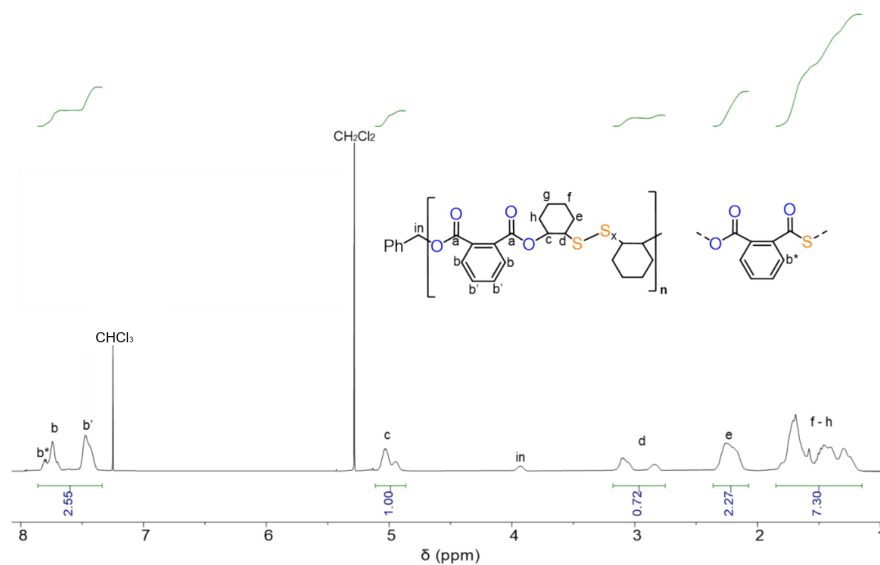


Figure S37:  $^1\text{H}$ -NMR spectrum (600 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #4.

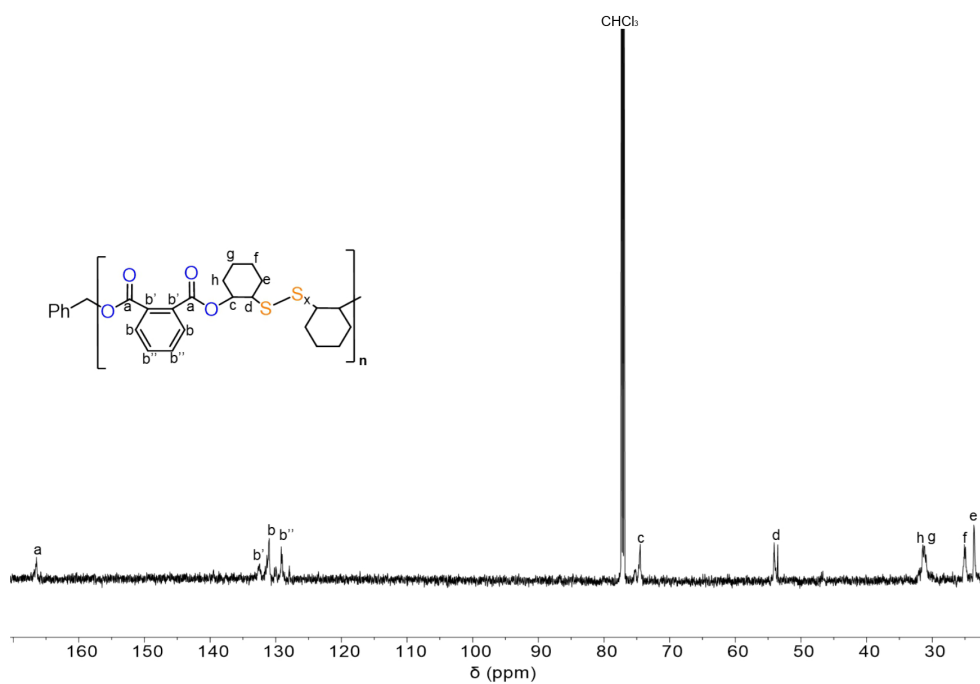


Figure S38:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #4.

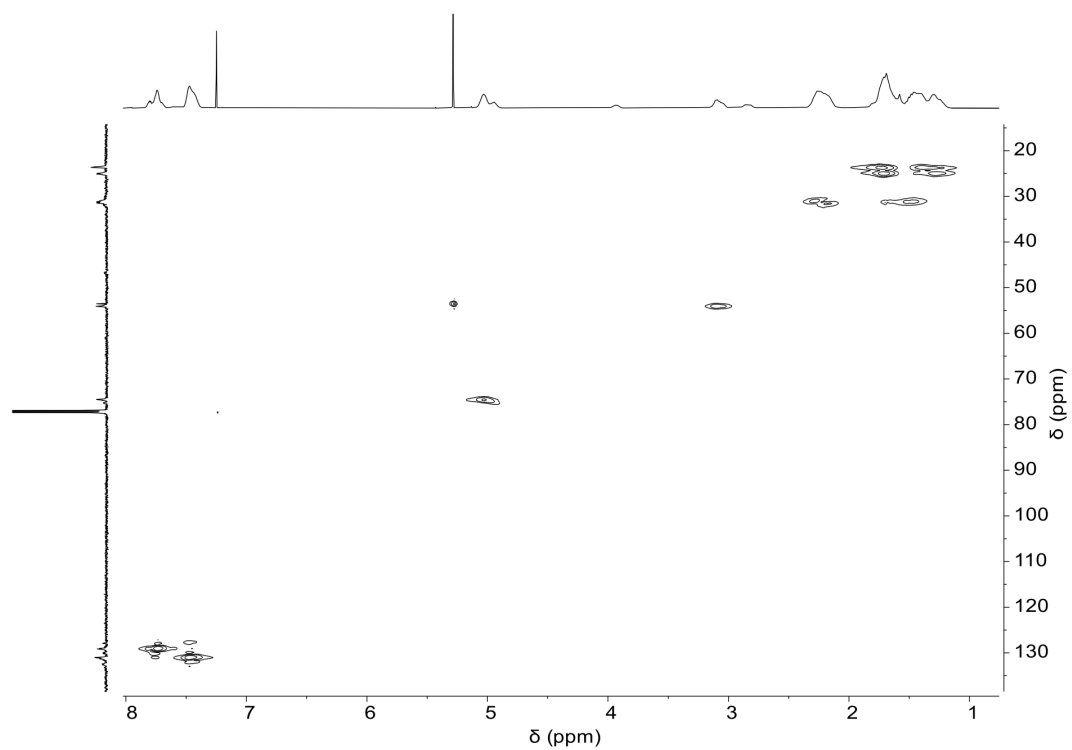


Figure S39:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #4.

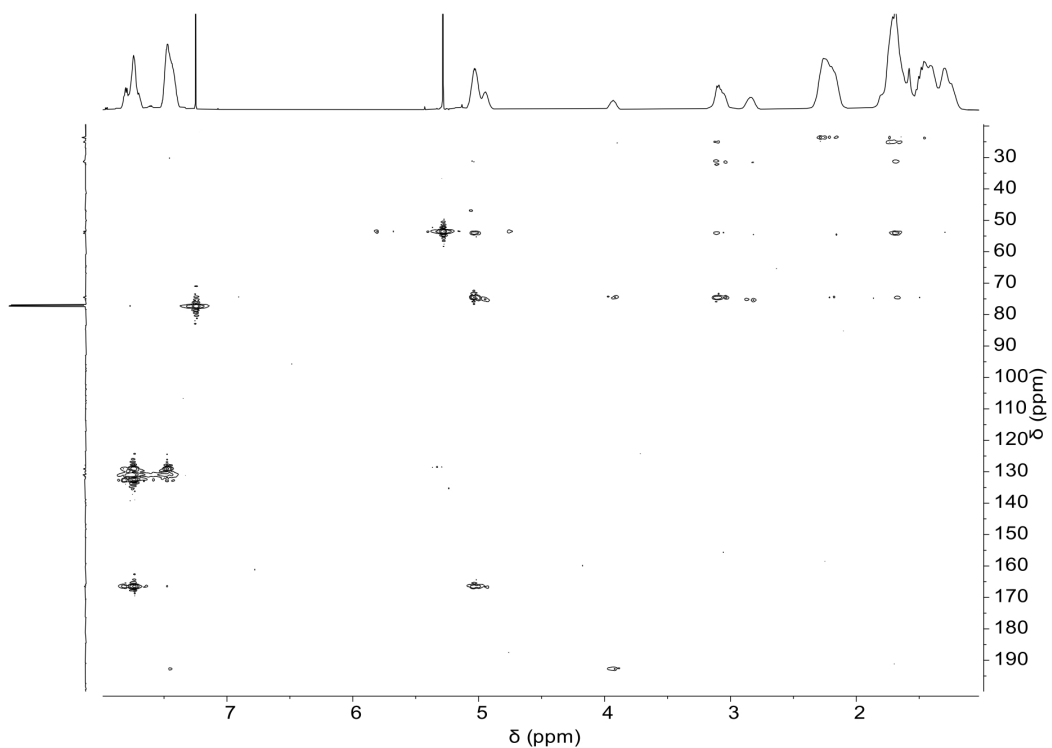


Figure S40:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #4.

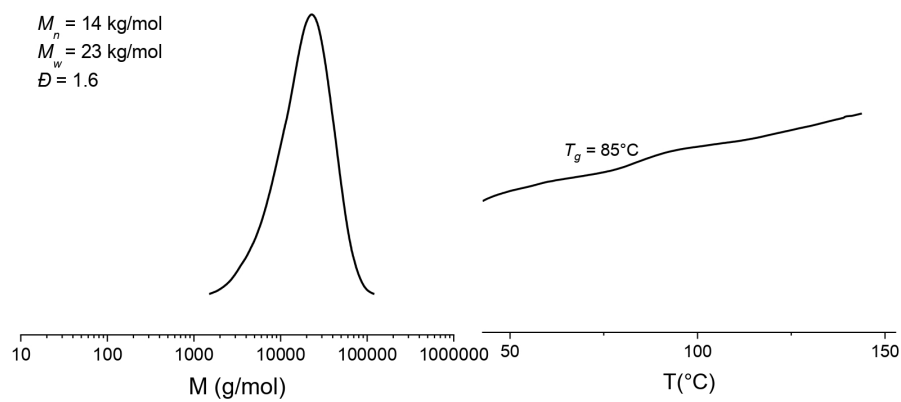


Figure S41: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #4.

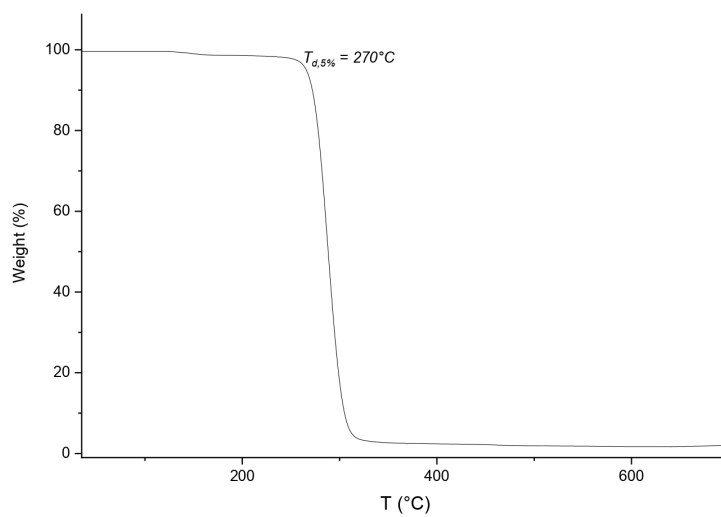


Figure S42: TGA data of the polymer corresponding to ESI table 1 run #4.

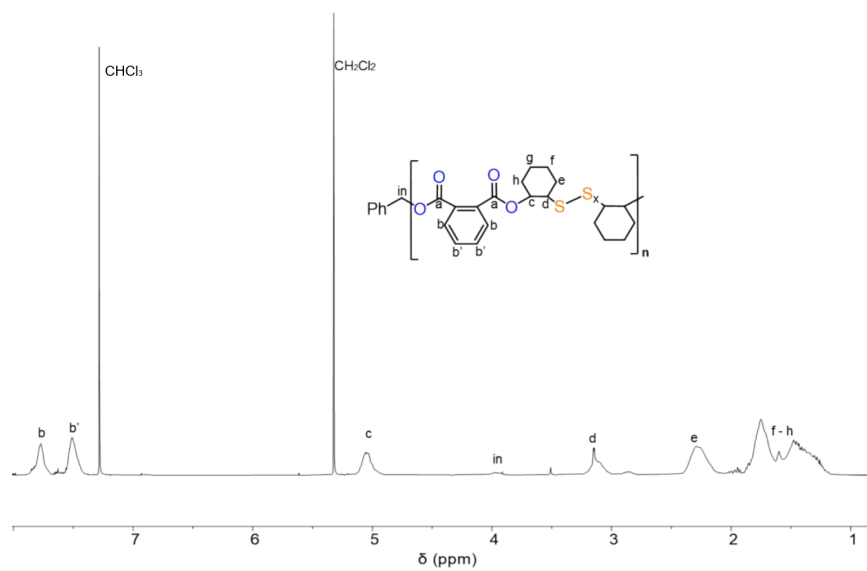


Figure S43:  $^1\text{H}$ -NMR spectrum (600 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #5.

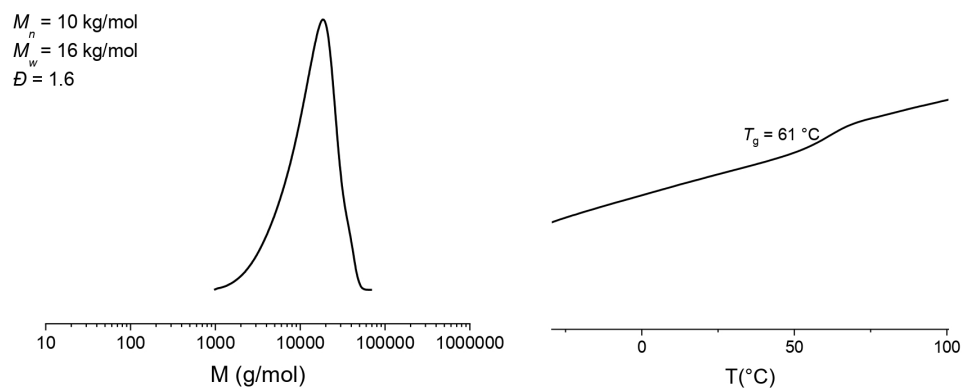


Figure S44: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #5.

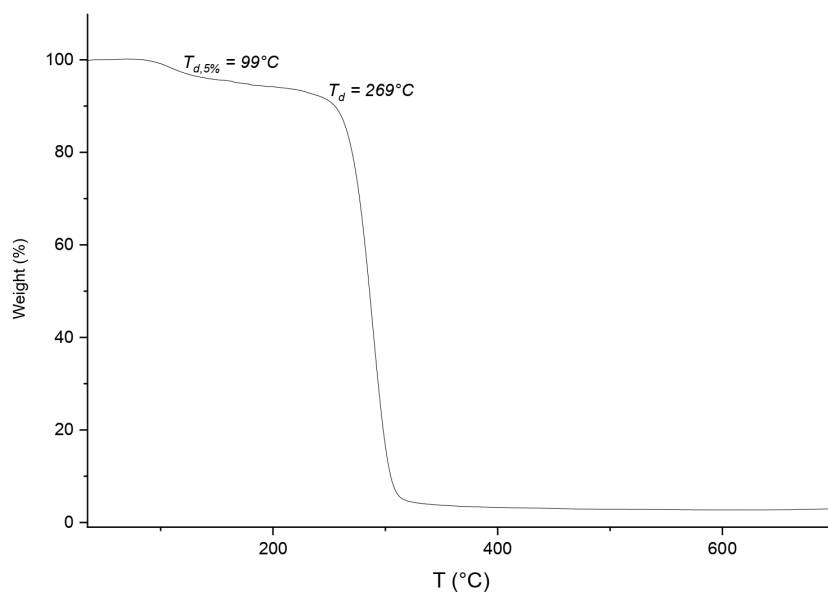


Figure S45: TGA data of the polymer corresponding to ESI table 1 run #5.

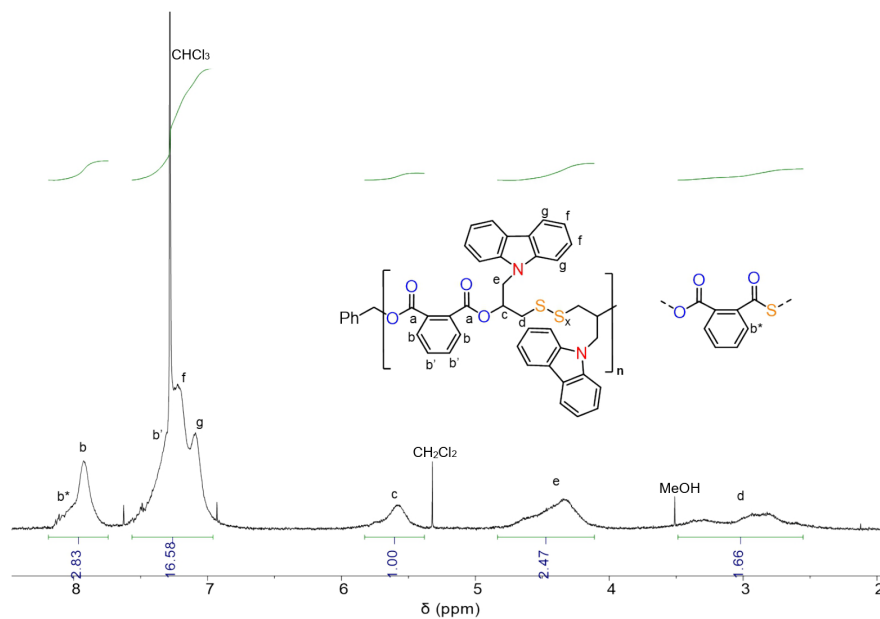


Figure S46:  $^1\text{H}$ -NMR spectrum (600 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #6.

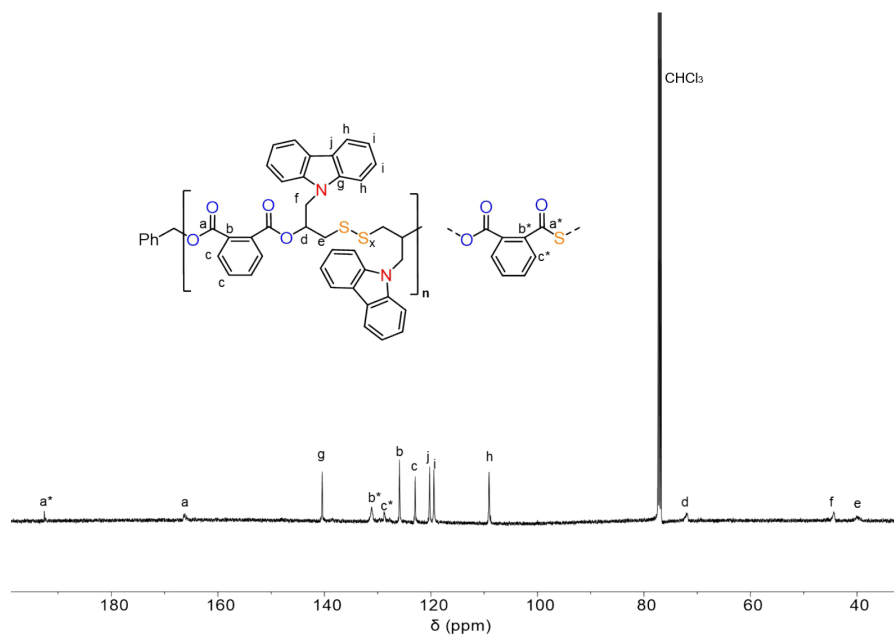


Figure S47:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #6.



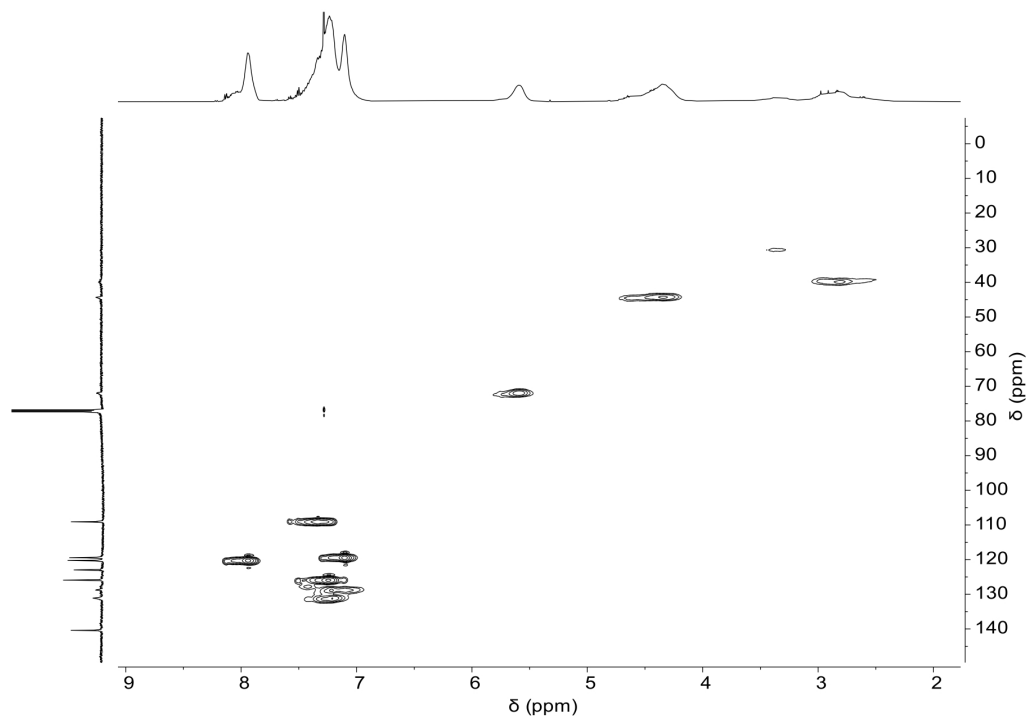


Figure S48:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #6.

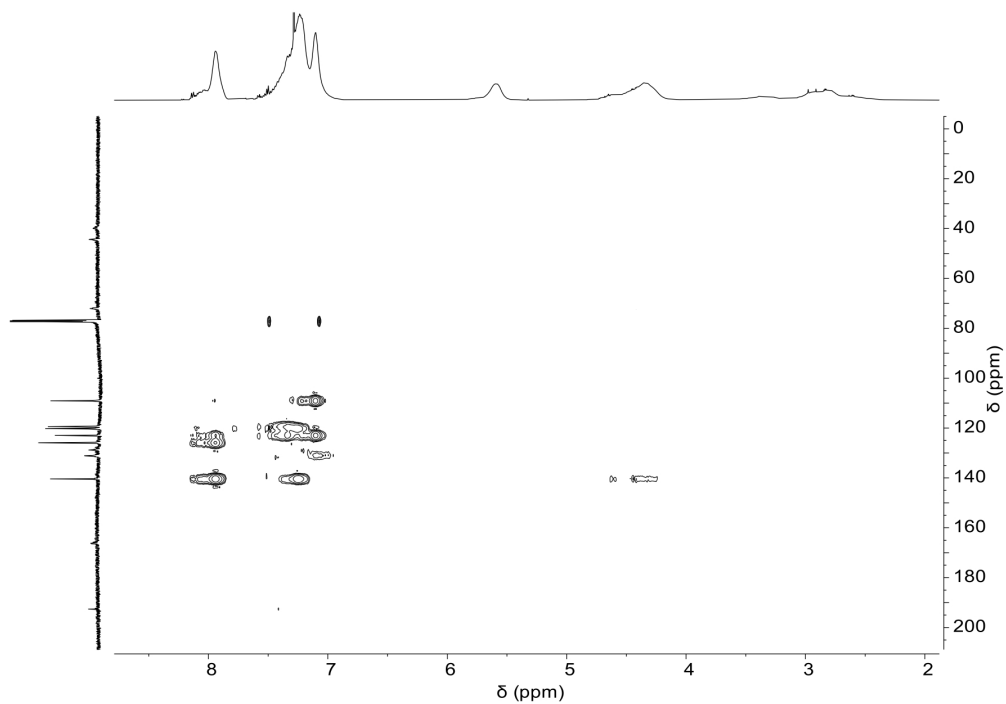


Figure S49:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #6.

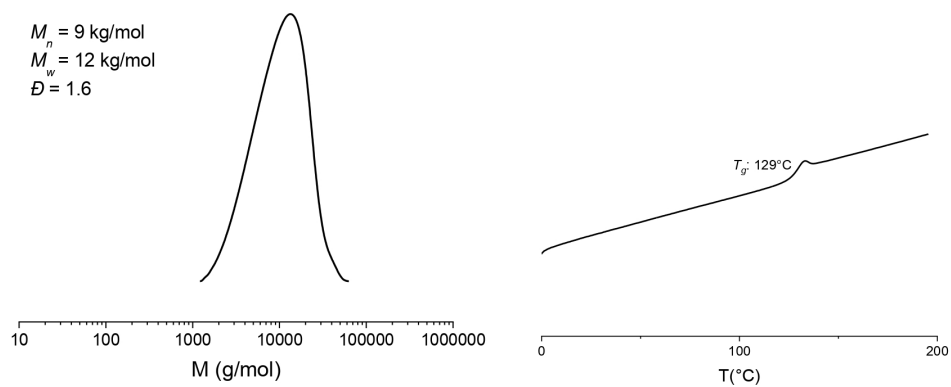


Figure S50: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #6.

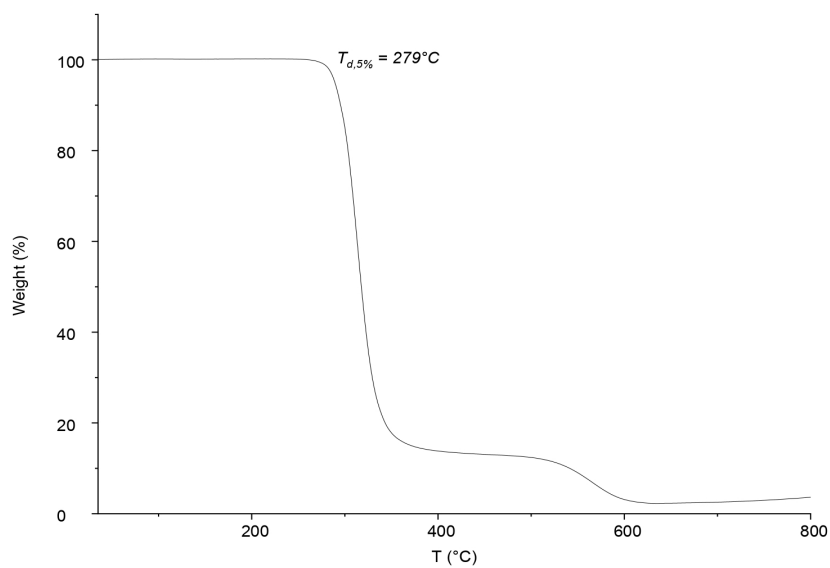


Figure S51: TGA data of the polymer corresponding to ESI table 1 run #6.

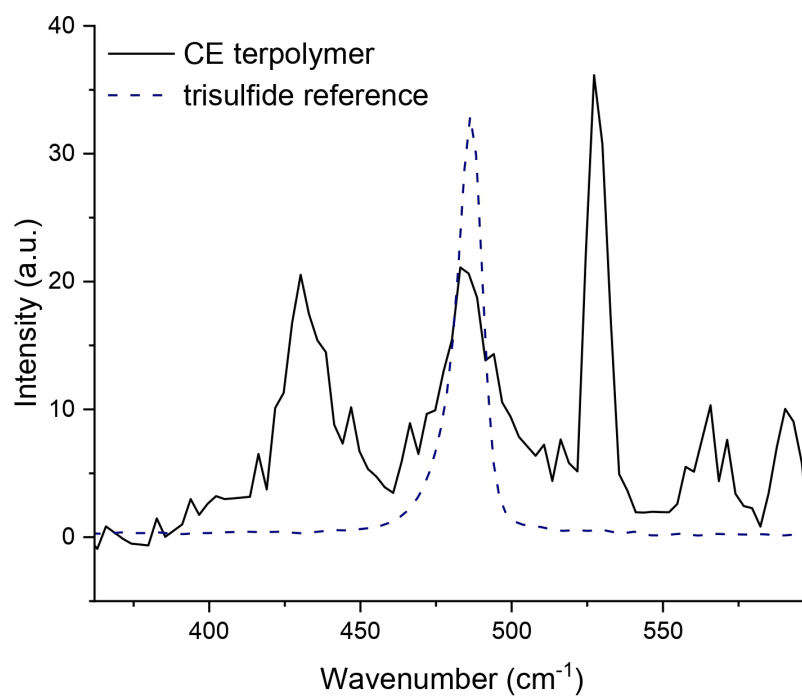


Figure S52: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectra of the polymer corresponding to ESI table 1 run #6, compared with dimethyl trisulfide reference compound.

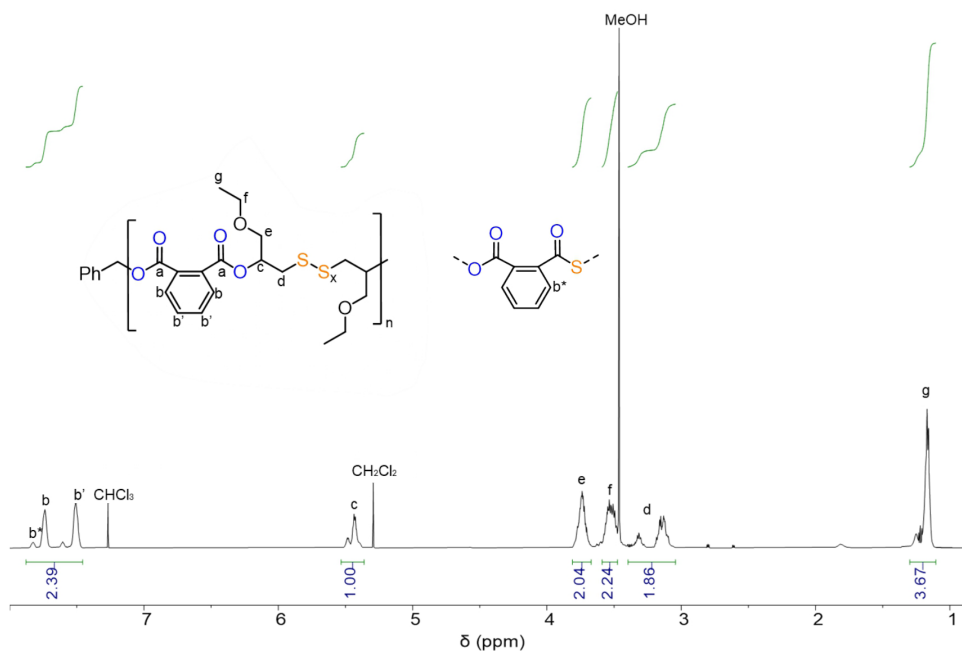


Figure S53: <sup>1</sup>H-NMR spectrum (600 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #7.

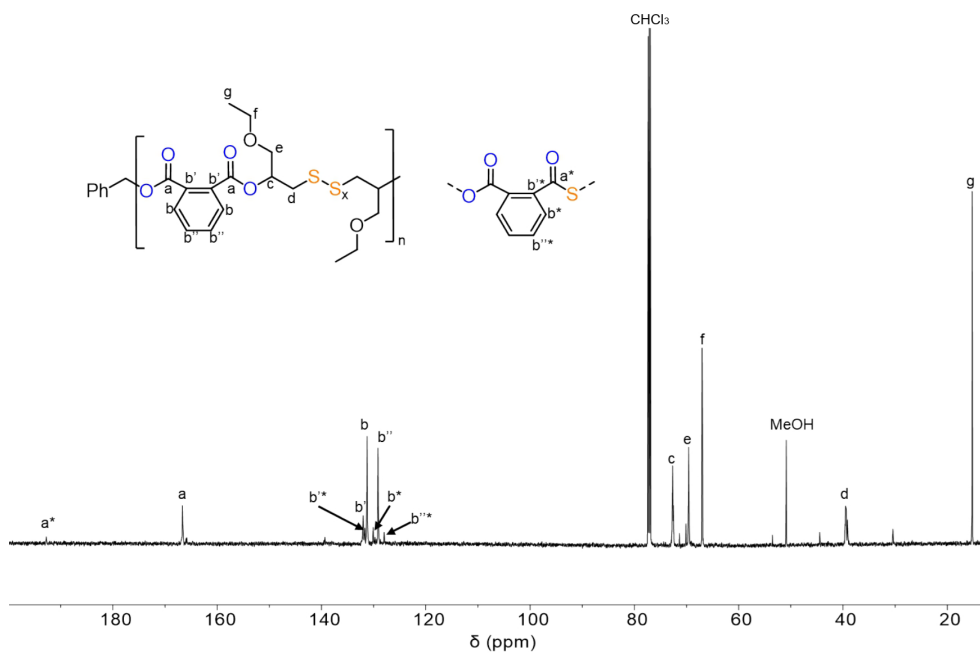


Figure S54: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #7.

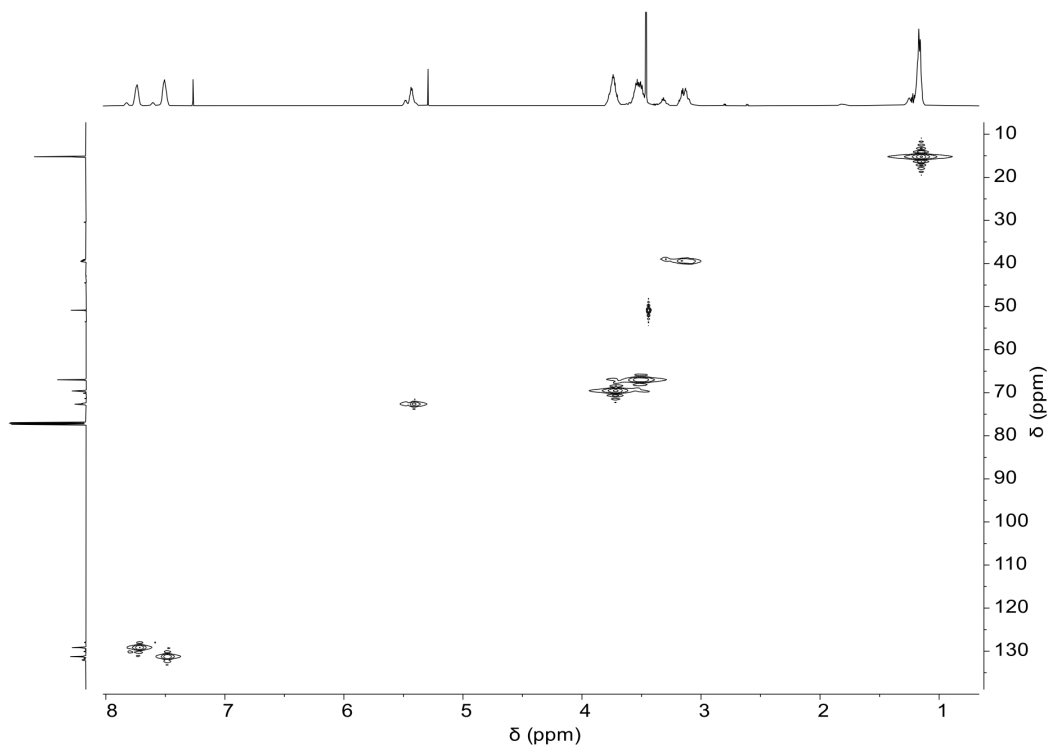


Figure S55:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #7.

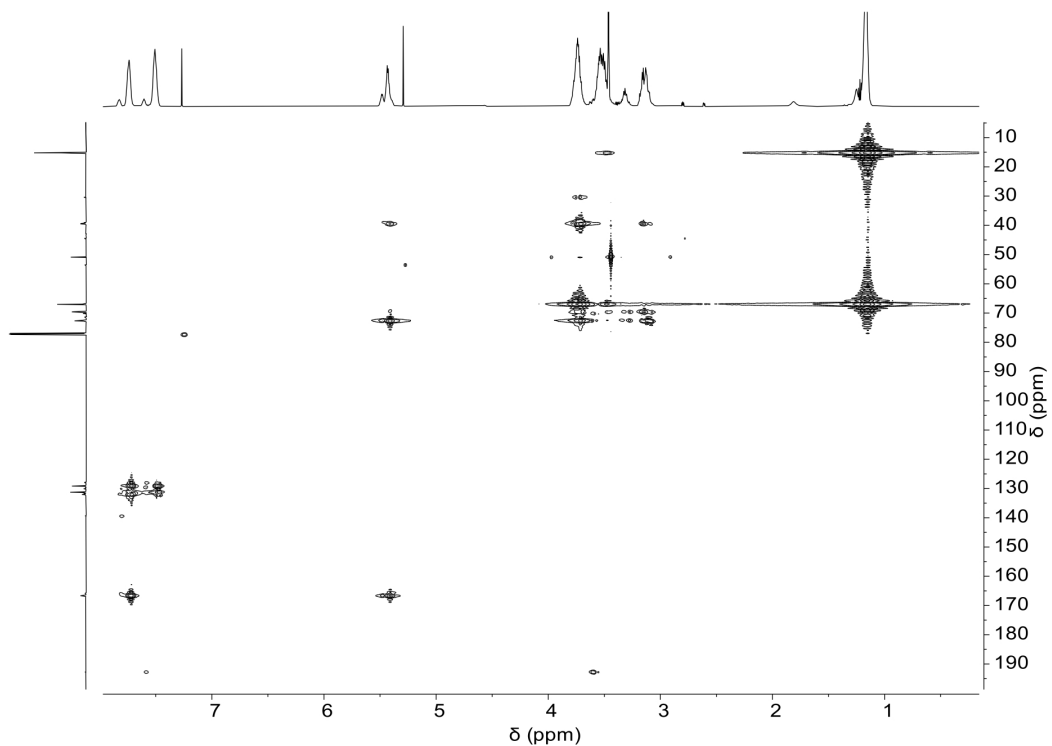


Figure S56:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #7.

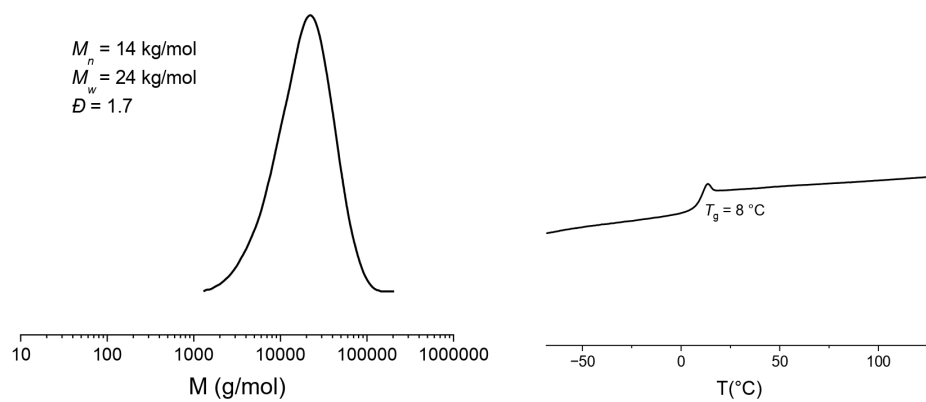


Figure S57: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #7.

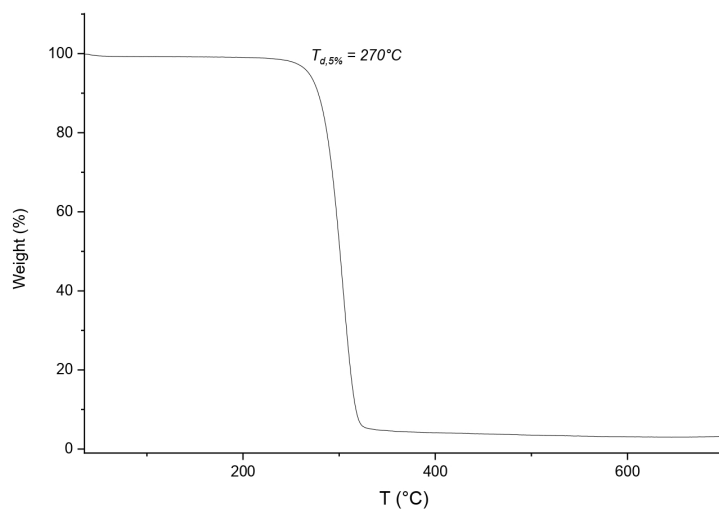


Figure S58: TGA data of the polymer corresponding to ESI table 1 run #7.

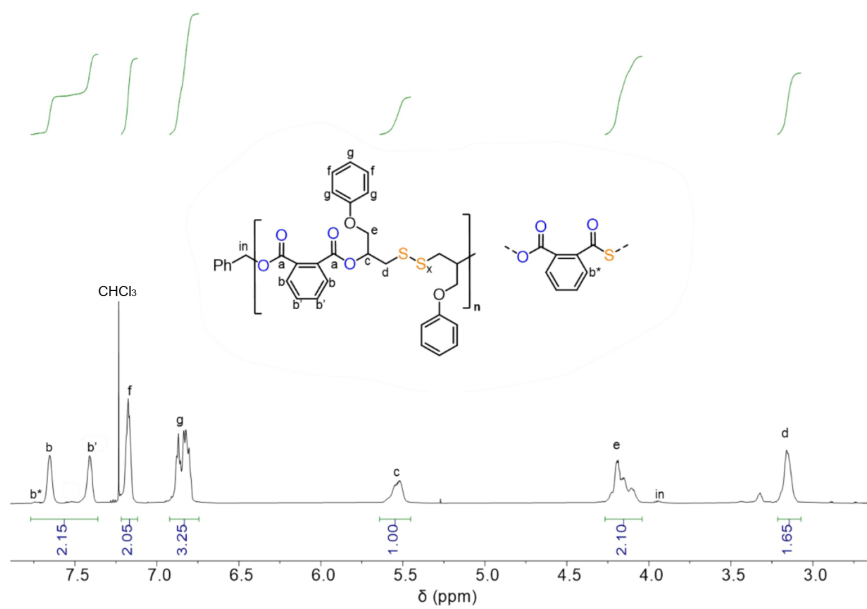


Figure S59:  $^1\text{H-NMR}$  spectrum (600 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #8.

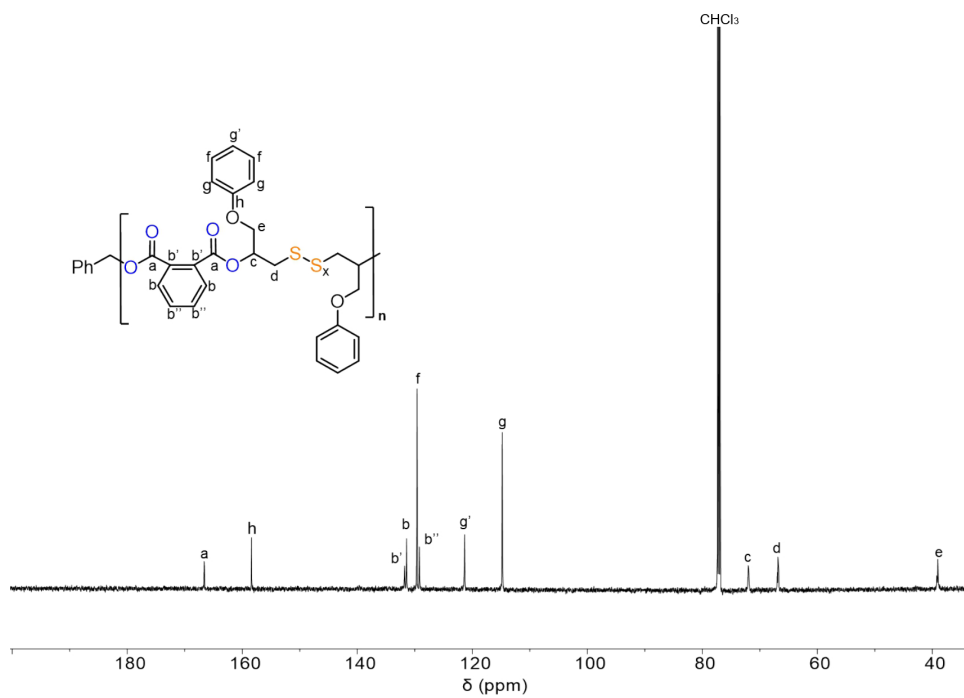


Figure S60:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #8.

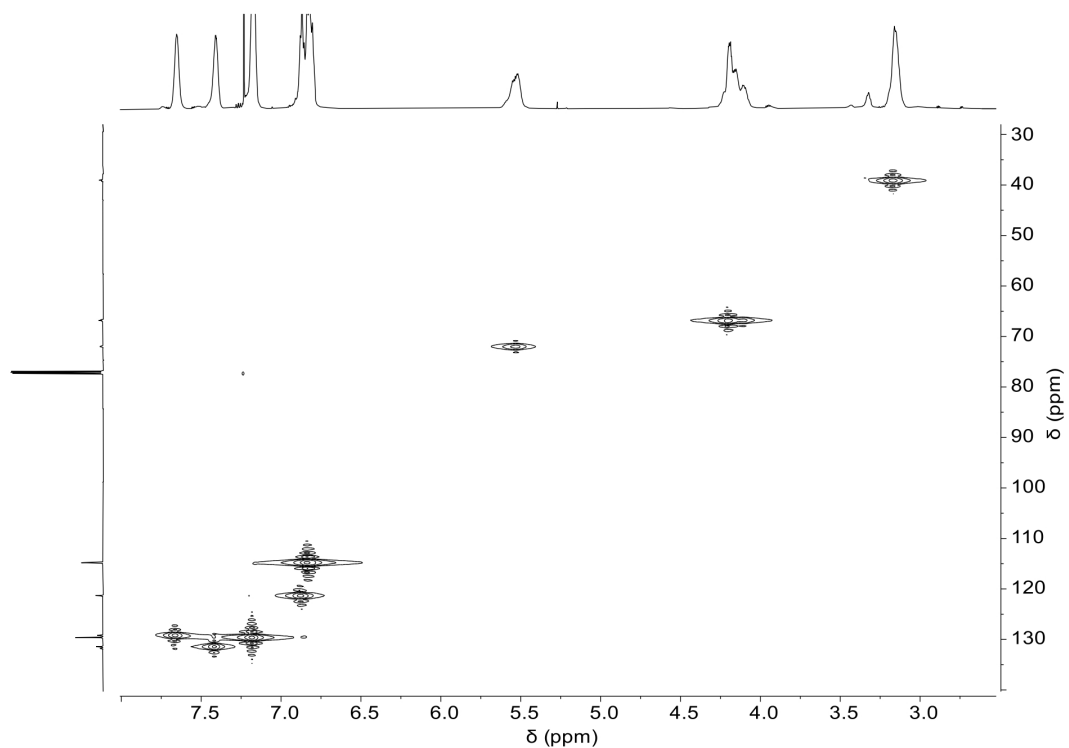


Figure S61:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #8.



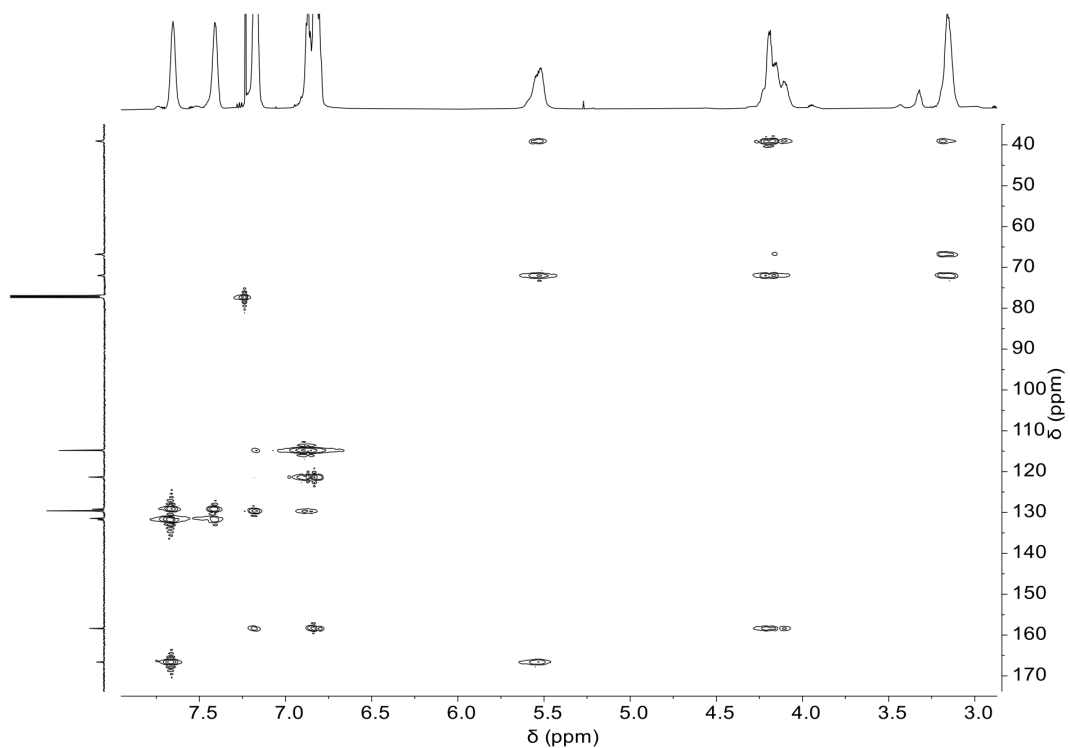


Figure S62:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #8.

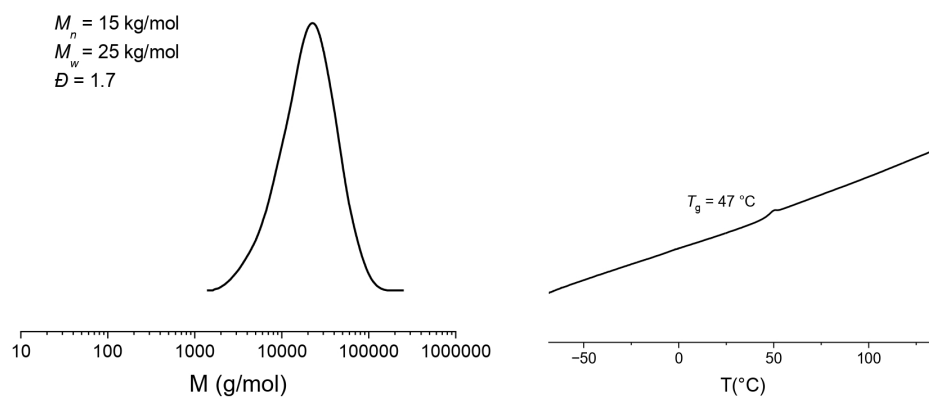


Figure S63: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #8.

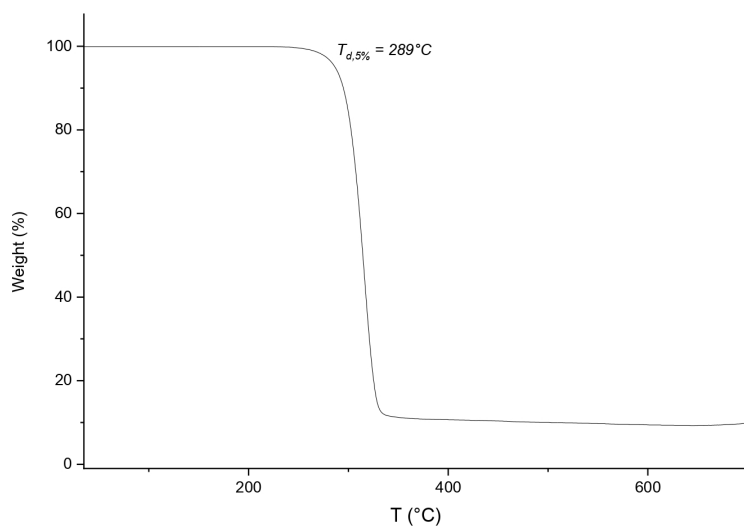


Figure S64: TGA data of the polymer corresponding to ESI table 1 run #8.

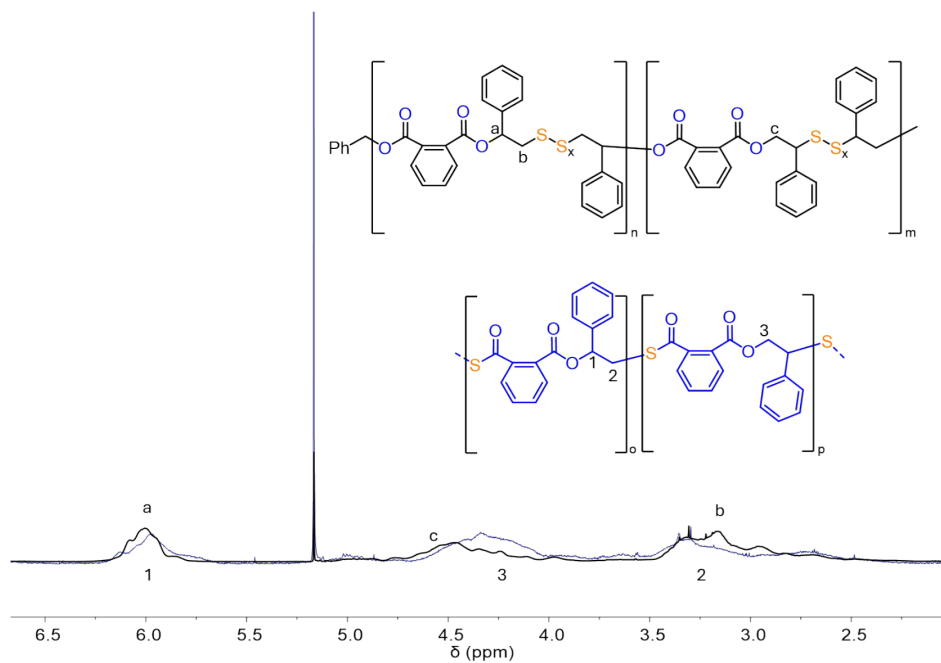


Figure S65: Zoom into the overlaid  $^1\text{H}$ -NMR spectra of the terpolymer obtained from SO, PTA and  $\text{S}_8$  (black) and the copolymer obtained from SO and PTA (blue).

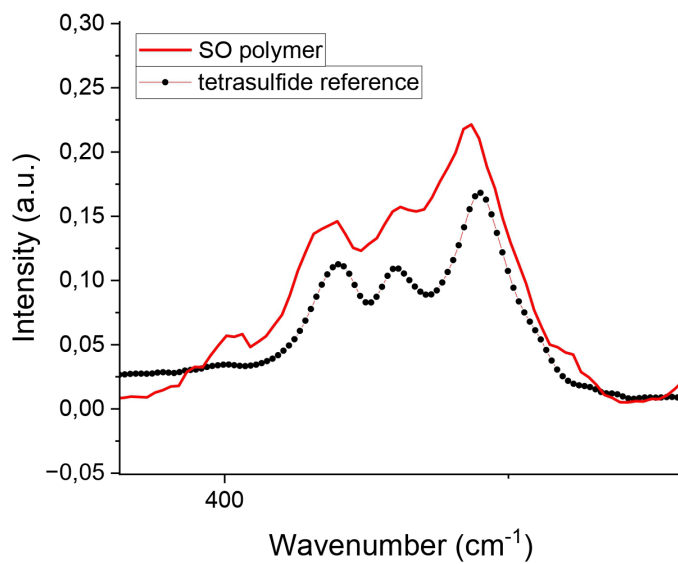


Figure S66: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectra of the polymer corresponding to ESI table 1 run # 9 compared with R<sub>2</sub>-tetrasulfide [R = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference compound.

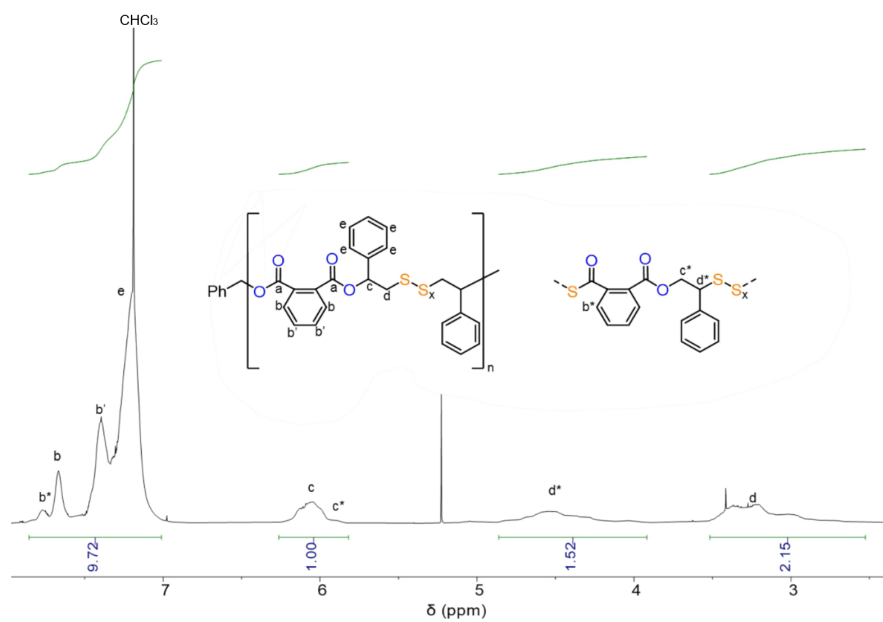


Figure S67: <sup>1</sup>H-NMR spectrum (600 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #9.

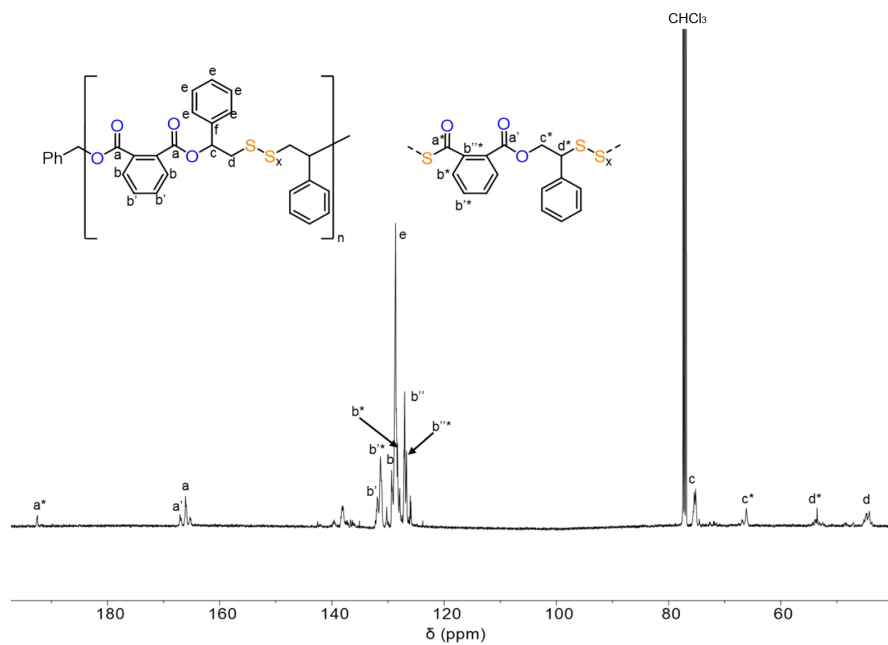


Figure S68:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #9.

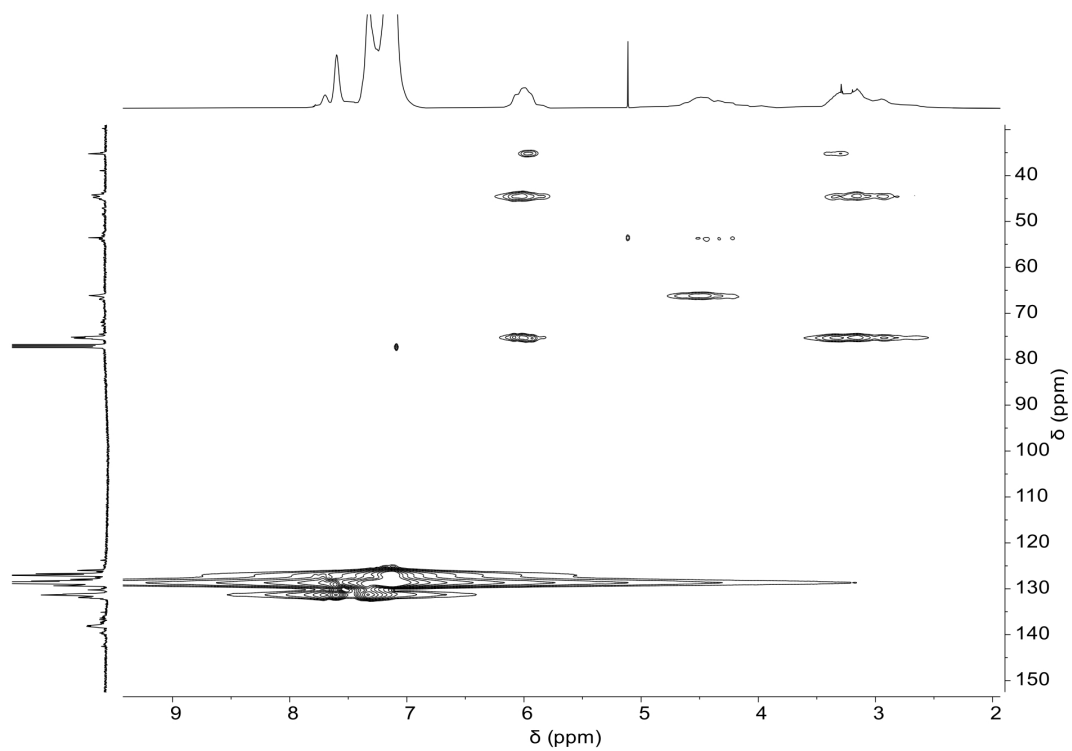


Figure S69:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #9.

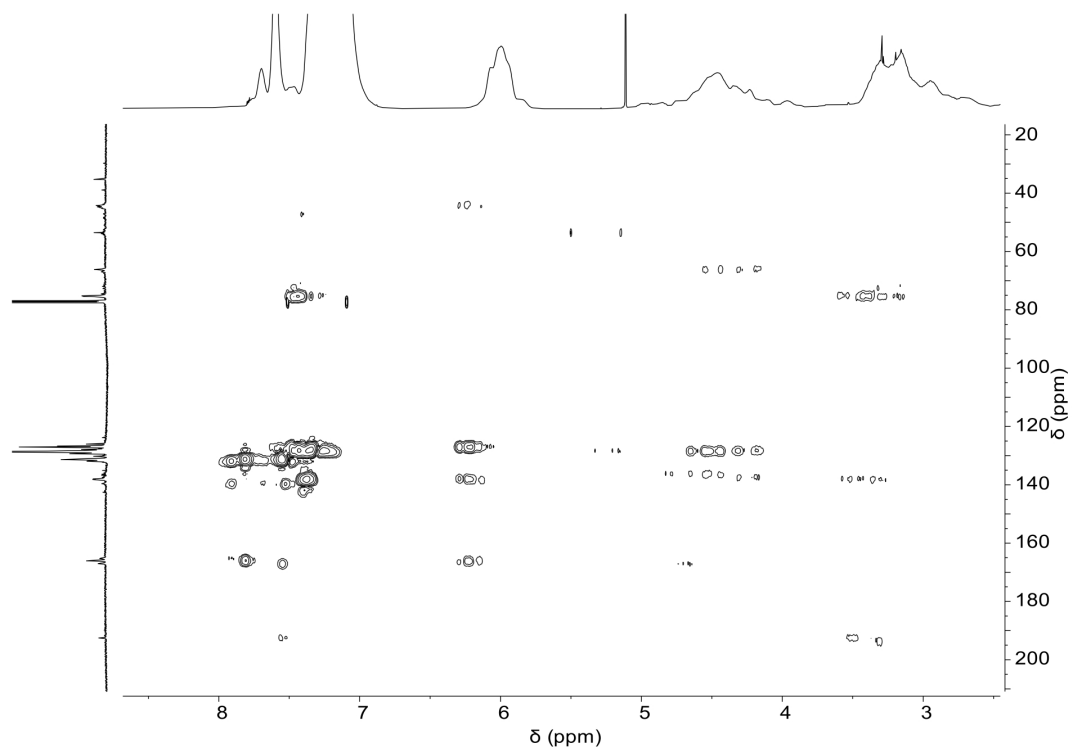


Figure S70:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #9.

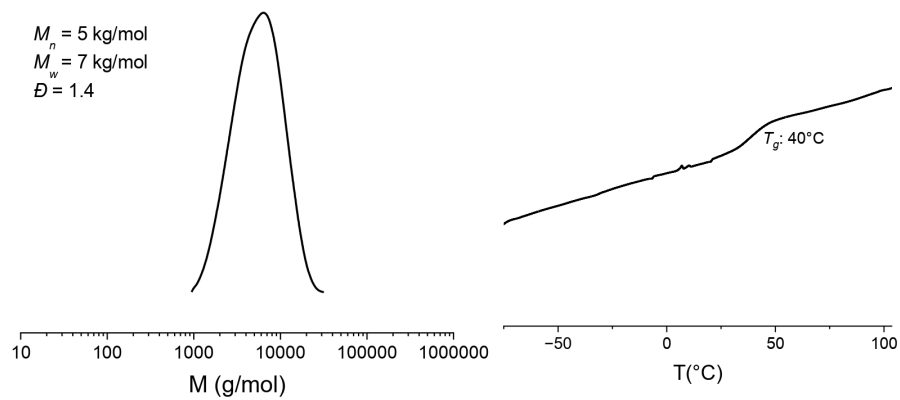


Figure S71: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #9.

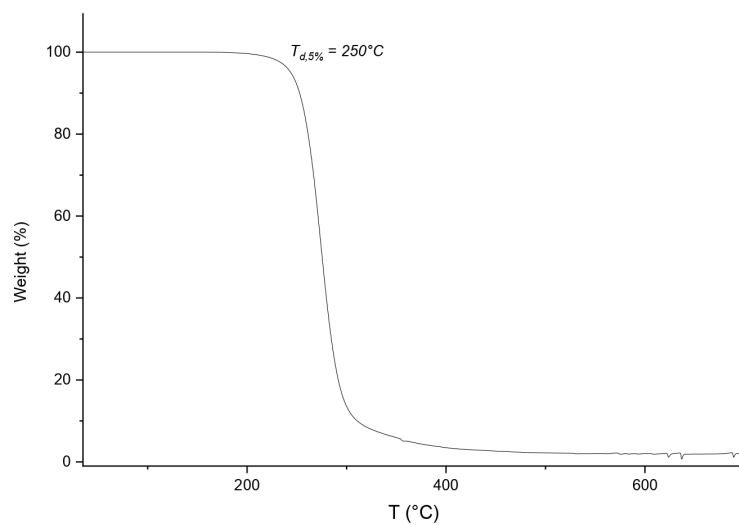


Figure S72: TGA data of the polymer corresponding to ESI table 1 run #9.

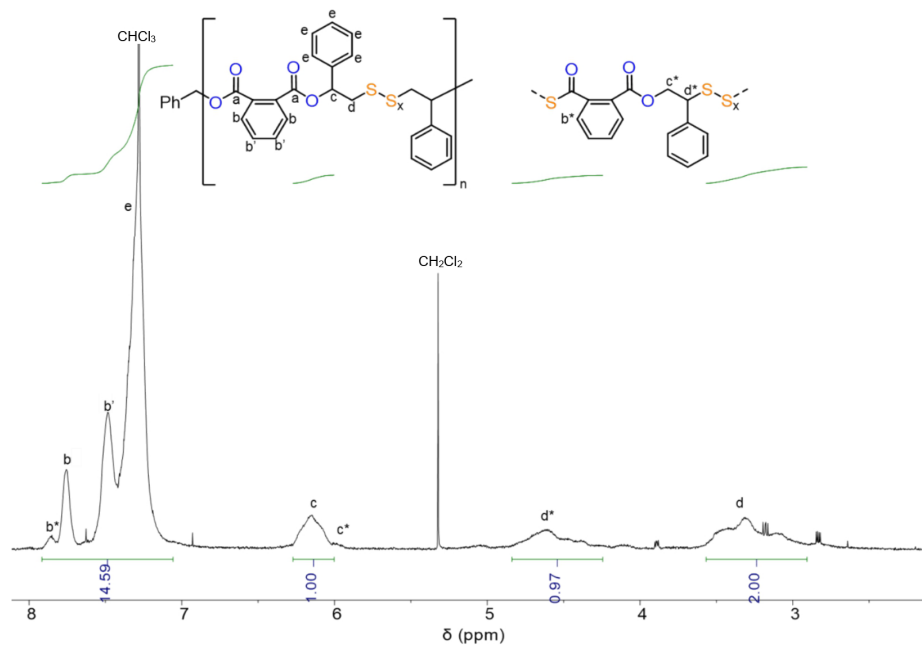


Figure S73:  $^1\text{H-NMR}$  spectra (600 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #10.

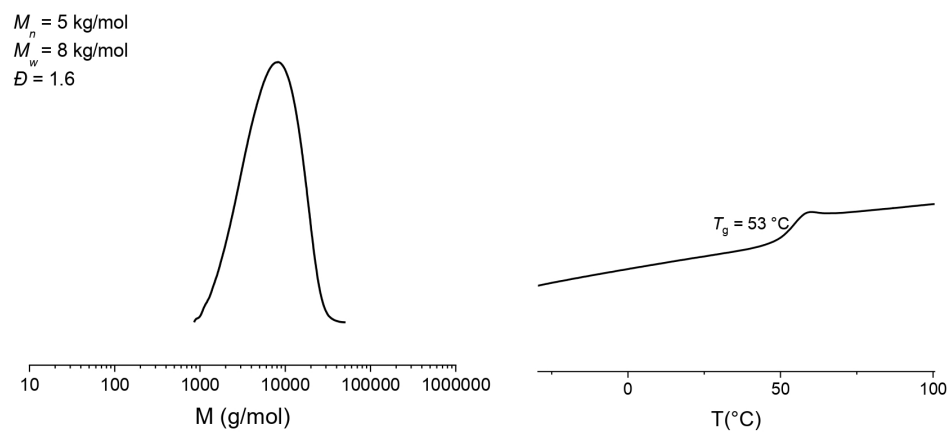


Figure S74: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #10.

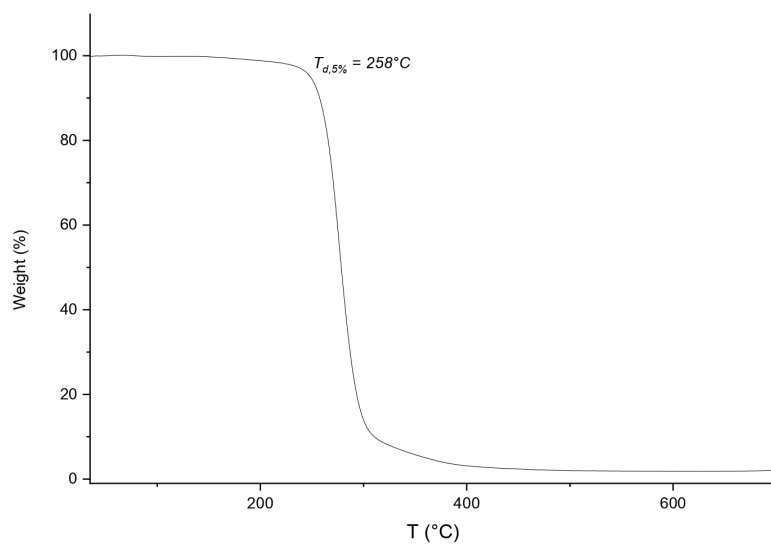


Figure S75: TGA data of the polymer corresponding to ESI table 1 run #10.

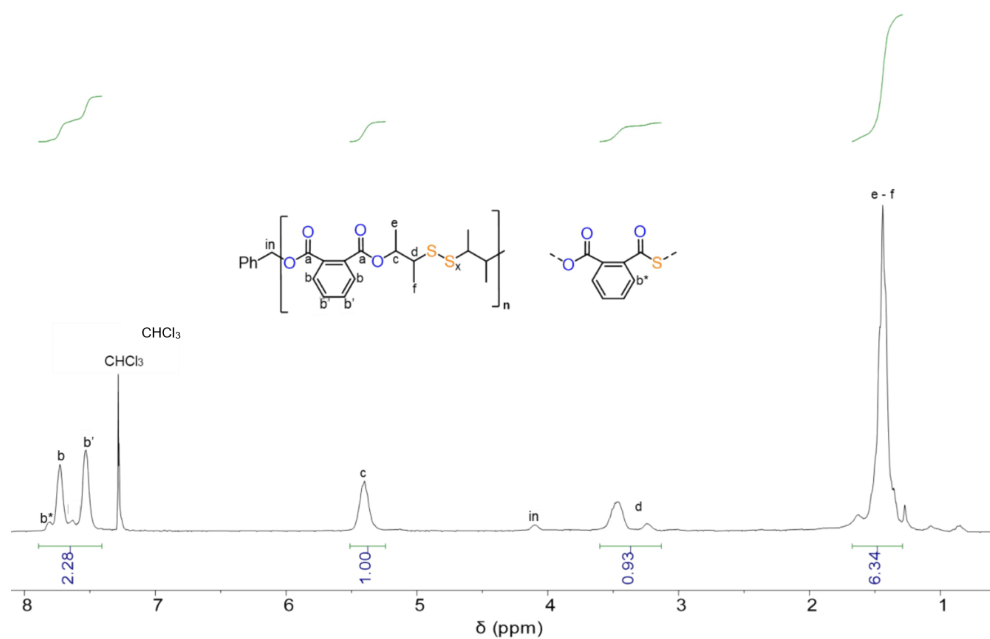


Figure S76: <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #11.

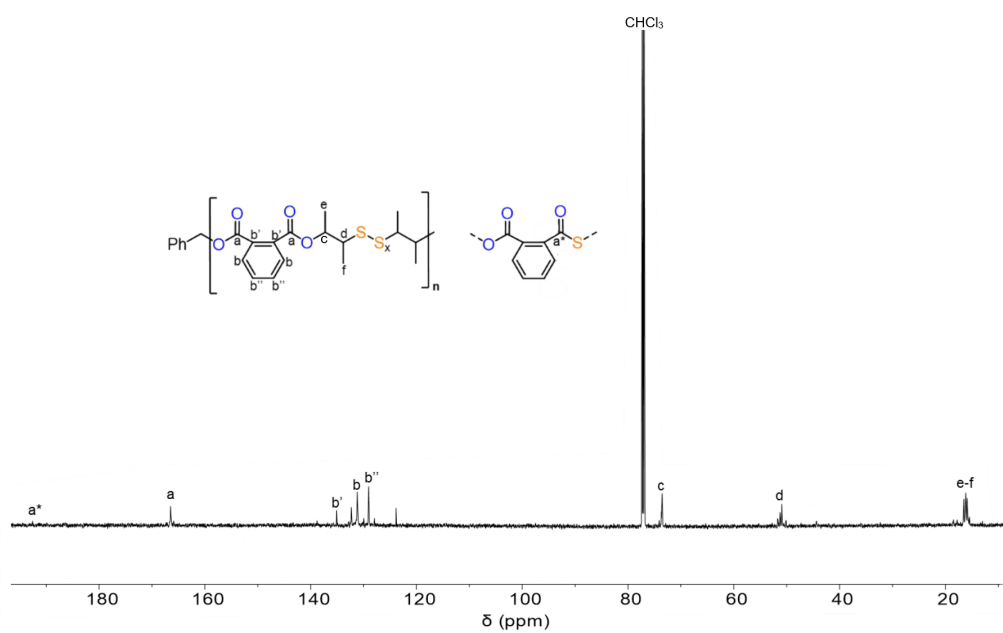


Figure S77: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #11.



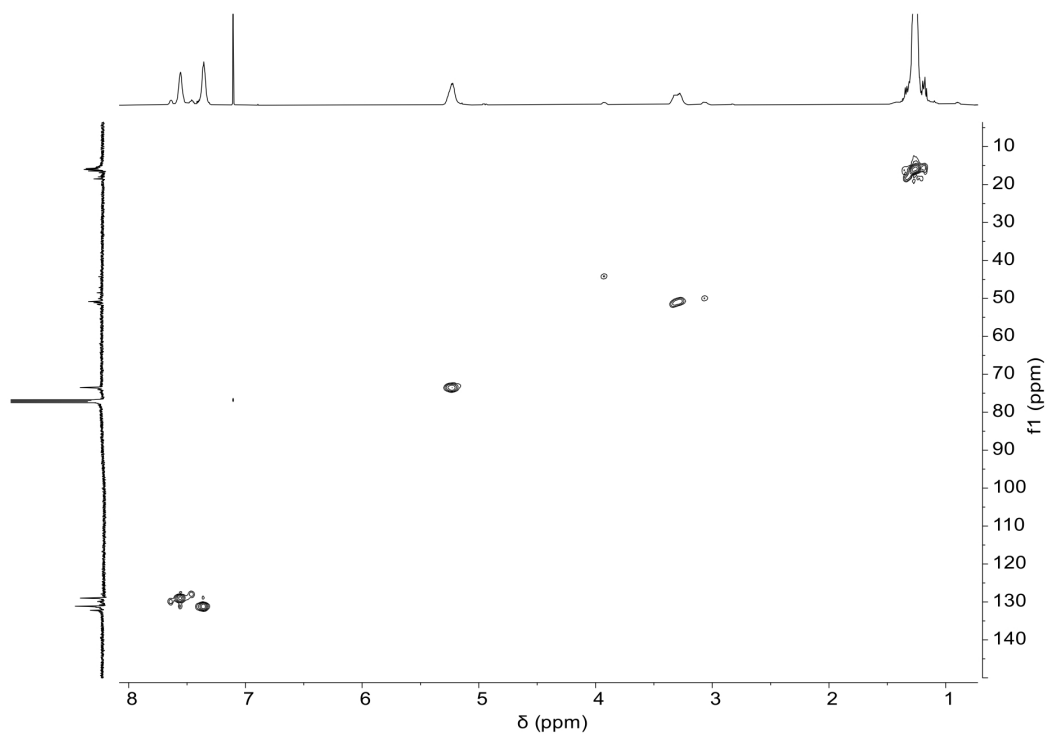


Figure S78:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #11.

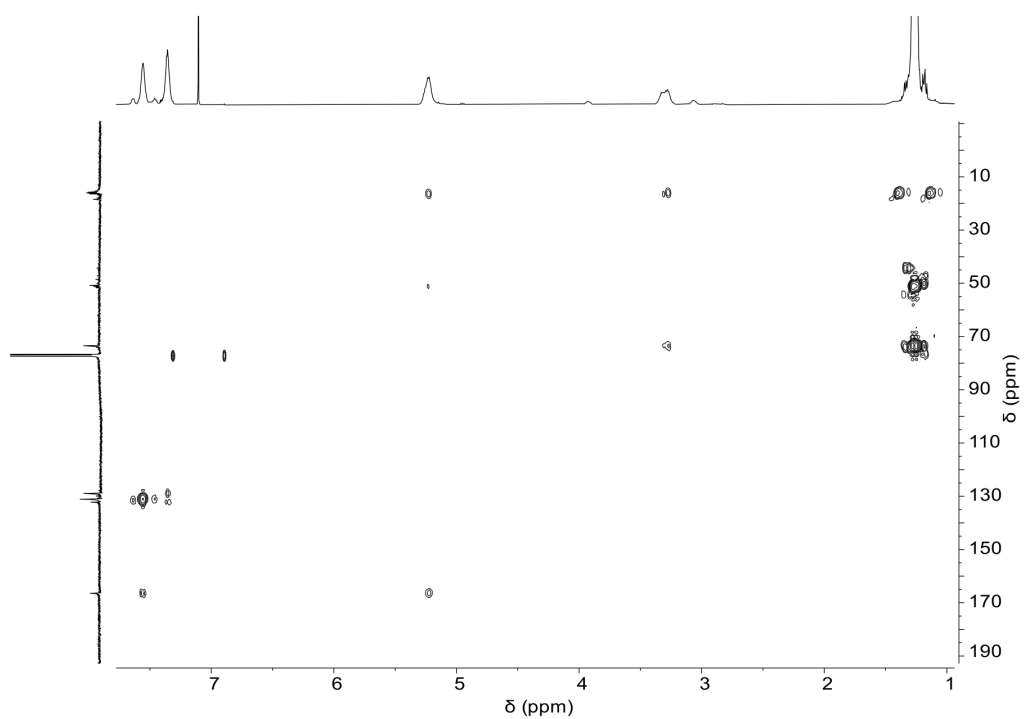


Figure S79:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #11.

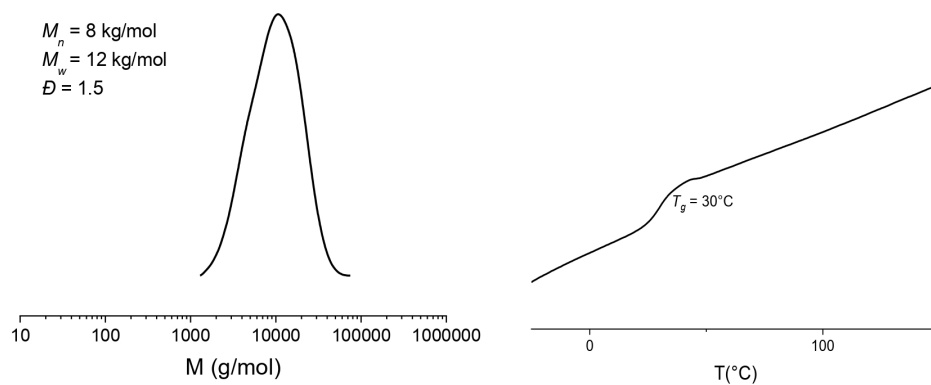


Figure S80: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #11.

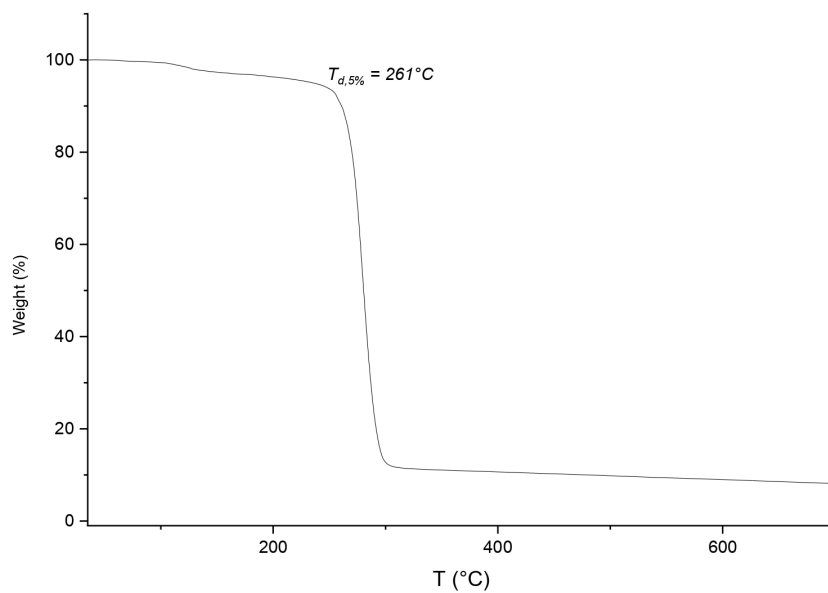


Figure S81: TGA data of the polymer corresponding to ESI table 1 run #11.

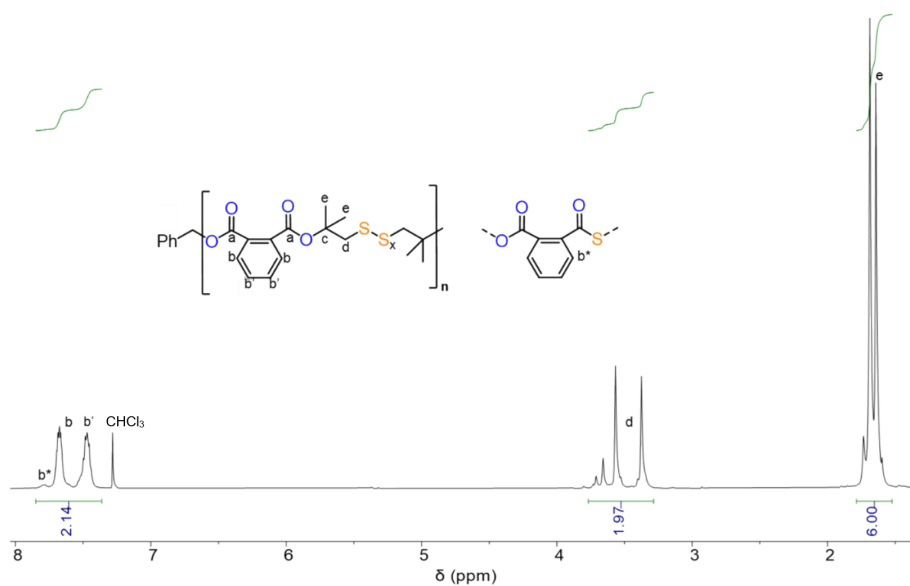


Figure S82: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #12.

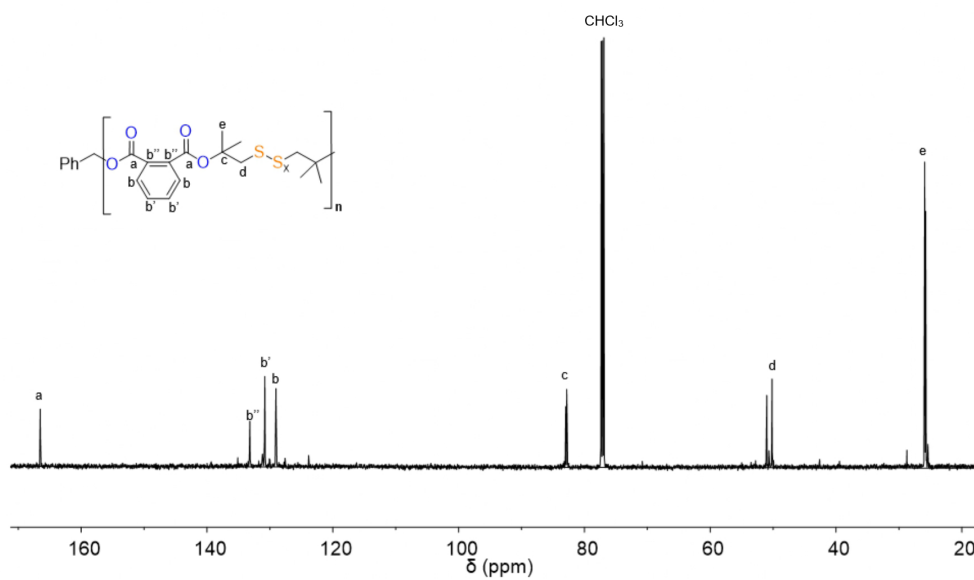


Figure S83: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #12.

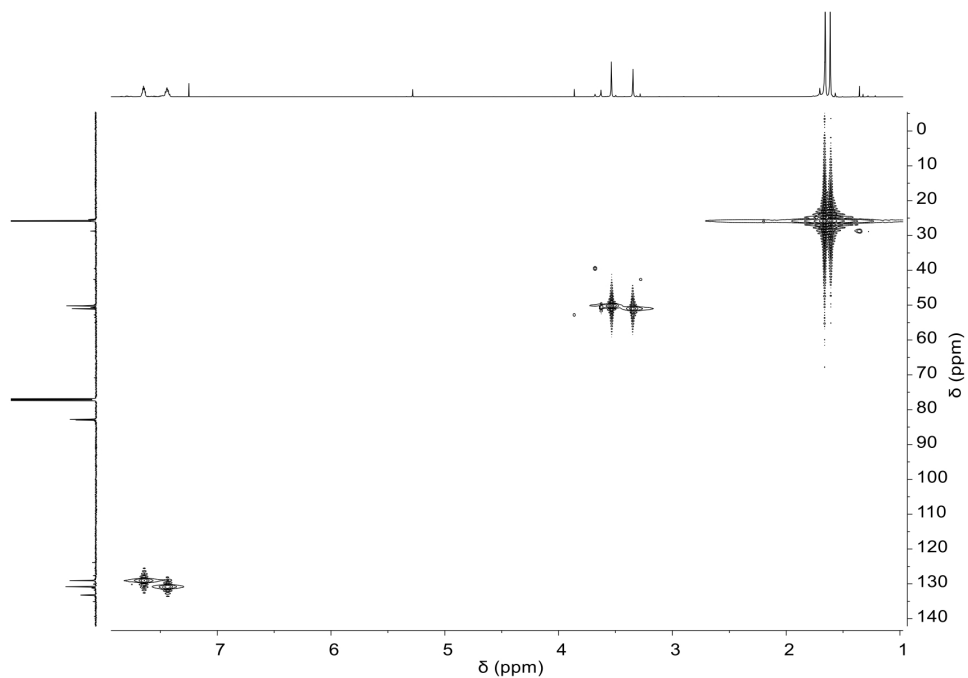


Figure S84:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #12.

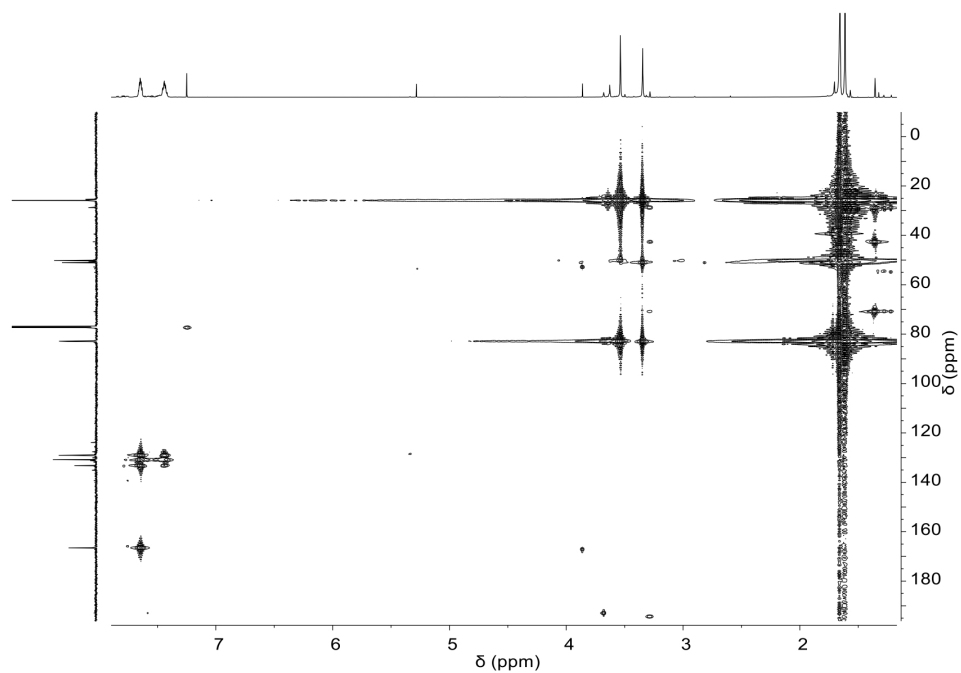


Figure S85:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #12.

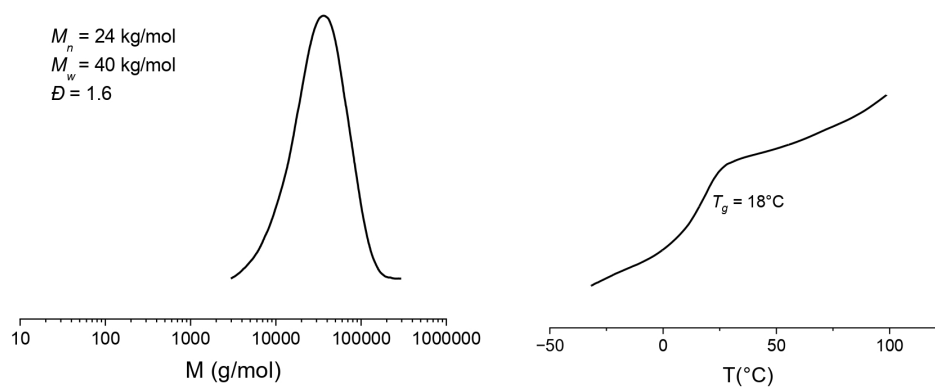


Figure S86: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #12.

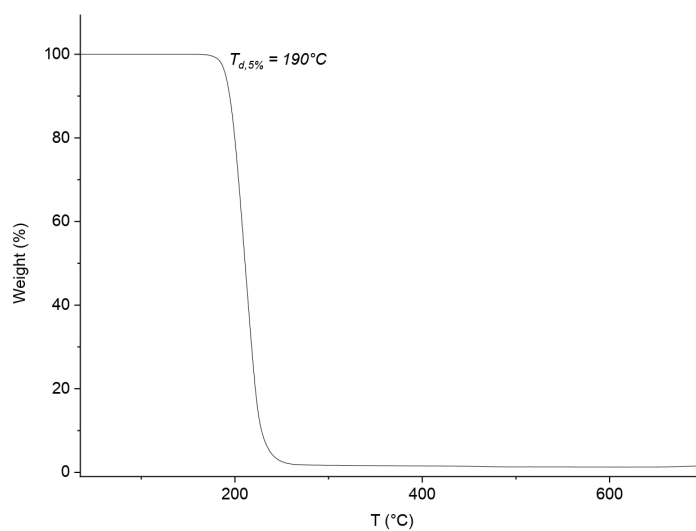


Figure S87: TGA data of the polymer corresponding to ESI table 1 run #12.

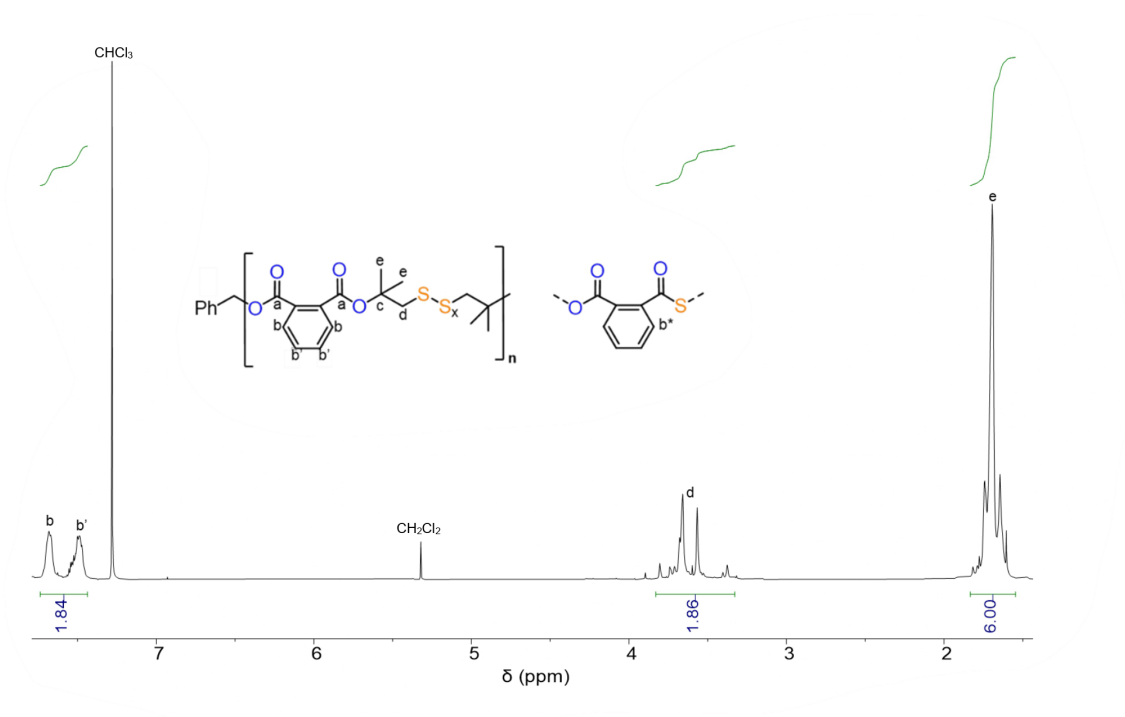


Figure S88:  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #13.

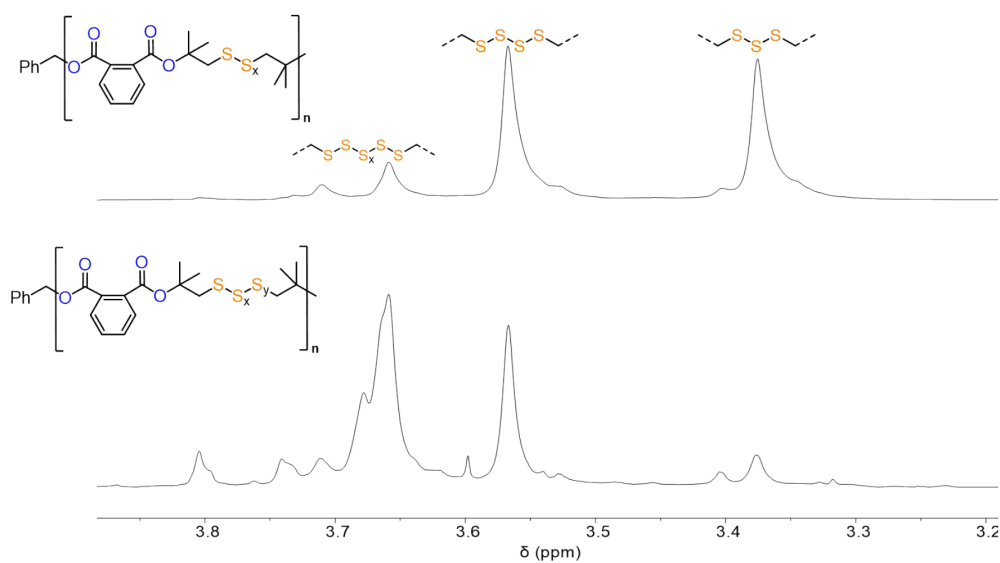


Figure S89:  $^1\text{H-NMR}$  spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to ESI table 1 run #12 (up) and #13 (down), zoomed in into the proton in alpha position to the polysulfide region.

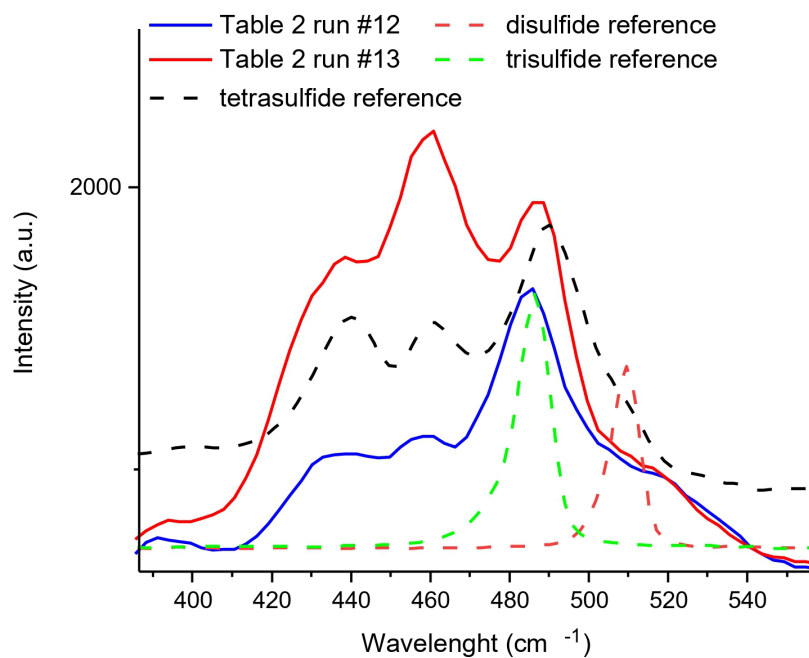


Figure S90: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectra of the polymer corresponding to ESI table 1 run # 12 and #13, compared with dimethyl disulfide, dimethyl trisulfide, and R<sub>2</sub>-tetrasulfide [R= -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] reference compounds.

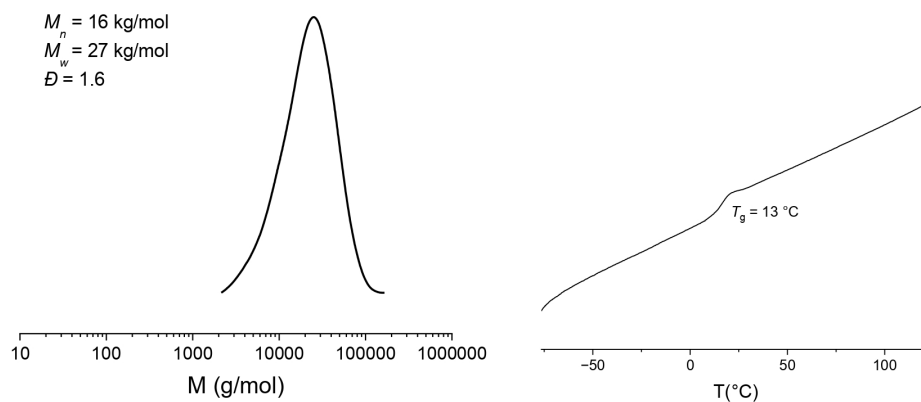


Figure S91: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #13.

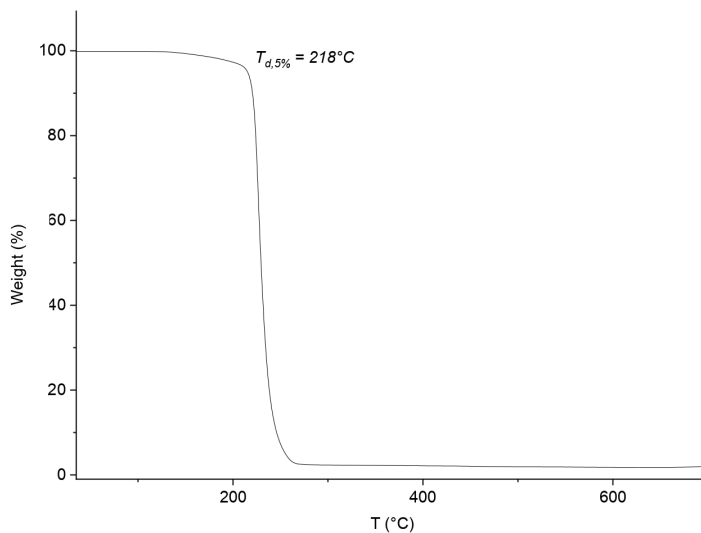


Figure S92: TGA data of the polymer corresponding to ESI table 1 run #13.

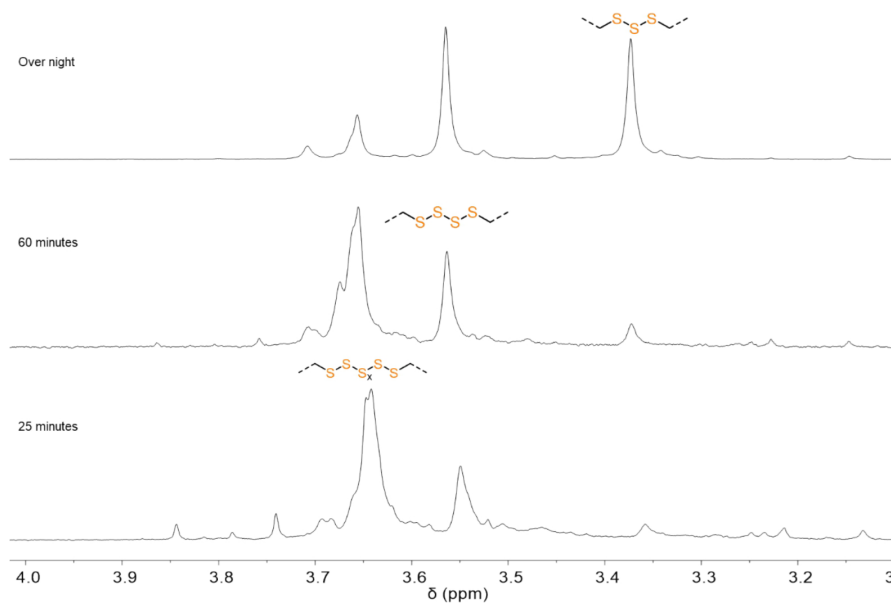


Figure S93: Zoom into overlaid  $^1\text{H}$ -NMR spectra of IBO terpolymerisation over time (1 eq. catalyst: 500 eq. IBO: 200 eq. PTA: 200 eq. S at  $100^{\circ}\text{C}$ ) revealing that over time longer polysulfide links decrease in quantity in favour of shorter trisulfide links and therefore polysulfide links remain reactive during ROTERP.



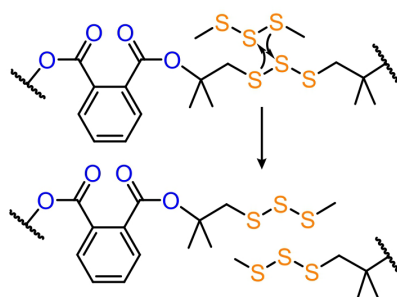
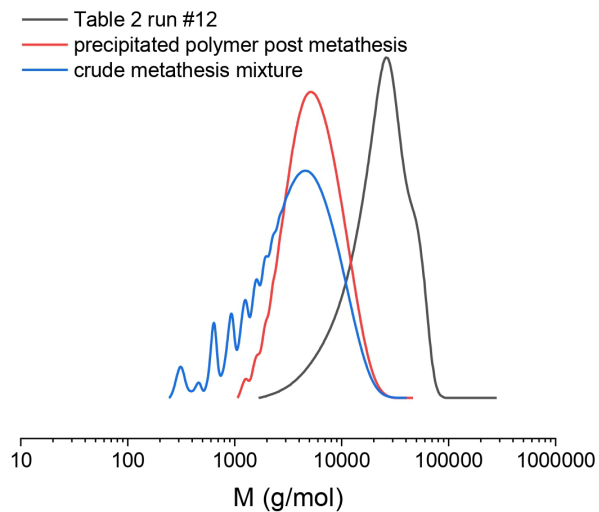


Figure S94: Comparison of the GPC signals obtained from the polymer corresponding to Table 2 run #12 and the same polymer after being exposed to dimethyl trisulfide at 100°C in a PO solution. The metathesis reaction was analysed with GPC before and after being purified by precipitation, the crude mixture shows the presence of smaller oligomers generated from the metathesis reaction. Scheme depicts an example chain cleavage pathway via spontaneous metathesis of polymer with  $\text{Me}_2\text{S}_3$ .

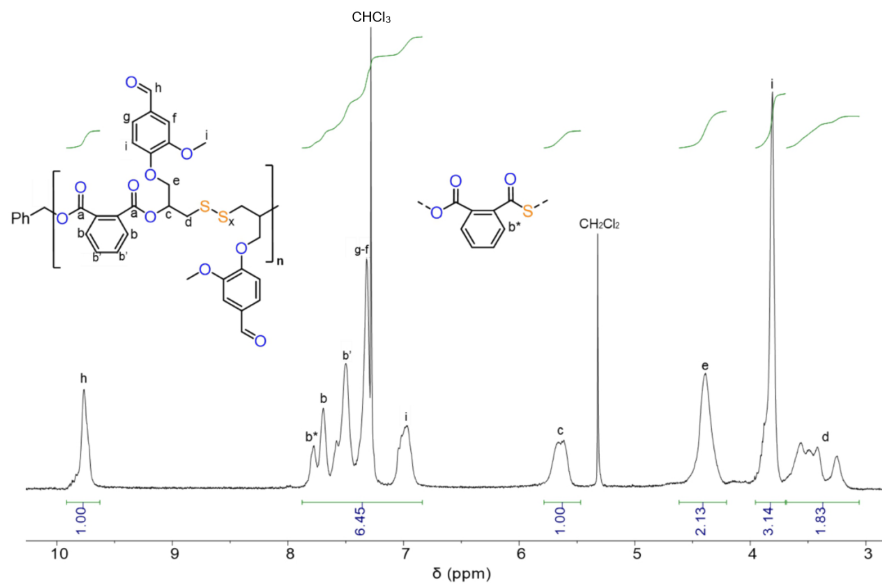


Figure S95:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #14.

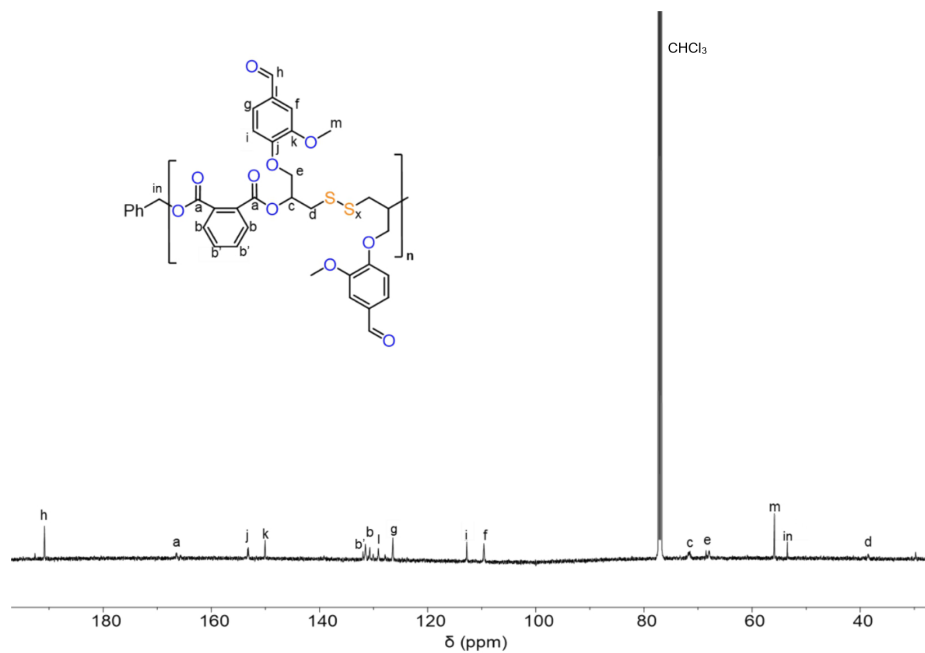


Figure S96:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #14.

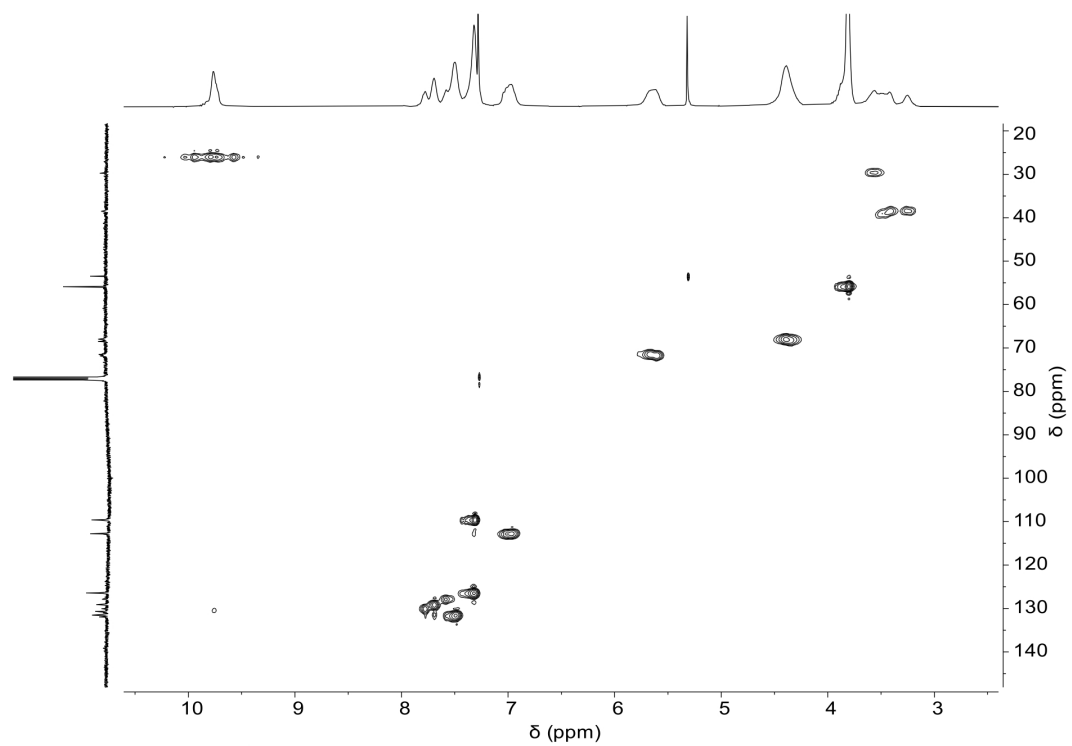


Figure S97:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #14.

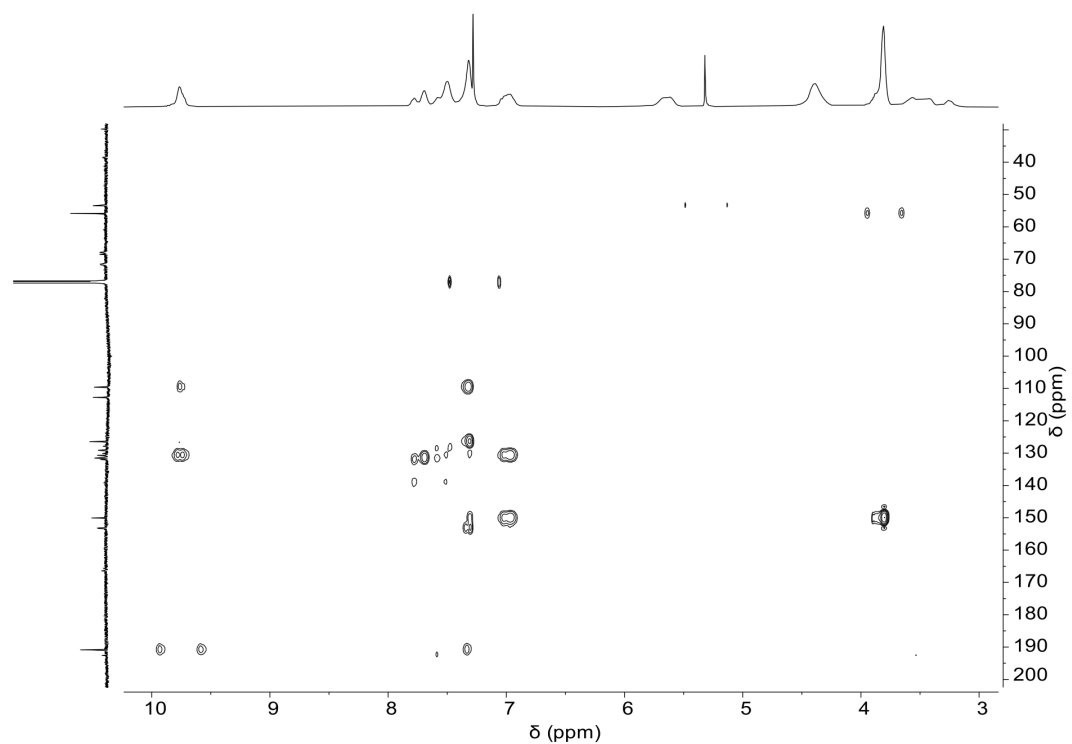


Figure S98:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #14.

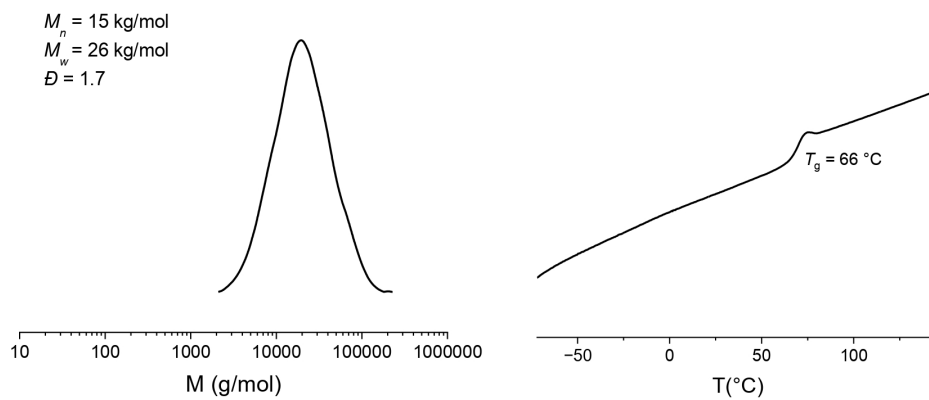


Figure S99: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #14.

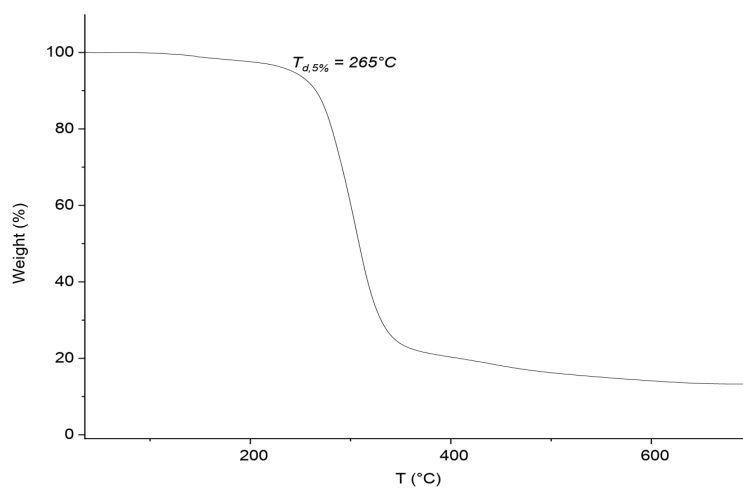


Figure S100: TGA data of the polymer corresponding to ESI table 1 run #14.

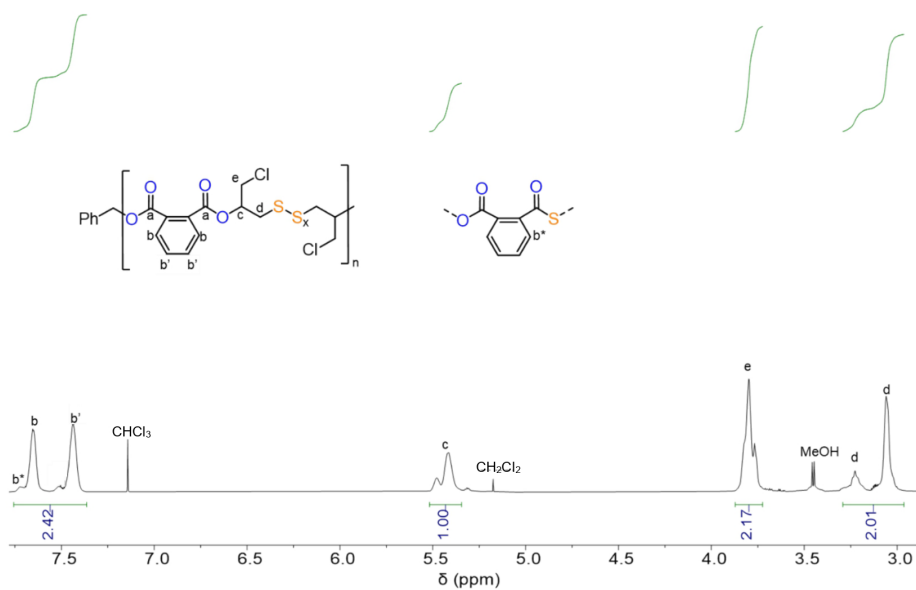


Figure S101:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #15.

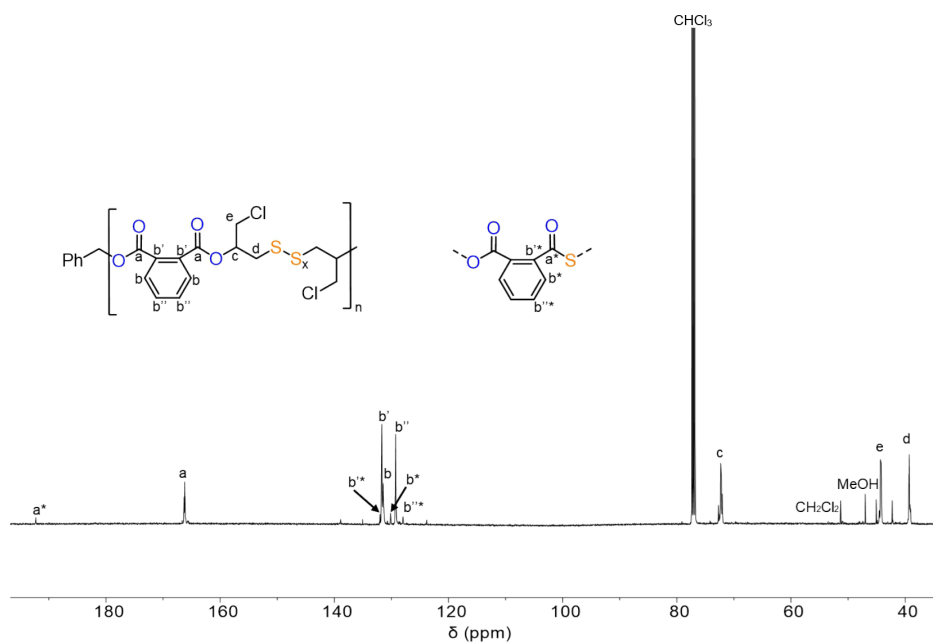


Figure S102:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #15.

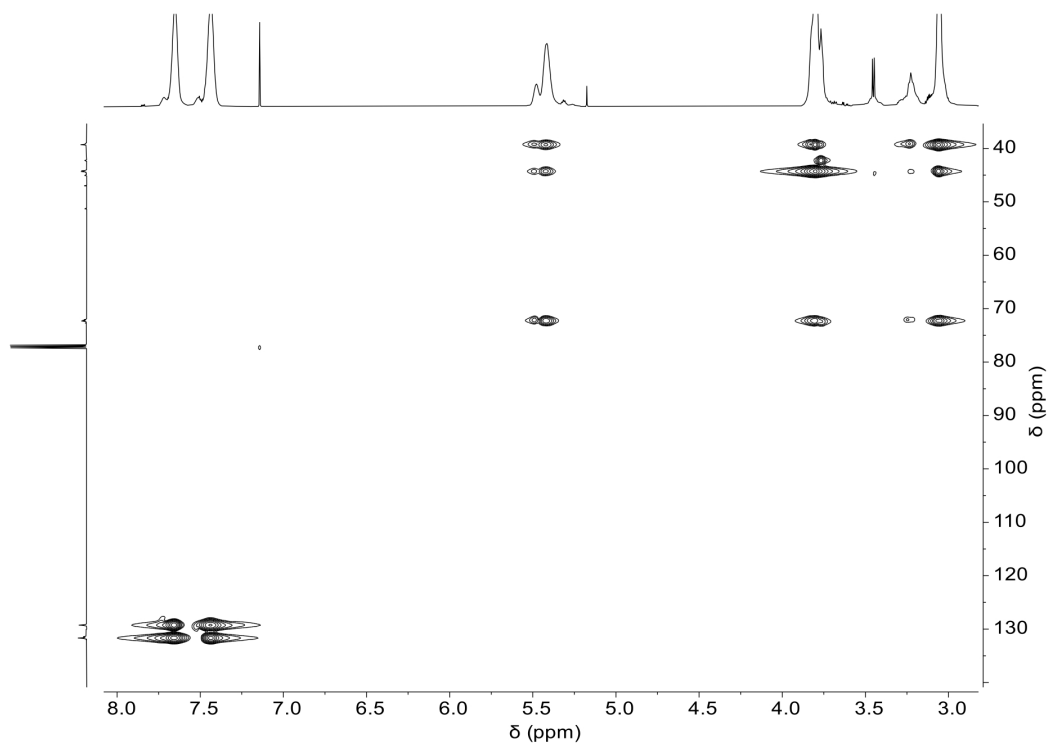


Figure S103:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #15.

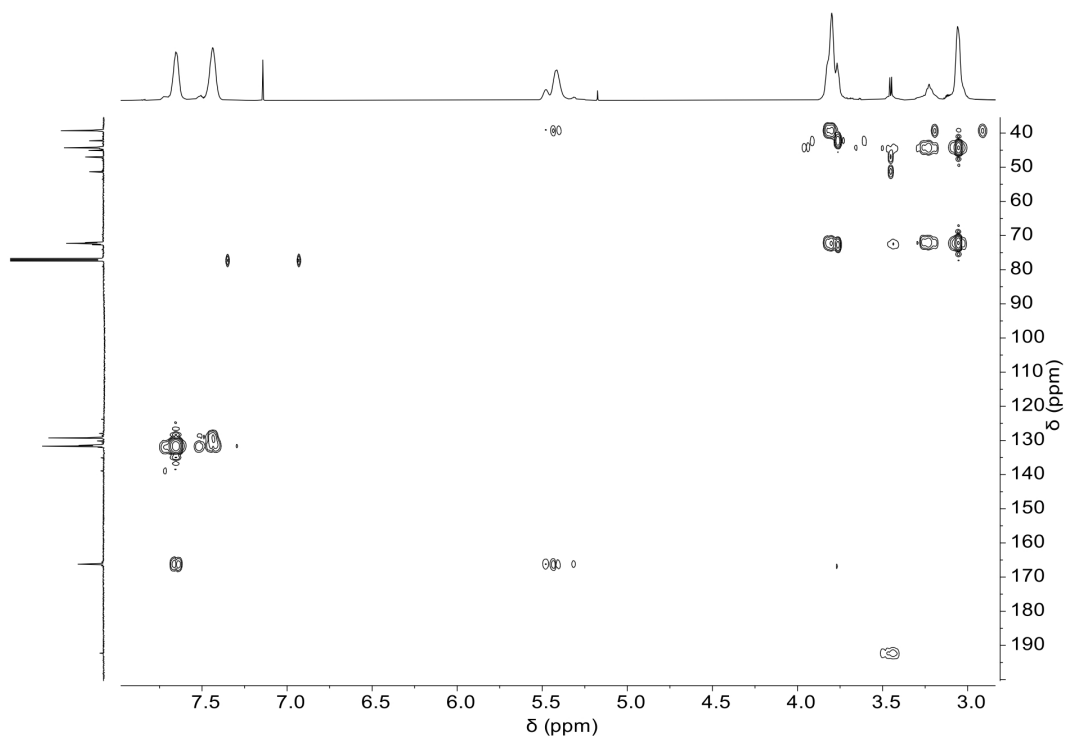


Figure S104:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #15.

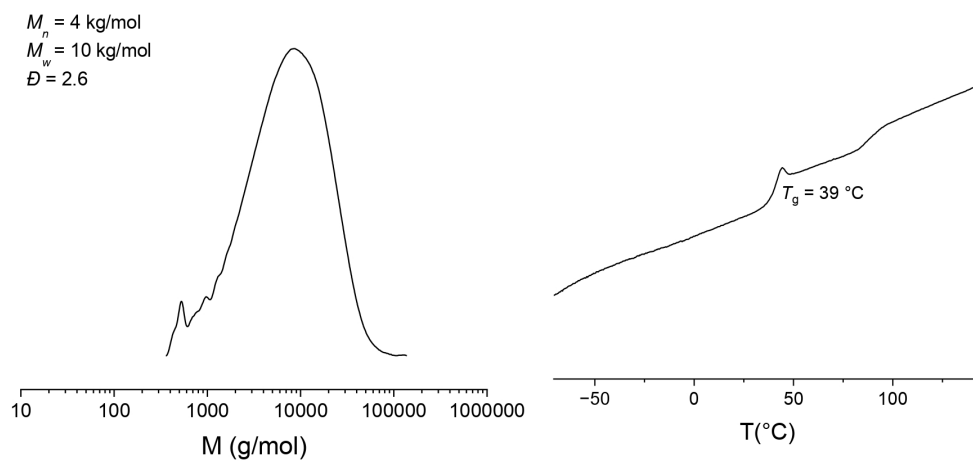


Figure S105: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #15.

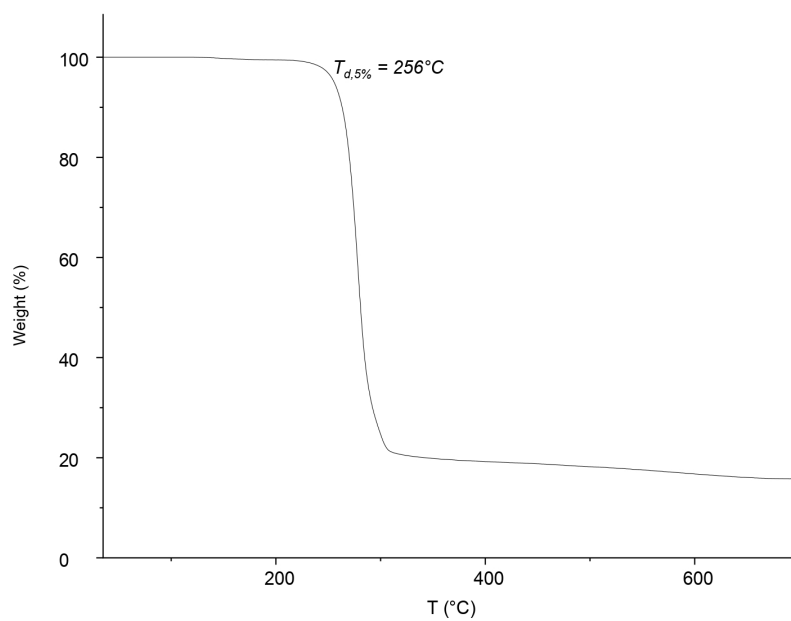


Figure S106: TGA data of the polymer corresponding to ESI table 1 run #15.

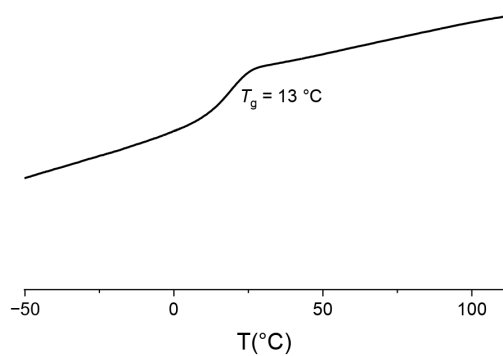


Figure S107: DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #16.

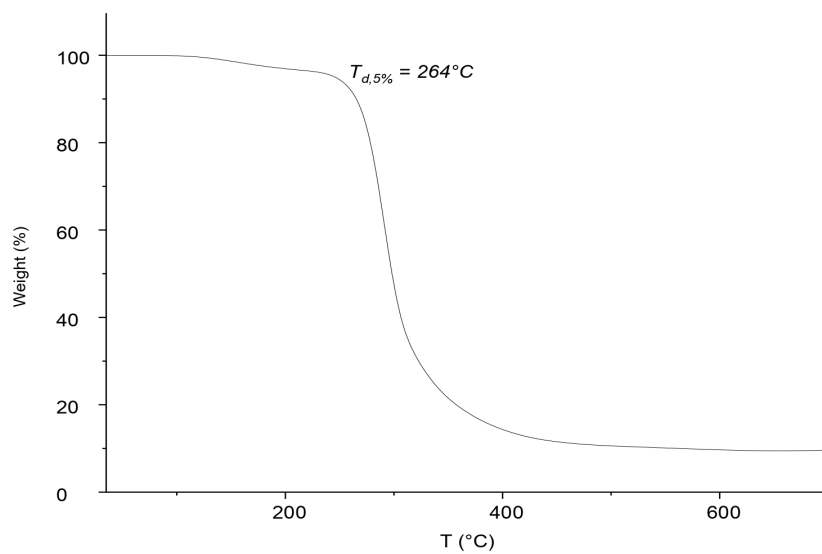


Figure S108: TGA data of the polymer corresponding to ESI table 1 run #16.



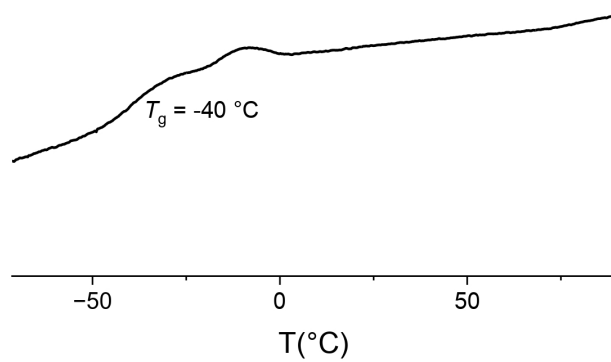


Figure S109: DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #17.

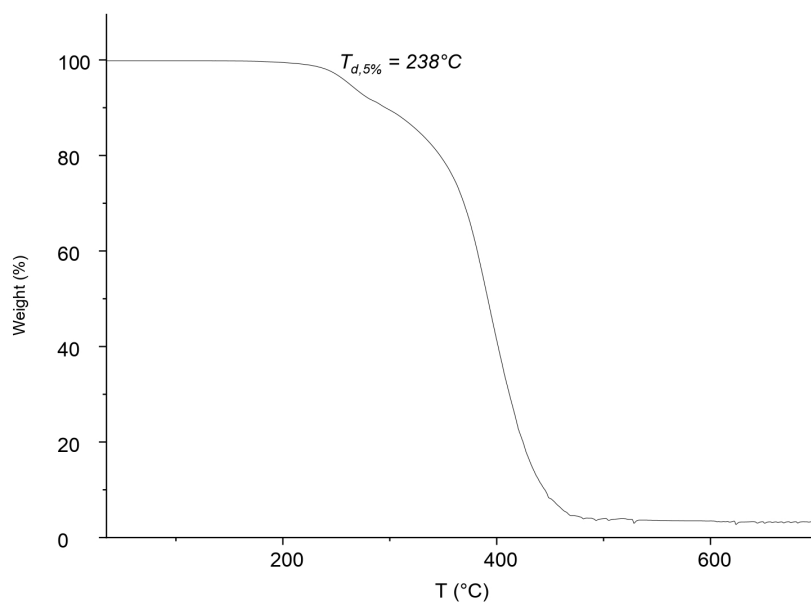


Figure S110: TGA data of the polymer corresponding to ESI table 1 run #17.

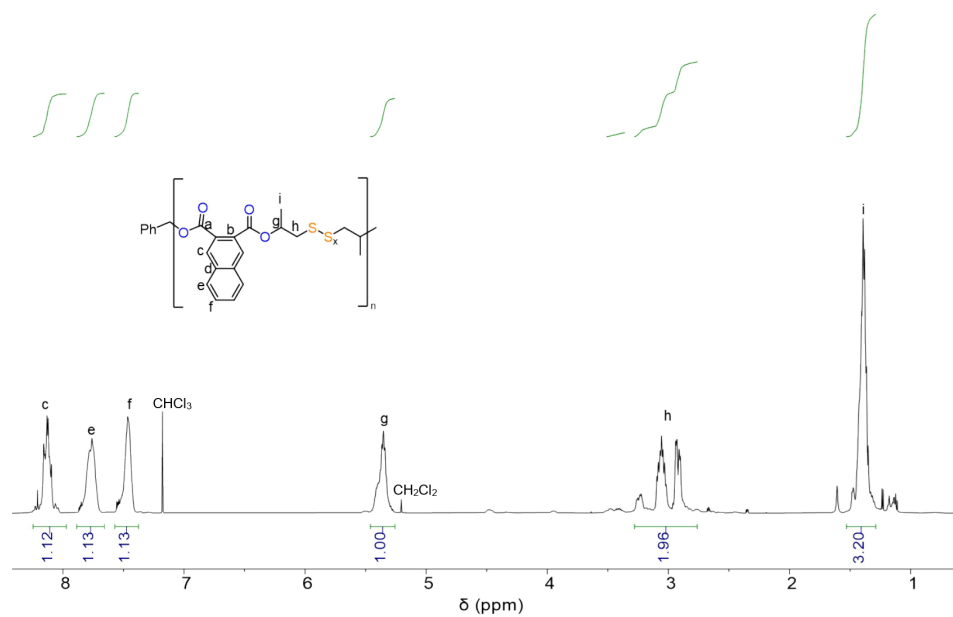


Figure S111:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #18.

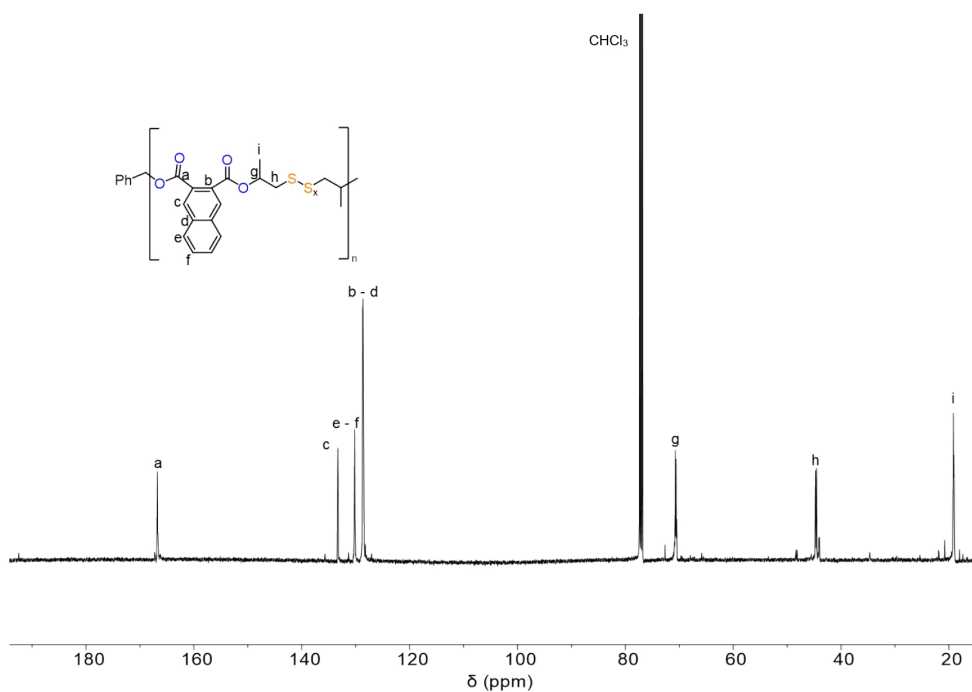


Figure S112:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to ESI table 1 run #18.

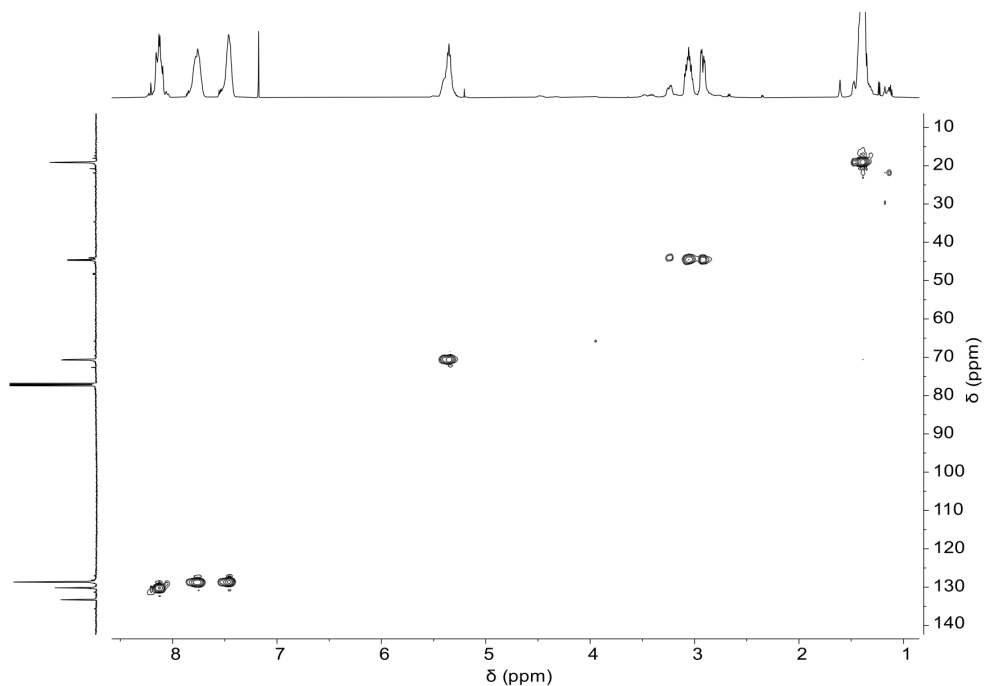


Figure S113:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #18.

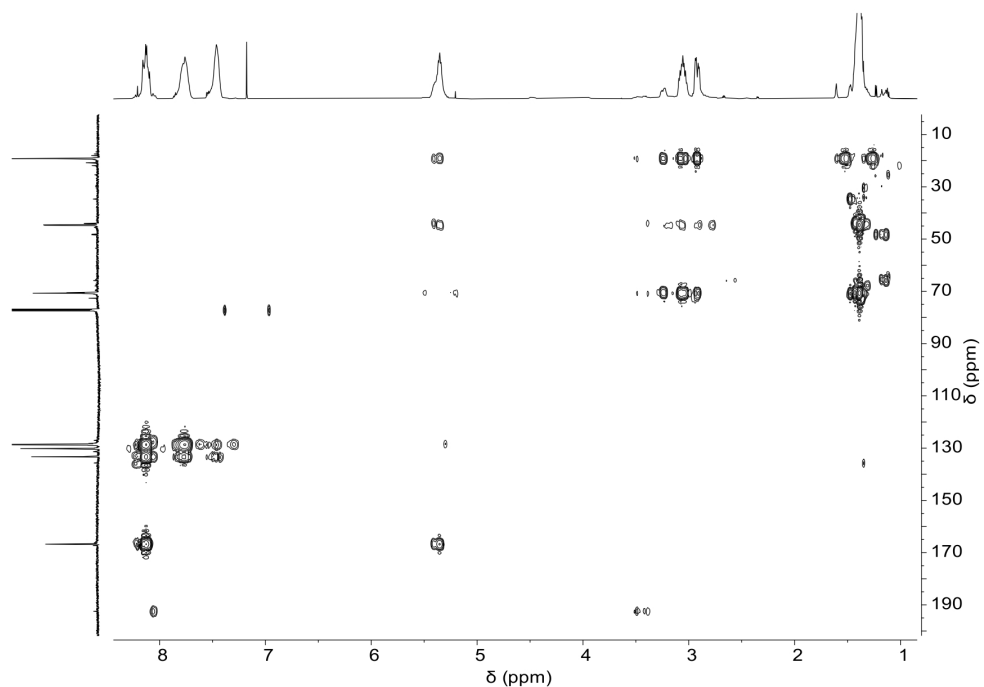


Figure S114:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #18.

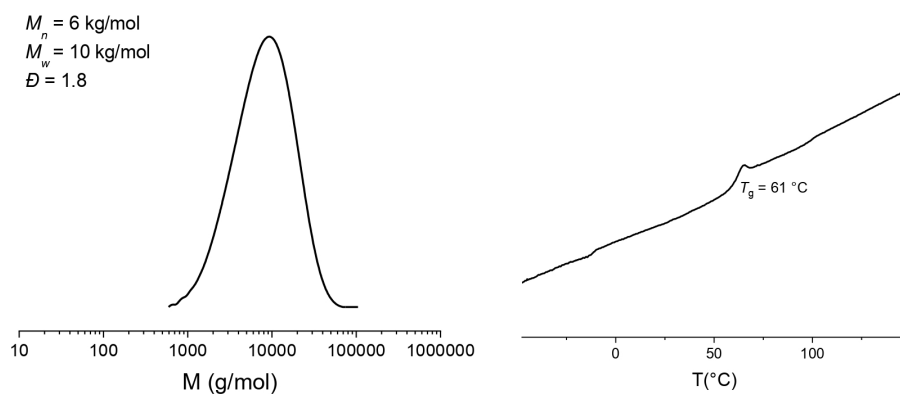


Figure S115: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #18.

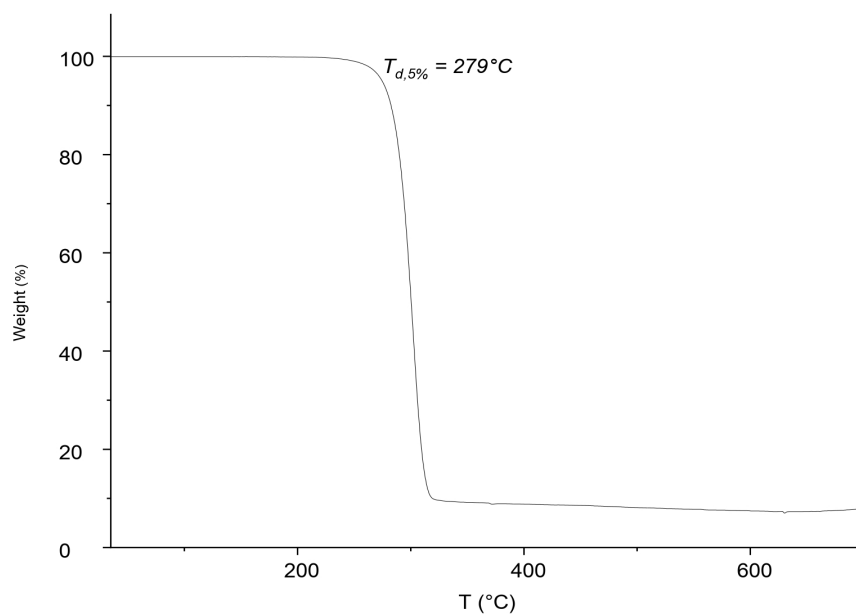


Figure S116: TGA data of the polymer corresponding to ESI table 1 run #18.

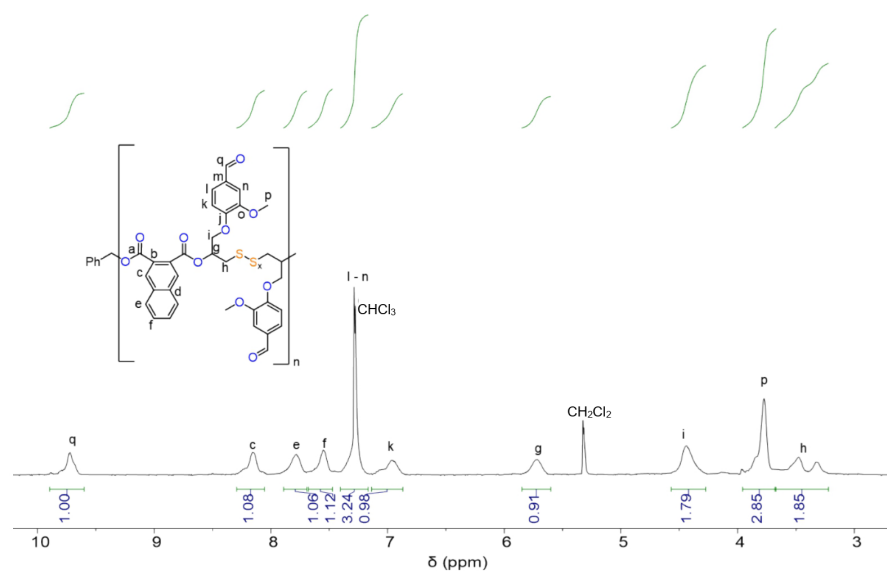


Figure S117: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #19.

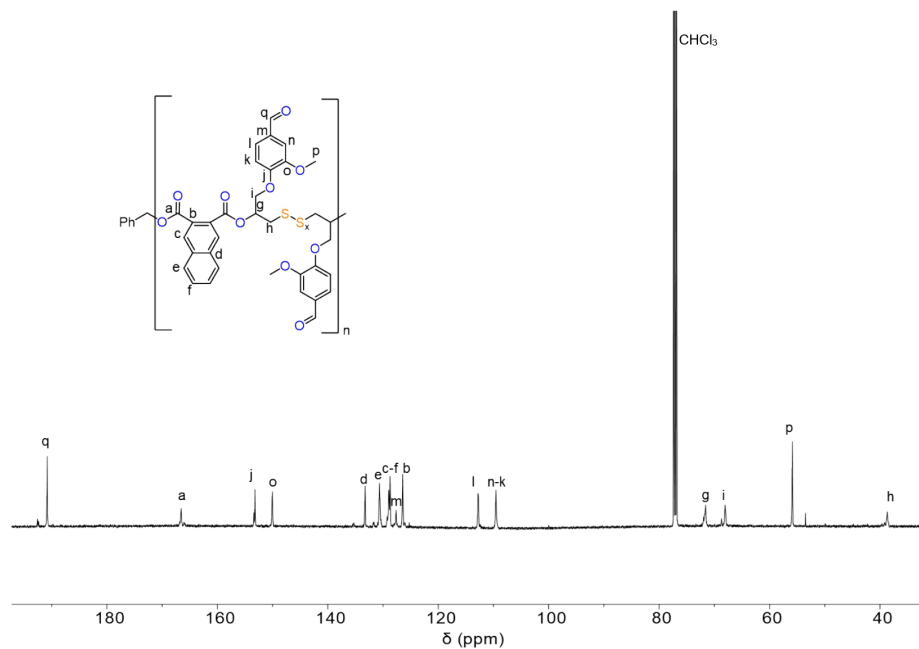


Figure S118: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #19.

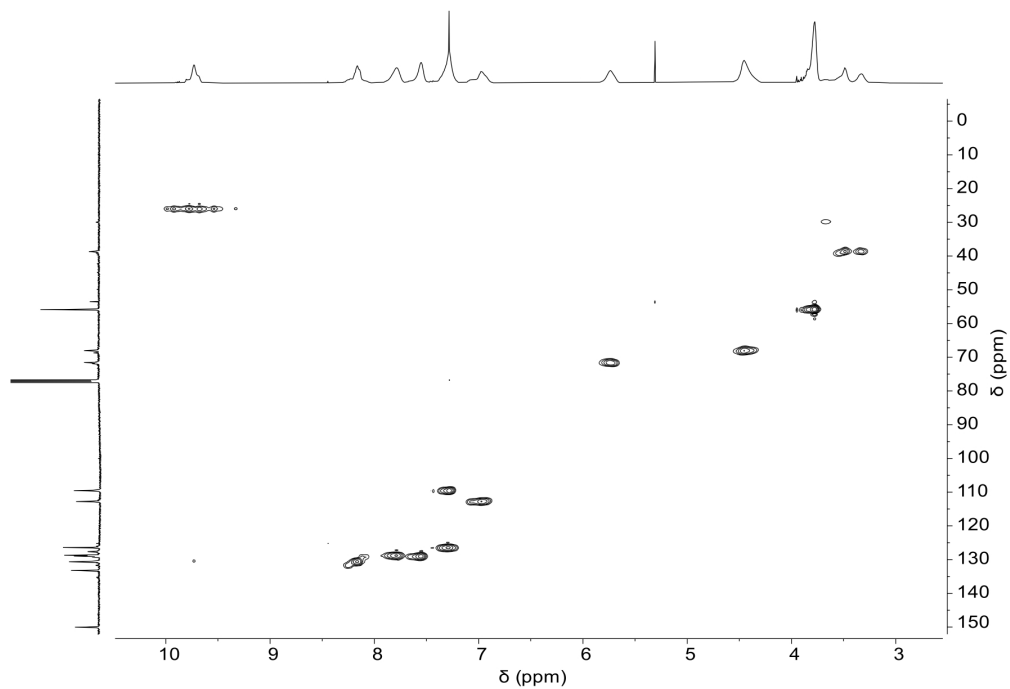


Figure S119:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #19.

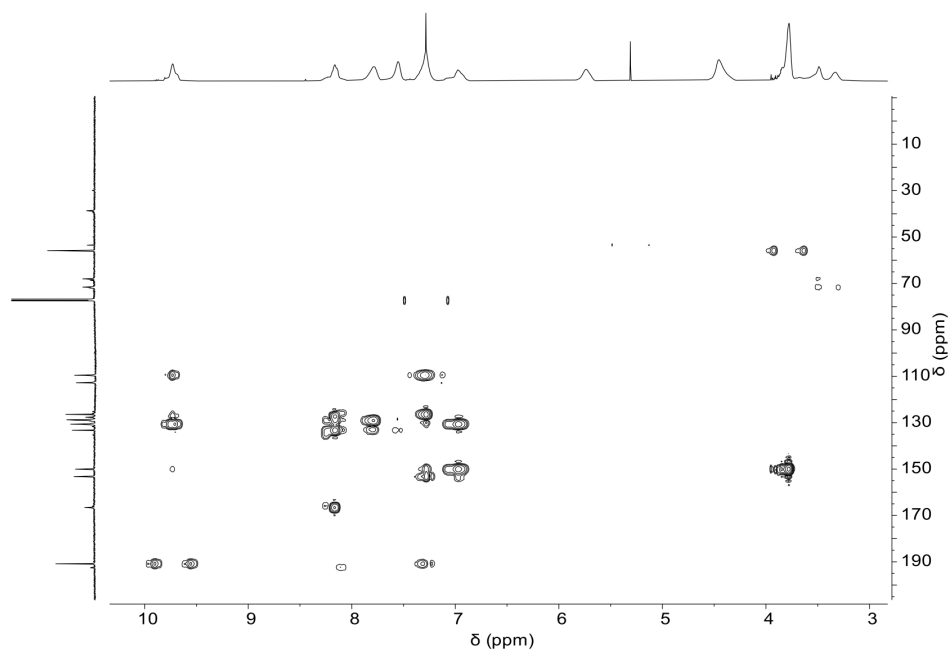


Figure S120:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #19.

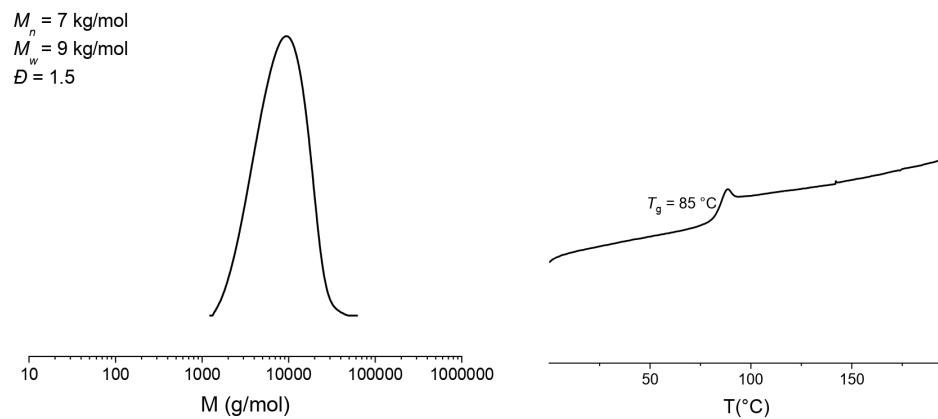


Figure S121: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #19.

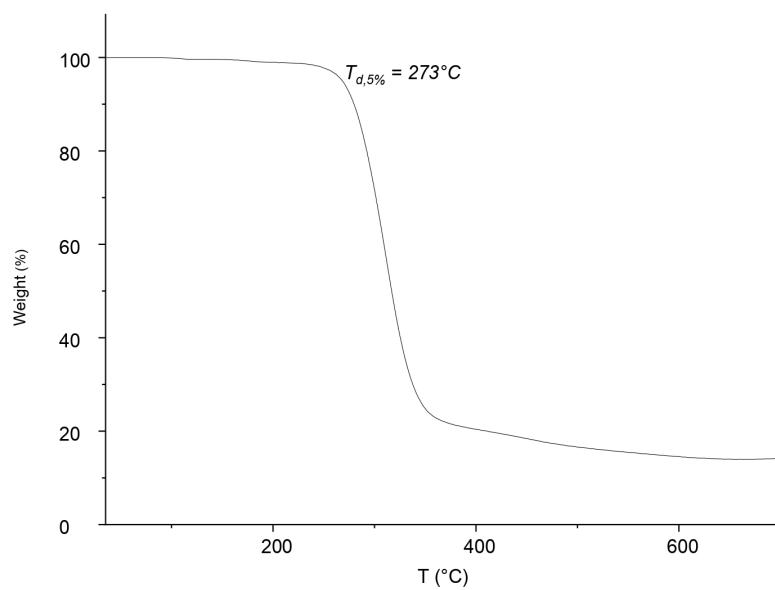


Figure S122: TGA data of the polymer corresponding to ESI table 1 run #19.

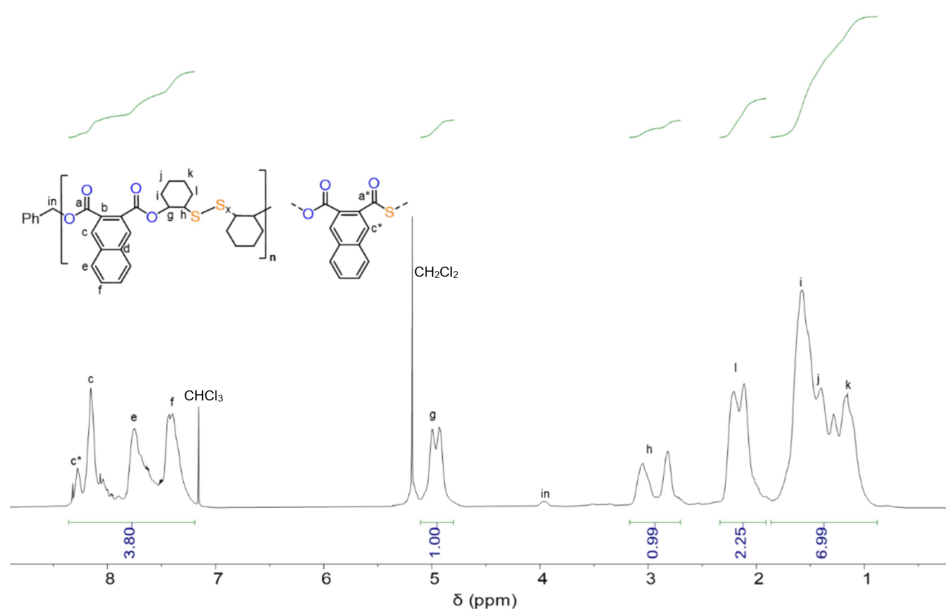


Figure S123: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #20.

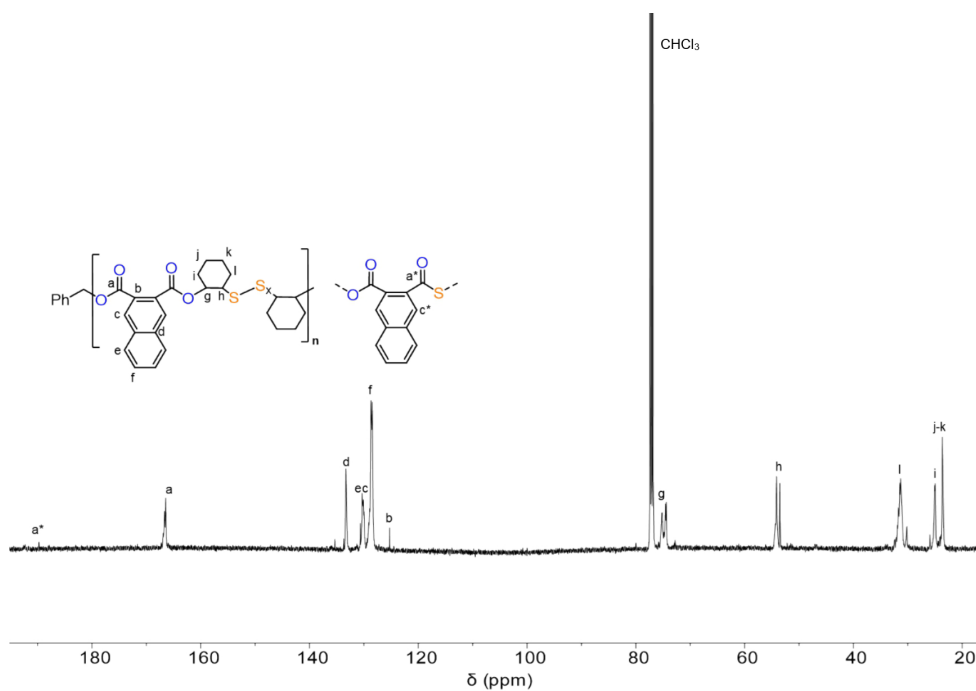


Figure S124: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #20.



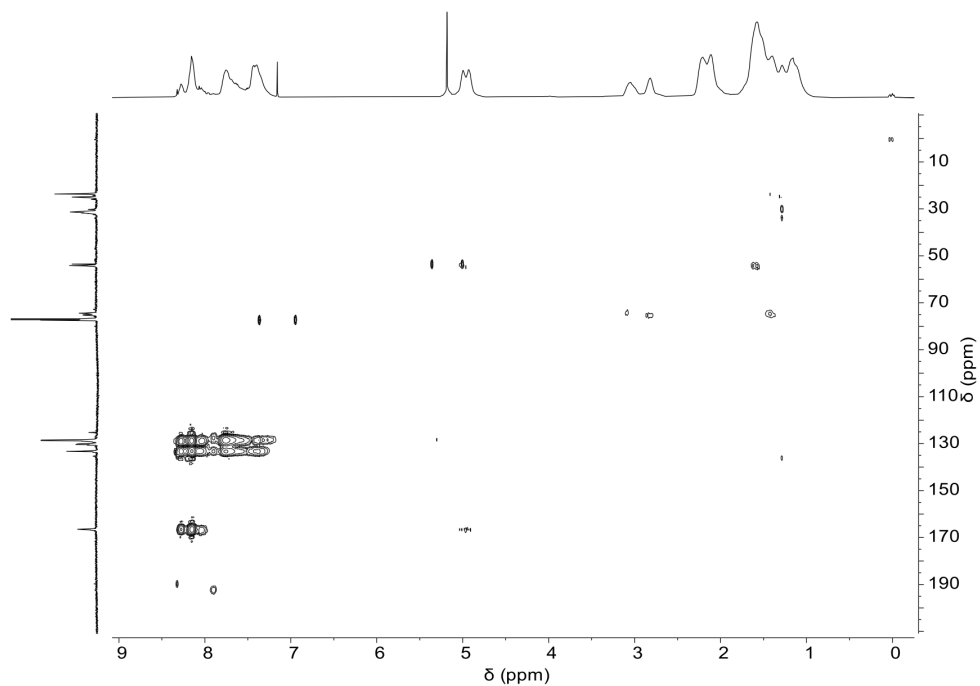


Figure S125:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #20.

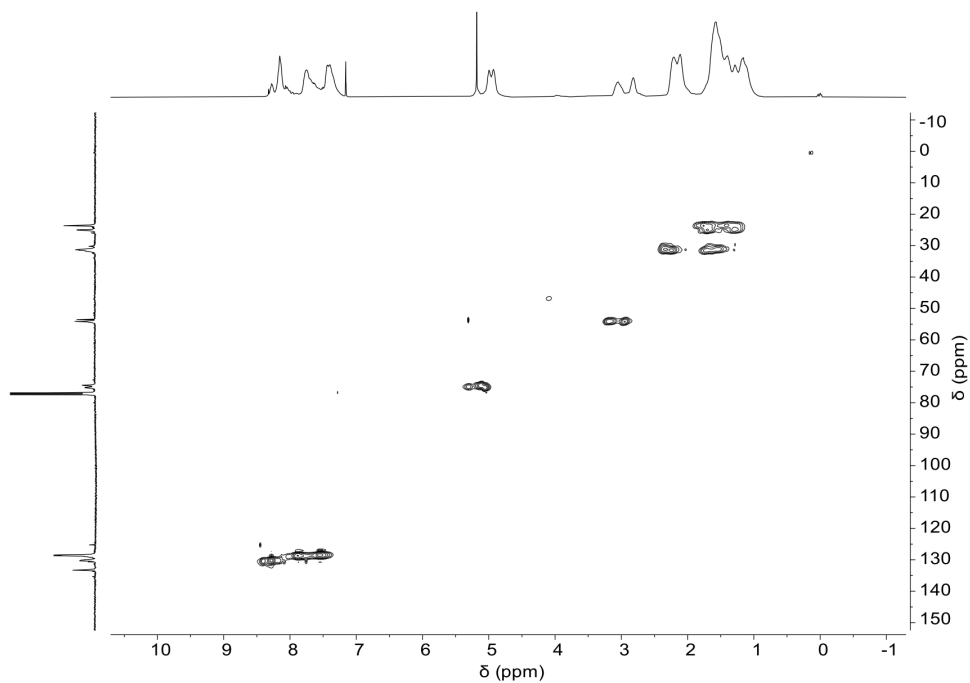


Figure S126:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to ESI table 1 run #20.

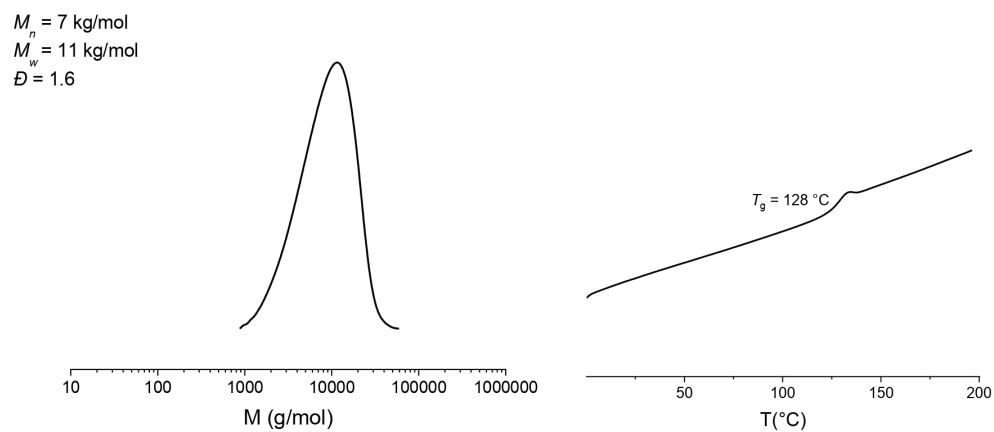


Figure S127: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to ESI table 1 run #20.

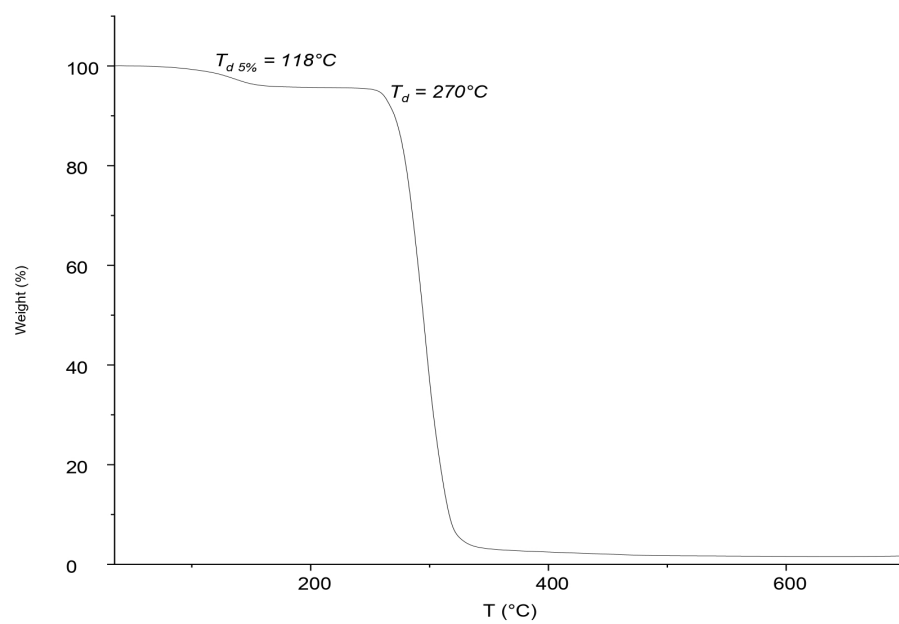


Figure S 128: TGA data of the polymer corresponding to ESI table 1 run #20.

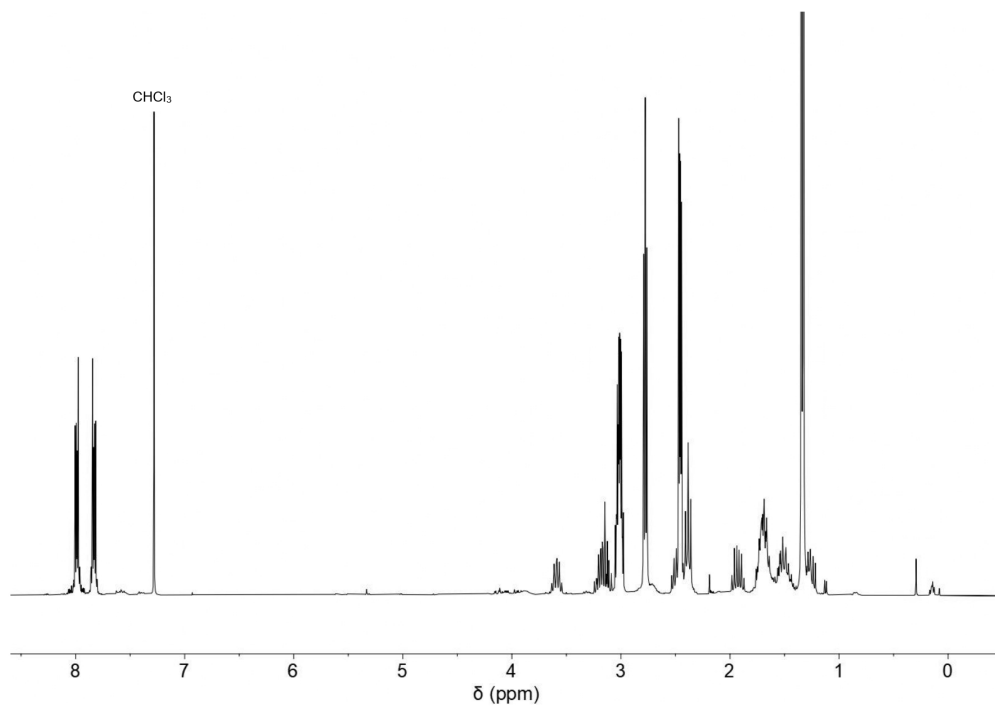


Figure S129:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25°C) of the crude mixture of S:lipoic acid:PTA:PO tetrapolymerization (1 eq. LiOBn: 200 eq. S : 200 eq. lipoic acid : 200 eq. PTA: 500 eq. epoxide).

## Section S5: Post functionalization

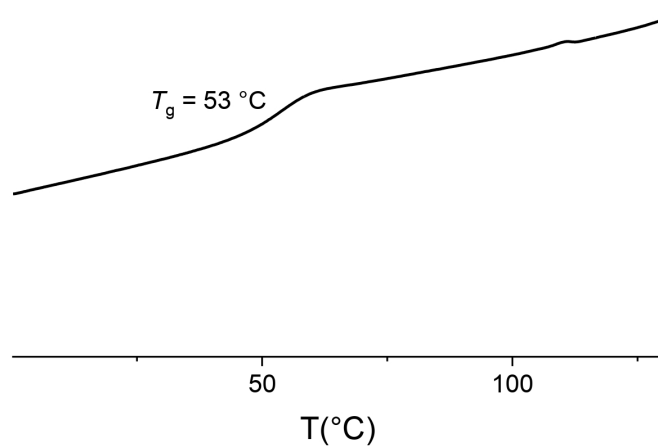
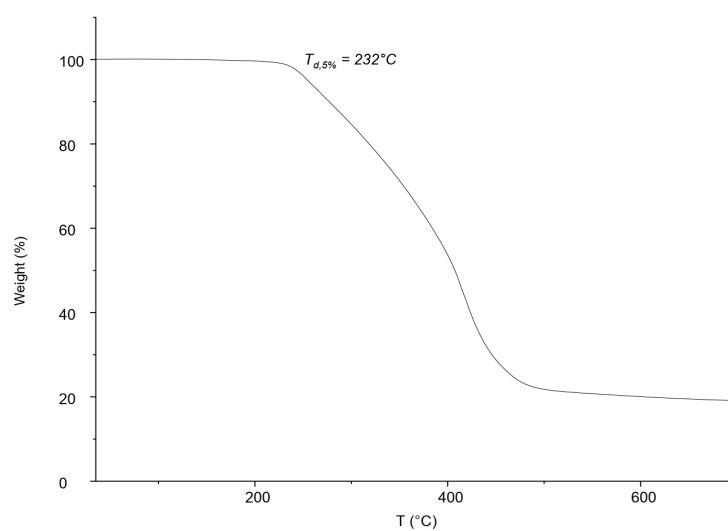
Figure S130: DSC 2<sup>nd</sup> heating curve of the imine cross-linked polymer.

Figure S131: TGA data of the imine cross-linked polymer.

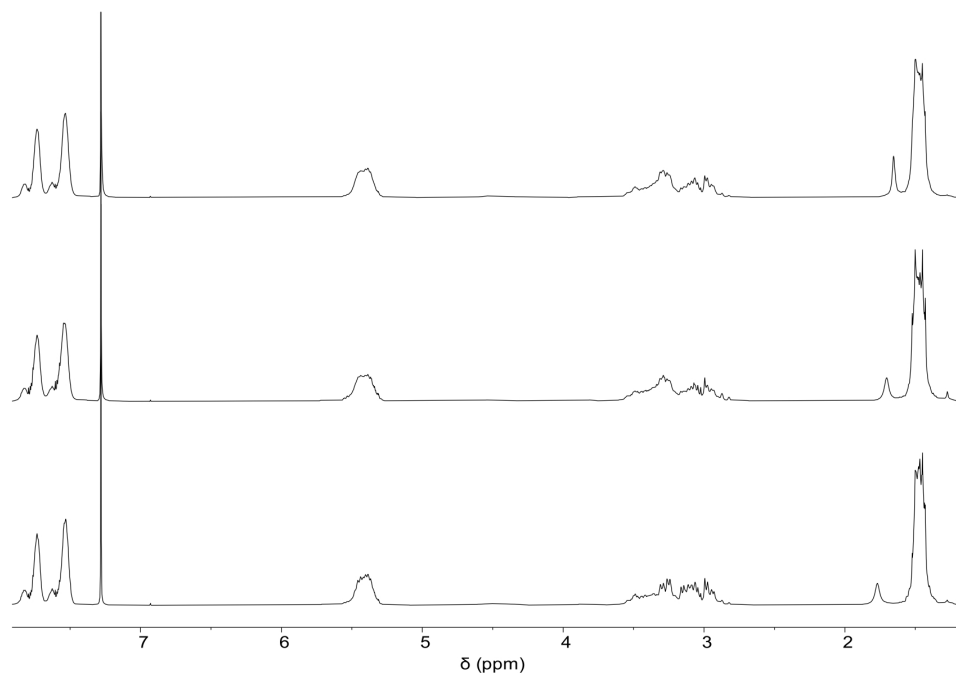


Figure S132:  $^1\text{H}$ -NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to table 1 run #9 and the same polymer after insertion of  $\text{S}_8$ . Bottom to top: table 1 run #9 (0%  $\text{S}_8$  inserted), 5%  $\text{S}_8$  w/w, 10% w/w  $\text{S}_8$ .

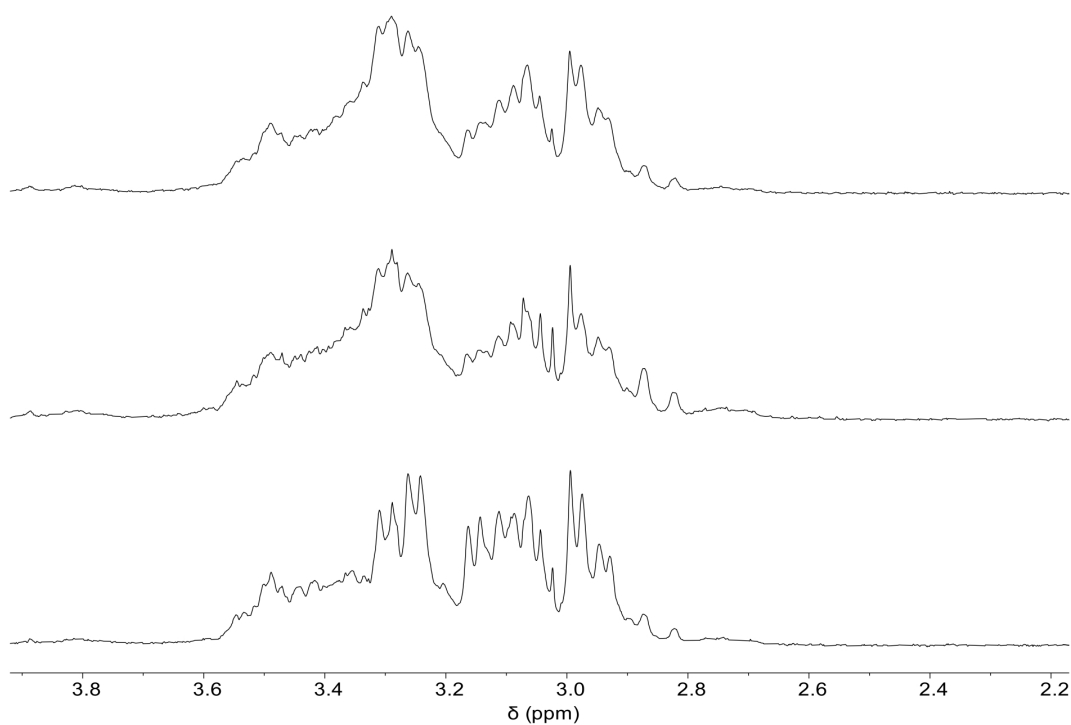


Figure S133:  $^1\text{H}$ -NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers corresponding to table 1 run #9 and the same polymer after insertion of  $\text{S}_8$ . Zoomed in into the polysulfide region.

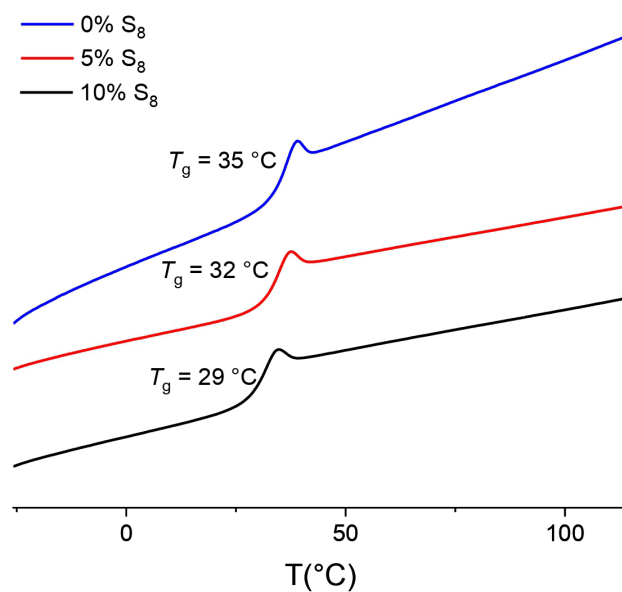


Figure S134: DSC 2<sup>nd</sup> heating curve of the precipitated polymer corresponding to table 1 run #9 and the same polymer after insertion of  $\text{S}_8$ .

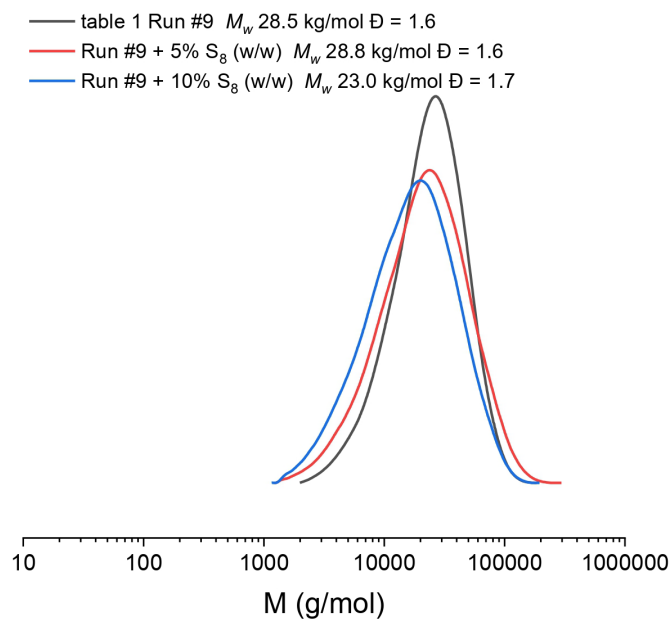


Figure S135: GPC curve of the precipitated polymer corresponding to table 1 run #9 and comparison with 2 batches of the same polymer, one after addition of 5%  $\text{S}_8$  (w/w) and the other after addition of 10%  $\text{S}_8$  (w/w).

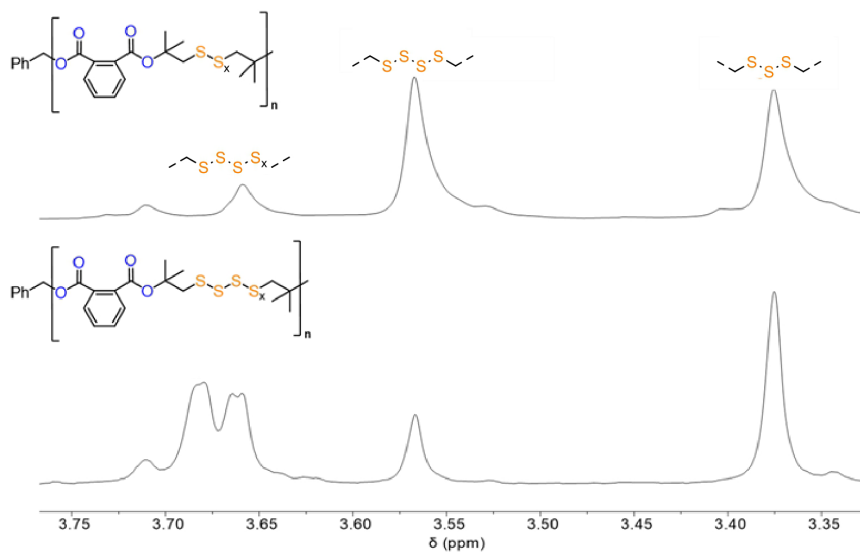


Figure S136: <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to ESI table 1 run #15 (top) and the same polymer after insertion of S<sub>8</sub> (10% w/w) (bottom), zoomed in into the polysulfide region.

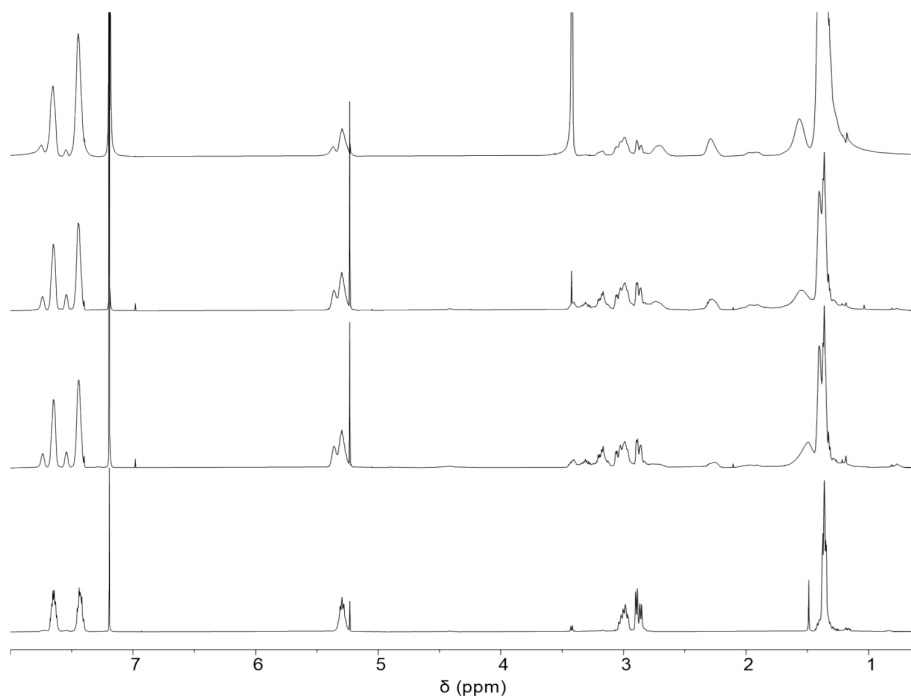


Figure S137: <sup>1</sup>H-NMR spectra (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymers from the lipoic acid insertion experiment. Respectively from bottom to top: linear polymer from table 1 run #9, 2:1 (weight ratio in starting mixture) pol:LA, 1:1 pol:LA, 1:2 pol:LA.

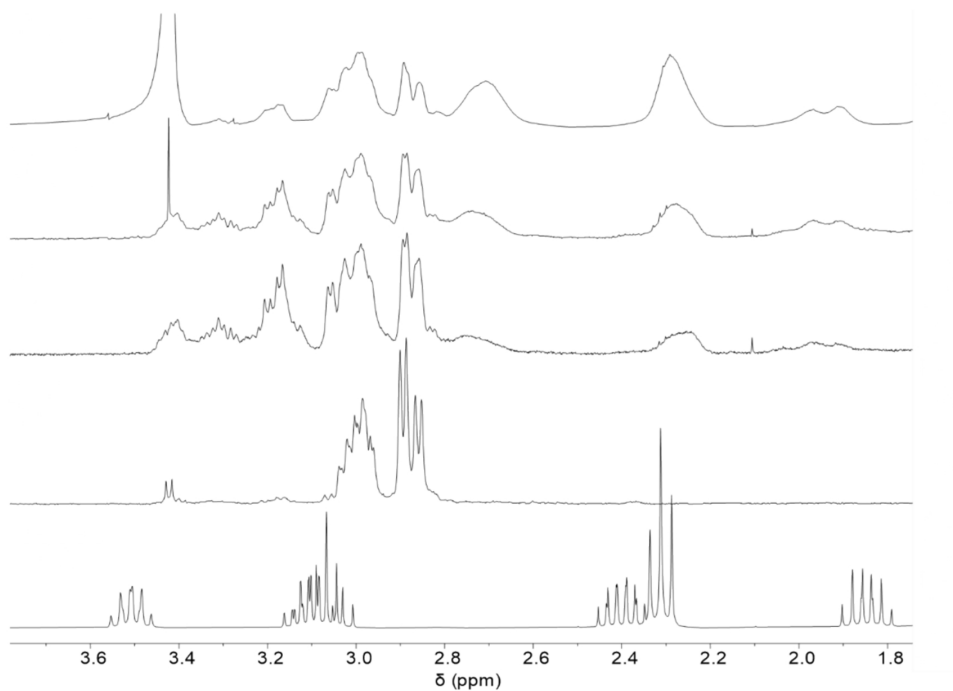


Figure S138:  $^1\text{H}$ -NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymers from the lipoic acid insertion experiment. Zoomed in into the polysulfide region. Respectively from bottom to top:  $\alpha$ -lipoic acid, linear polymer from table 1 run #9, 2:1 (weight ratio in starting mixture) pol:LA, 1:1 pol:LA, 1:2 pol:LA.

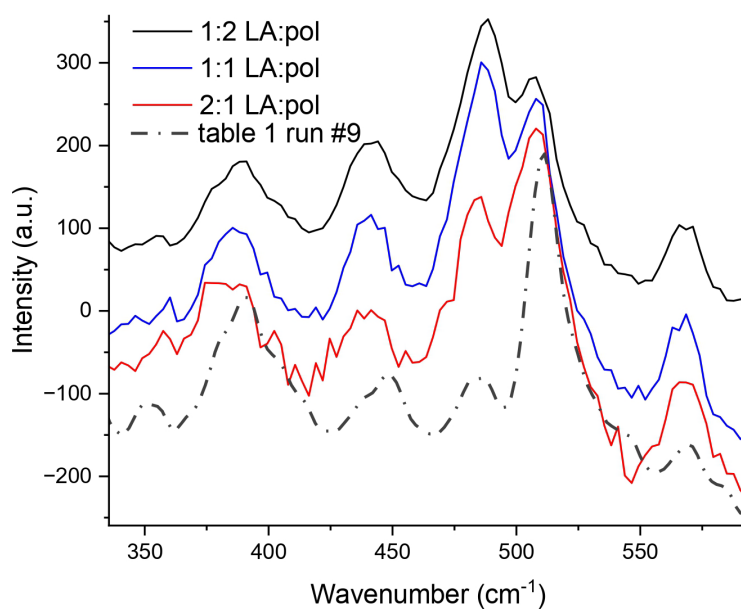


Figure S139: Zoom into the  $\text{C-S}_x\text{-C}$  stretching vibrations of the Raman spectrum of the polymer corresponding to table 1 run # 9 after the insertion of different amount of lipoic acid.



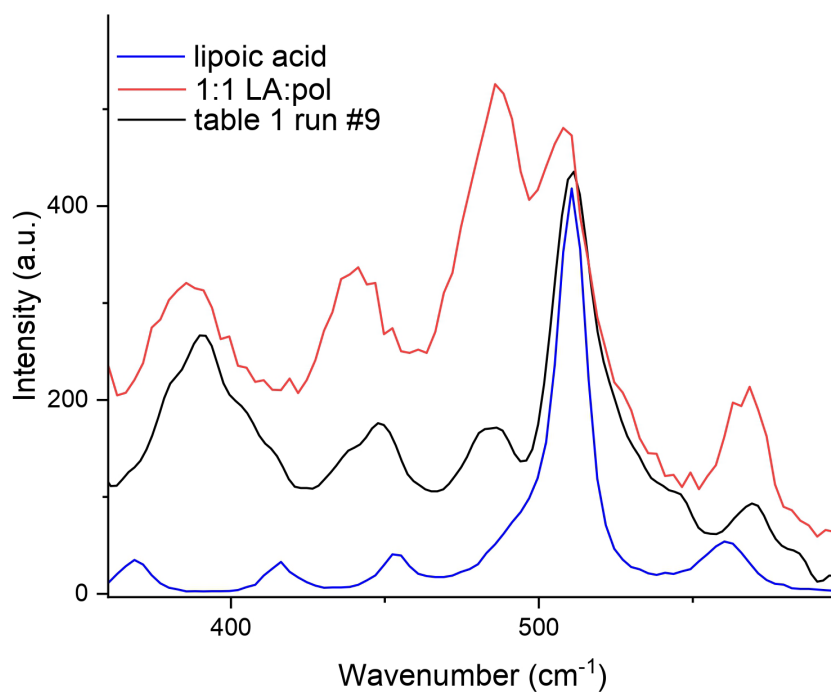


Figure S140: Zoom into the C-S<sub>x</sub>-C stretching vibrations of the Raman spectrum of the polymer corresponding to table 1 run # 9, lipoic acid and the 1:1 mixture after insertion.

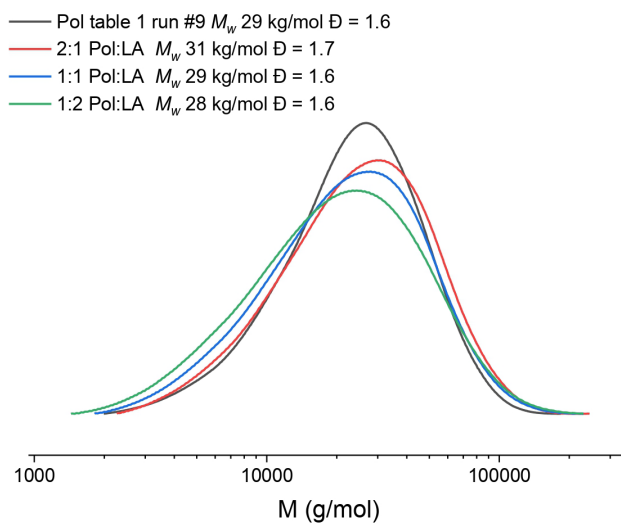


Figure S141: GPC curve of the precipitated polymer corresponding to table 1 run #9 and the polymers obtained from the lipoic acid insertion.

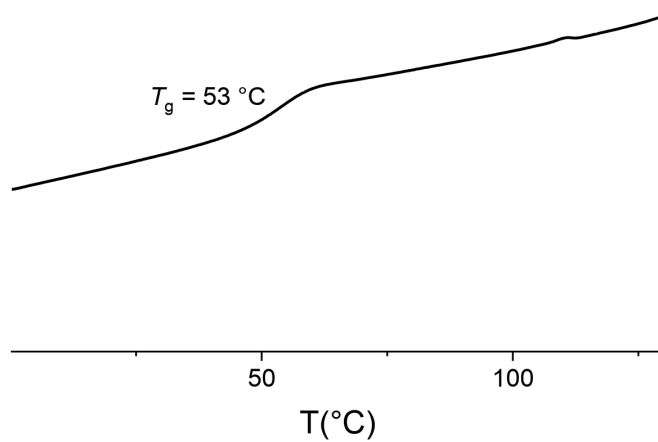


Figure S142: DSC 2<sup>nd</sup> heating curve of the imine cross-linked polymer after lipoic acid insertion.

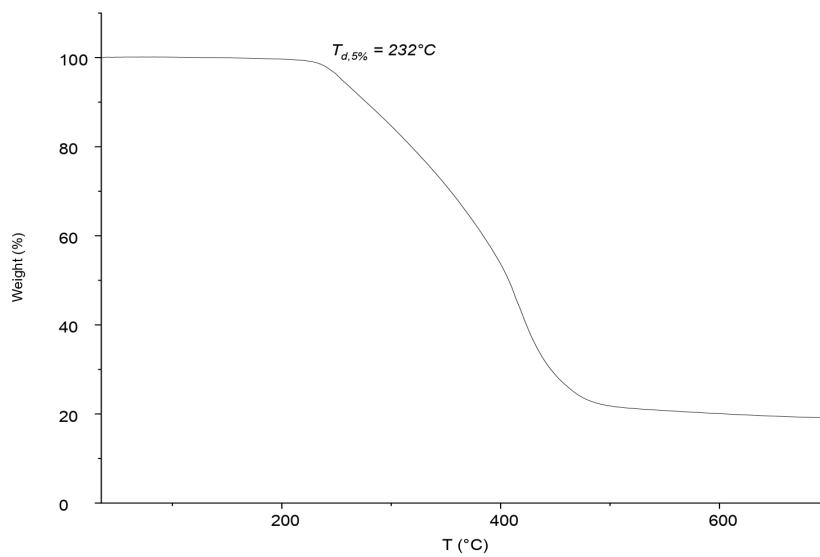


Figure S143: TGA data of the imine cross-linked polymer after lipoic acid insertion.

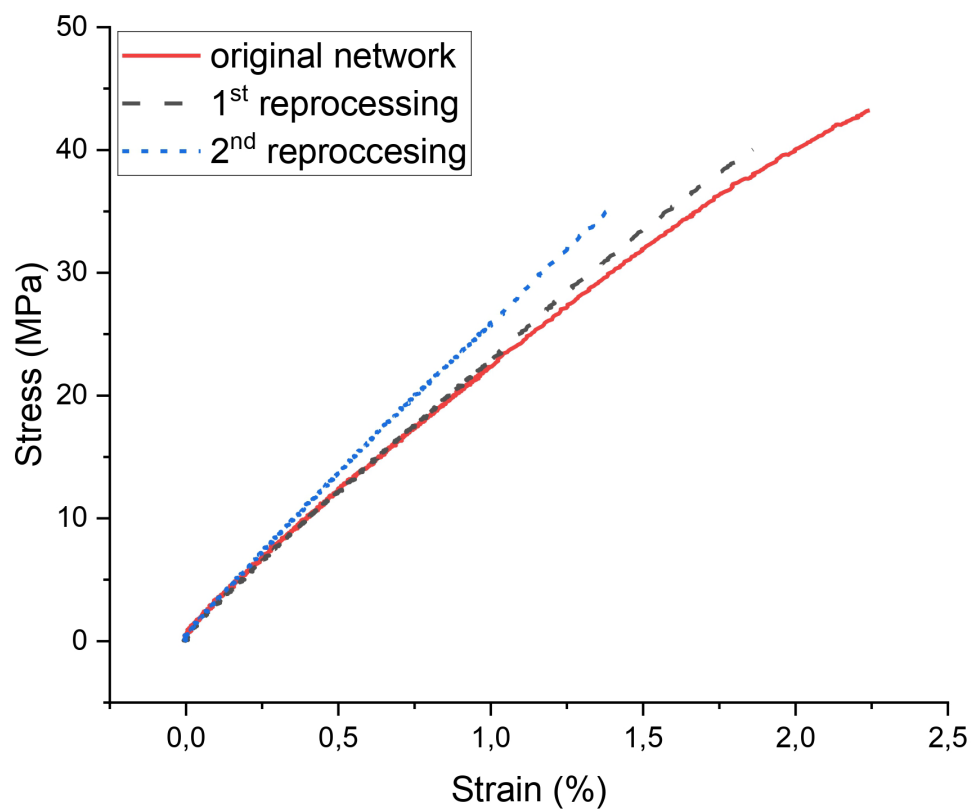


Figure S144: Evaluation of mechanical properties of the imine cross-linked material after reprocessing.

|                  | $E_y$ [Gpa]       | $\sigma$ [Mpa]   | $\epsilon$ [%]  |
|------------------|-------------------|------------------|-----------------|
| Virgin material  | $2.337 \pm 0.096$ | $49.93 \pm 4.6$  | $2.73 \pm 0.34$ |
| 1st reprocessing | $2.450 \pm 0.113$ | $43.98 \pm 10.6$ | $2.12 \pm 0.83$ |
| 2nd reprocessing | $2.521 \pm 0.105$ | $30.41 \pm 7.1$  | $1.31 \pm 0.24$ |

Table S2: Results from the tensile test strength of dog bones cut from cross linked networks. Average values and associated errors are calculated from 3 samples.



Figure S145: Before and after reprocessing for 1 h at 130°C.

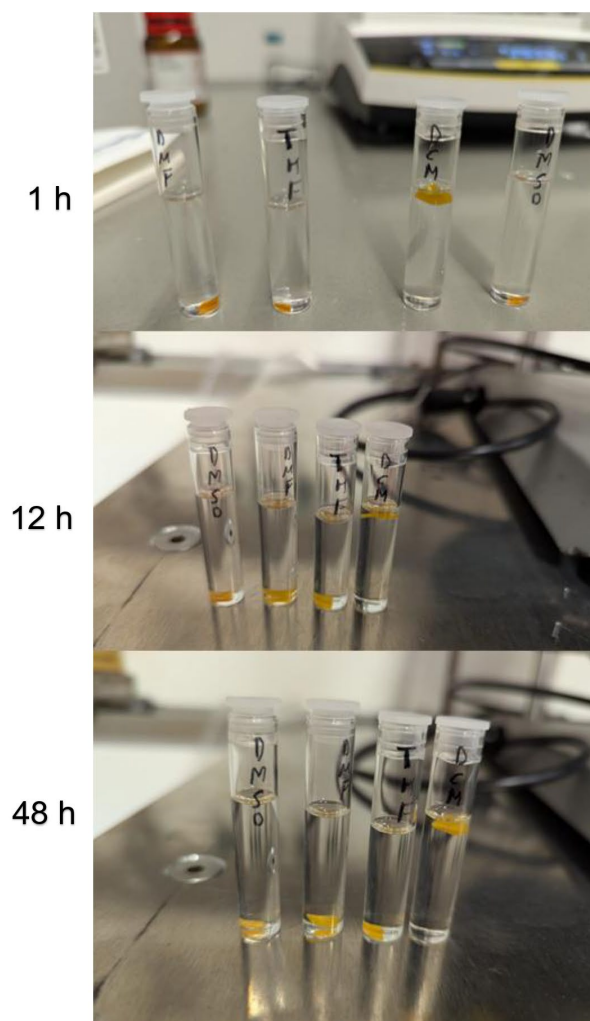


Figure S146: Solubility test on the imine cross-linked material.

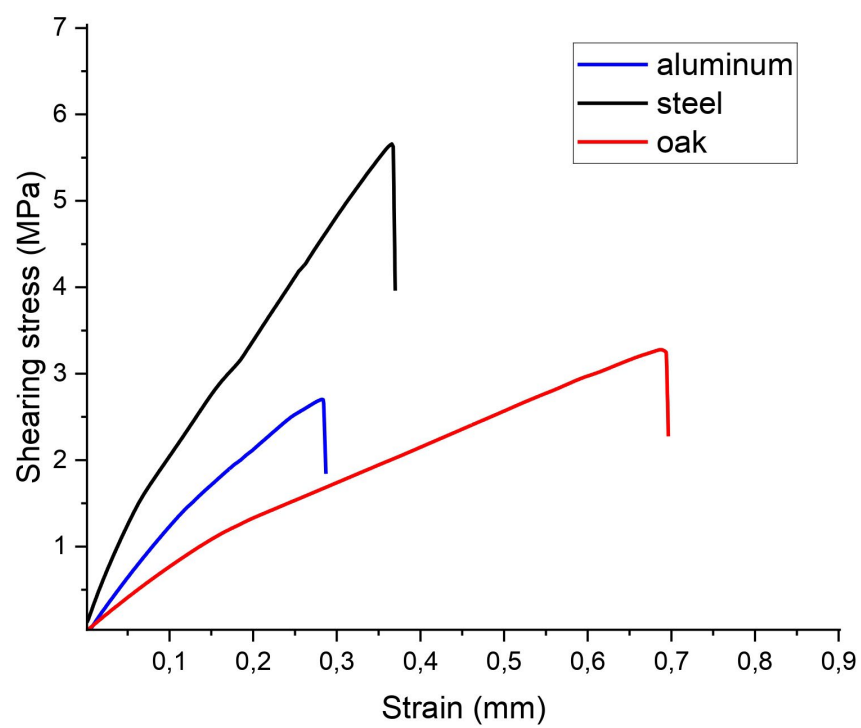


Figure S147: Example lap shear test on different substrates bonded with the imine cross-linked material.

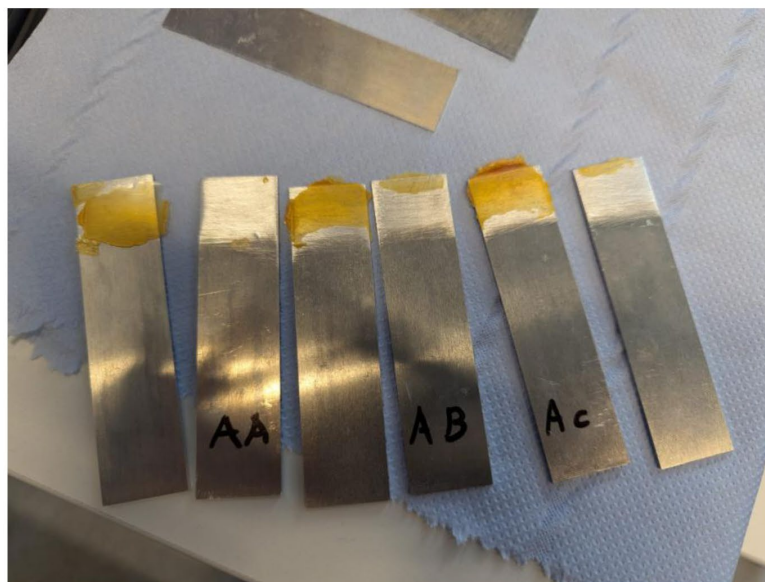


Figure S148: Aluminum plates after lap shear measurement, the almost complete detachment from one of the two plates suggests an adhesive type of failure.

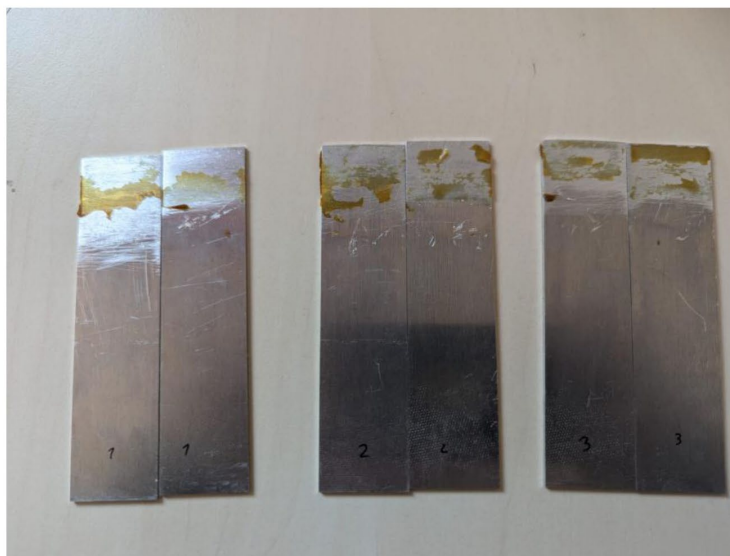


Figure S149: Aluminum plates after lap shear measurement with the lipic acid functionalized material. The high presence of rupture points within the materials suggests a mostly cohesive failure type.

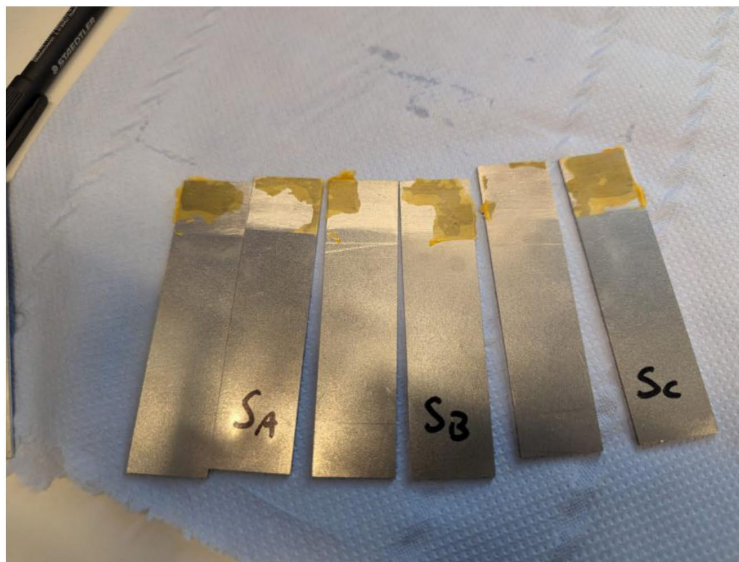


Figure S150: Steel plates after lap shear measurement, the almost complete detachment from one of the two plates suggests an adhesive type of failure but also some degree of cohesive failure can't be excluded.



Figure S151: Wood (oak) plate after lap shear measurement, the chunks of wood that remain attached to the polymer suggest a structural type of failure.

|          | Steel  | Steel reprocessed | Reference epoxy glue - steel | Aluminum | Aluminum + lipoic acid | Reference epoxy glue - aluminum |
|----------|--------|-------------------|------------------------------|----------|------------------------|---------------------------------|
| average  | 5.42   | 6.58              | 0.34                         | 2.79     | 5.55                   | 0.83                            |
| St. dev. | 1.1829 | 1.103             | 0.162                        | 0.774    | 0.297                  | 0.498                           |

Table S3: Averaged values and standard deviation (three runs) of lap shear tests on different substrates.

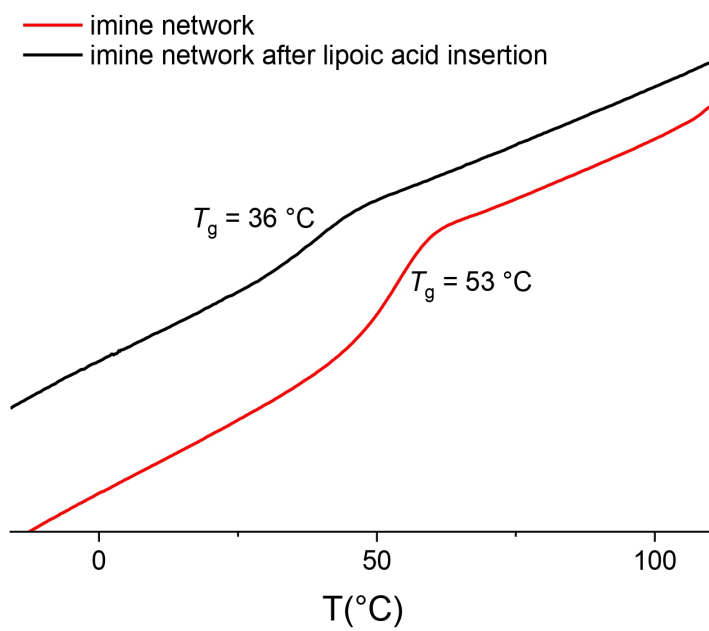


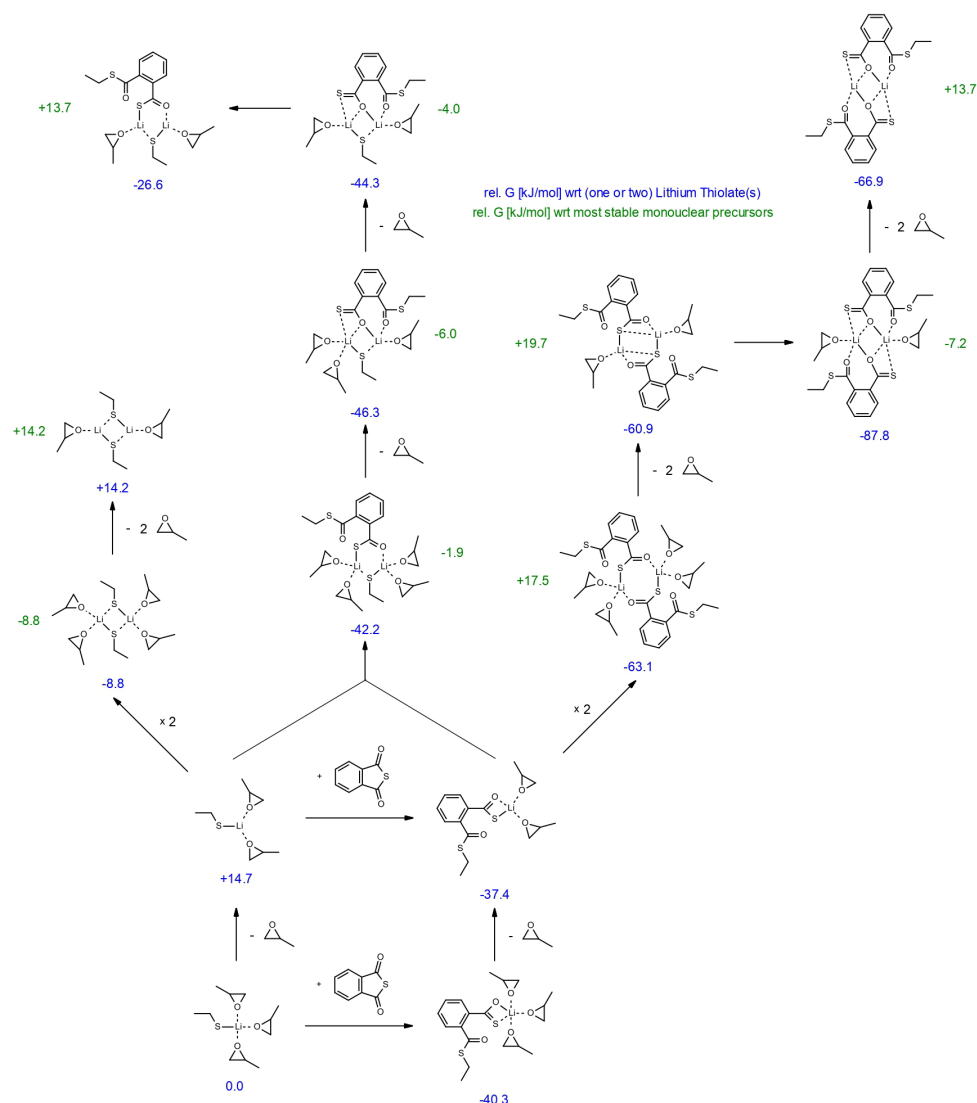
Figure S152: DSC 2<sup>nd</sup> heating curve of the imine cross-linked polymer before after lipoic acid insertion.

#### Section S6: DFT calculations

|                         |                                                               |
|-------------------------|---------------------------------------------------------------|
| DFT:                    | M06-2X/def2-TZVPD   TPSSH/def-TZVP/COSMO( $\epsilon=\infty$ ) |
| Solvation:              | COSMO-RS (parameters: BP_TZVPD_FINE_C30_1801.ctd)             |
| Solvent:                | 5:1 mixture of PO and PTA                                     |
| Temperature:            | 30°C                                                          |
| Reference state:        | $x=1$ for all species                                         |
| Dimerization threshold: | -15.0 kJ/mol                                                  |
| "reaction"-call:        | -qvib -ct_version 18                                          |

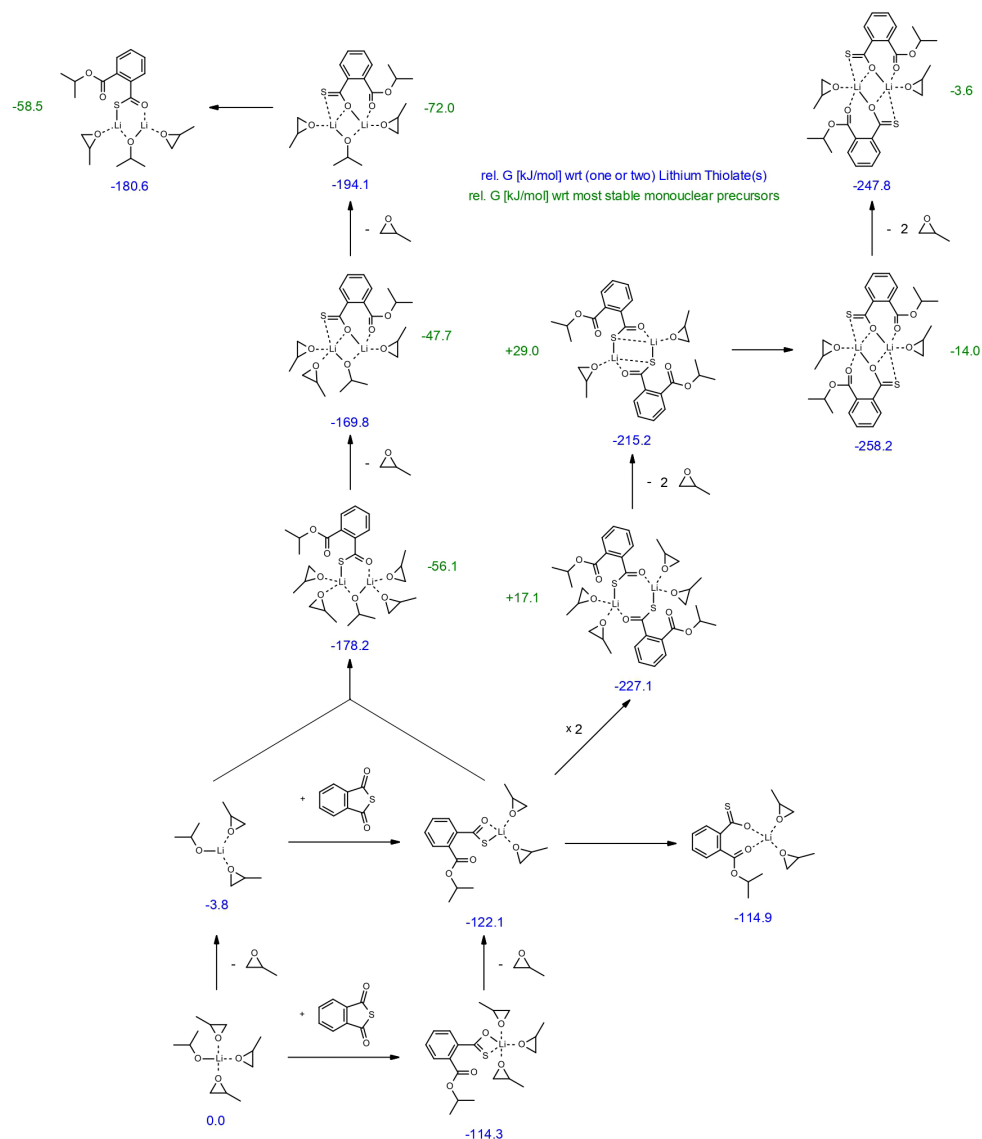
Primary Thiolate Addition to PTA (in the Absence of S<sub>8</sub>)





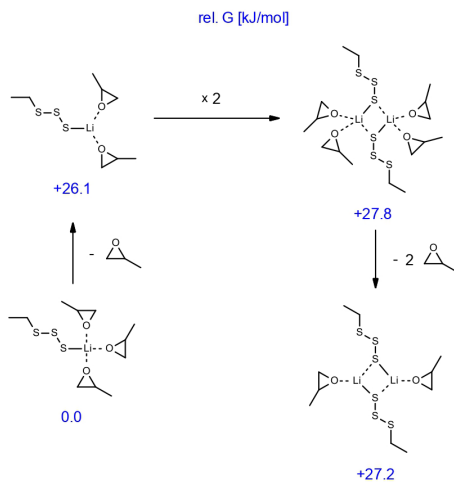
Thiocarboxylate formation by addition of thiolates to PTA (yielding at the same time a thioester linkage) is significantly exergonic. The addition reaction is not expected to exhibit huge activation barriers, PTA being an activated carbonyl compound. Thus, the resting state of the catalytic cycle in copolymerization of PO and PTA is expected to be the thiocarboxylate. With an only weakly exergonic dimerization, the resting state would be a dinuclear complex at the hypothetical reference state of  $x=1$  but is the mononuclear complex at all realistic catalyst concentrations ( $x \sim 0.001$ ).

Secondary Alkoxide Addition to PTA (in the Presence of  $S_8$ ) – Assuming a Thiocarboxylate Resting State



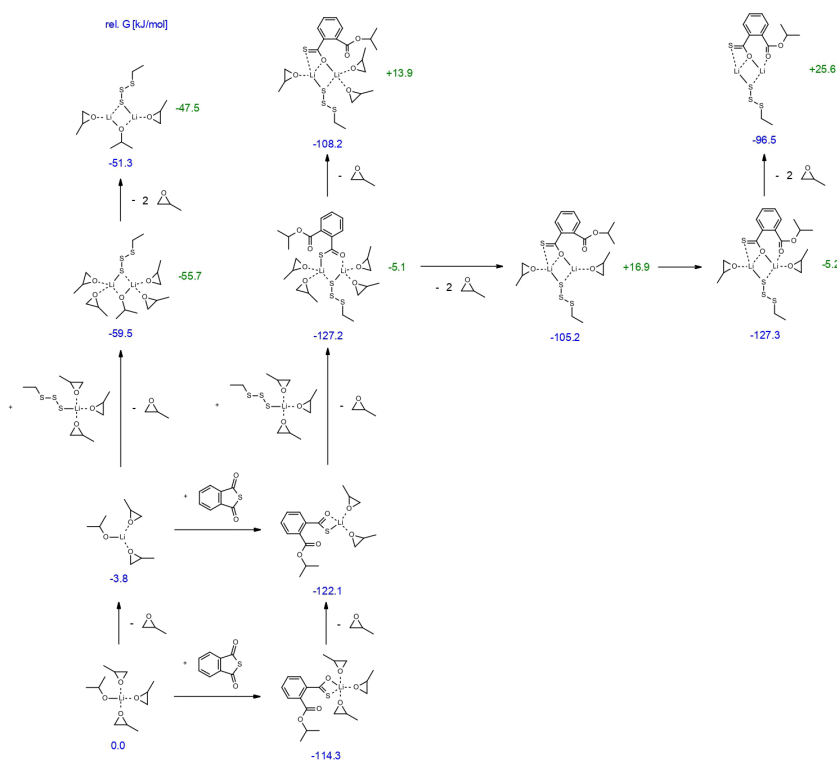
Thiocarboxylate formation by addition of alkoxides to PTA (yielding at the same time an ester linkage) is highly exergonic. The ester linkage is preferred by around 85 kJ/mol over the thioester linkage. Dimerization is also here not strongly exergonic (but more exergonic than in the above case), the resting state would be a dinuclear complex at the hypothetical reference state of  $x=1$  and will be most probably a mixture of mono- and dinuclear complexes at realistic catalyst concentrations (at 30°C, a  $\Delta G$  of -16.9 kJ would correspond to an equilibrium constant  $K=1000$ ). Thus, also here for the sake of simplicity mononuclear resting states were assumed.

### Trithiolate Speciation



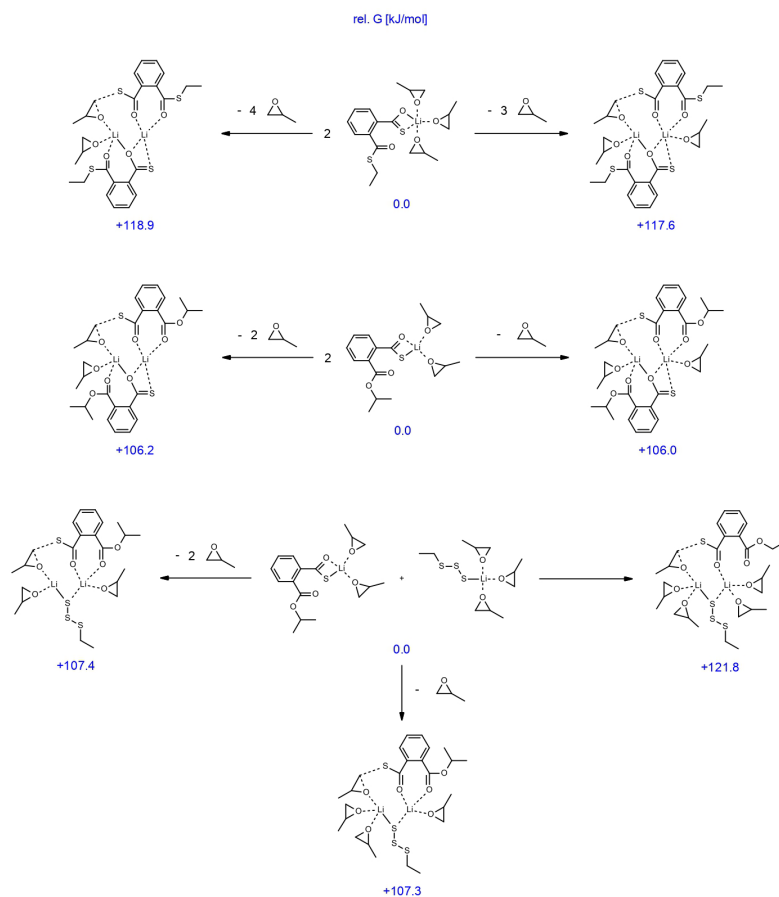
At the trithiolate stage, a mononuclear species with three PO ligands is clearly preferred.

### Secondary Alkoxide Addition to PTA (in the Presence of $S_8$ ) – Assuming a Trithiolate Resting State



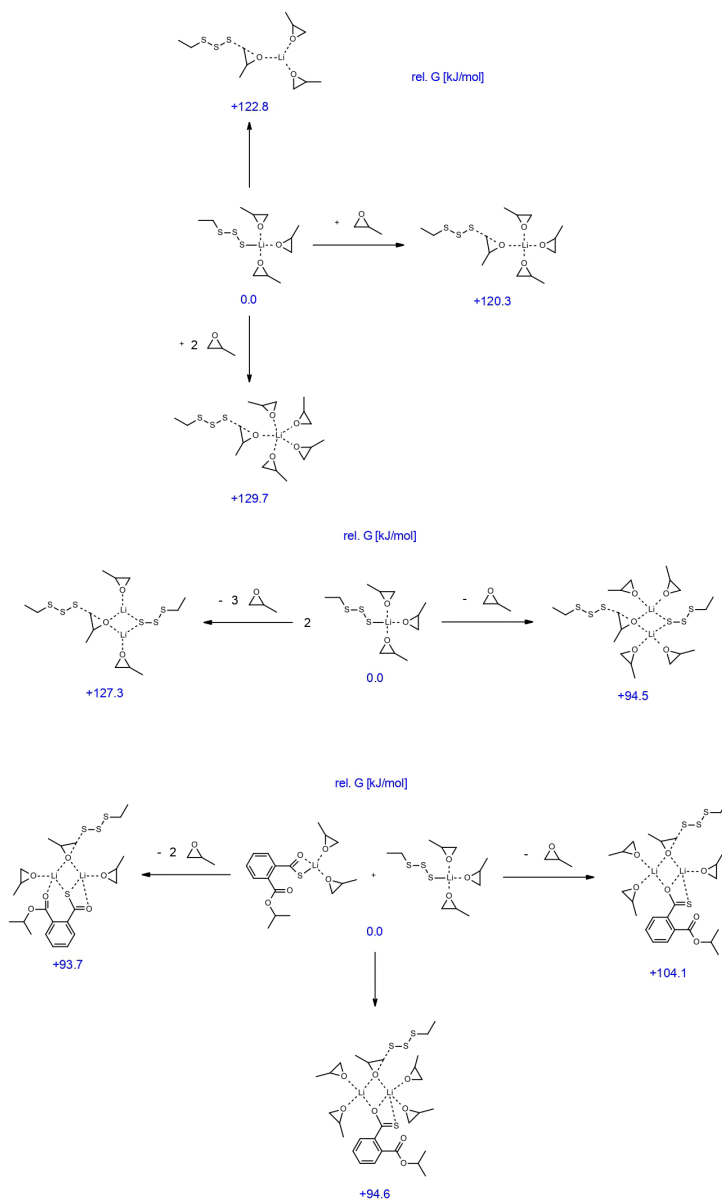
In case of trithiolate as counter ion to form dimeric species, there is a higher preference for mononuclear species than in case of thiocarboxylates, which can be explained by the weaker electron donating ability of trithiolate. However, the general trends are similar as above.

## PO Ring Opening by Thiocarboxylates Starting from Potential Resting States



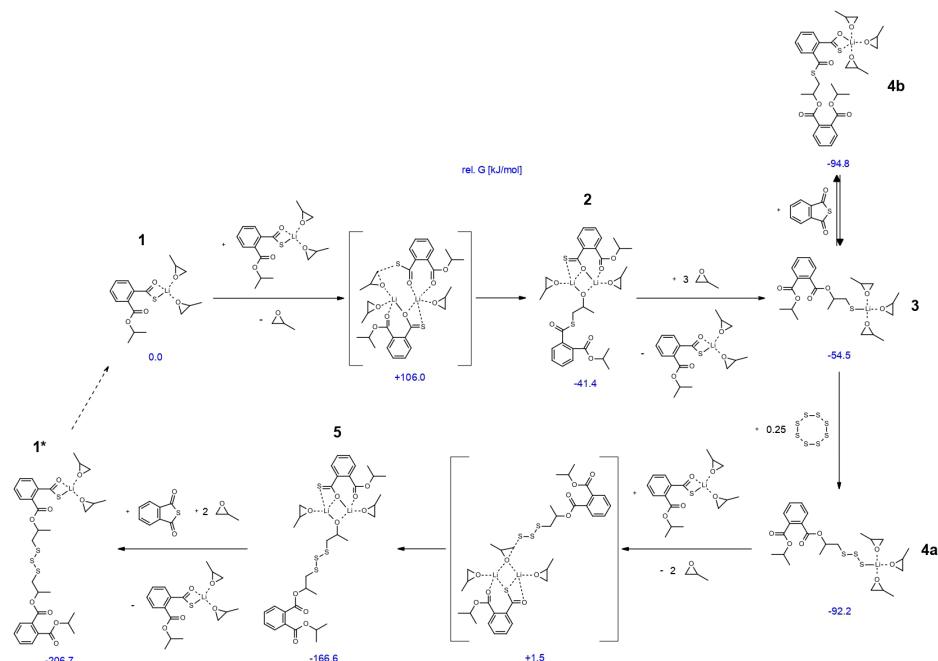
In case of thiocarboxylates with an ortho-ester group, the lowest barrier for PO ring opening is 106.0 kJ/mol. The barrier in case of thiocarboxylates with an ortho-thioester group is with 117.6 kJ/mol significantly higher.

## PO Ring Opening by Trithiolates Starting from Potential Resting States



The lowest barriers for PO ring opening are obtained – counter ion independent – via zwitterionic transition states and amount to less than 95 kJ/mol. Thus, PO ring opening by trithiolate is faster than by thiocarboxylates, which leads to the conclusion that the systems exhibits a thiocarboxylate resting state.

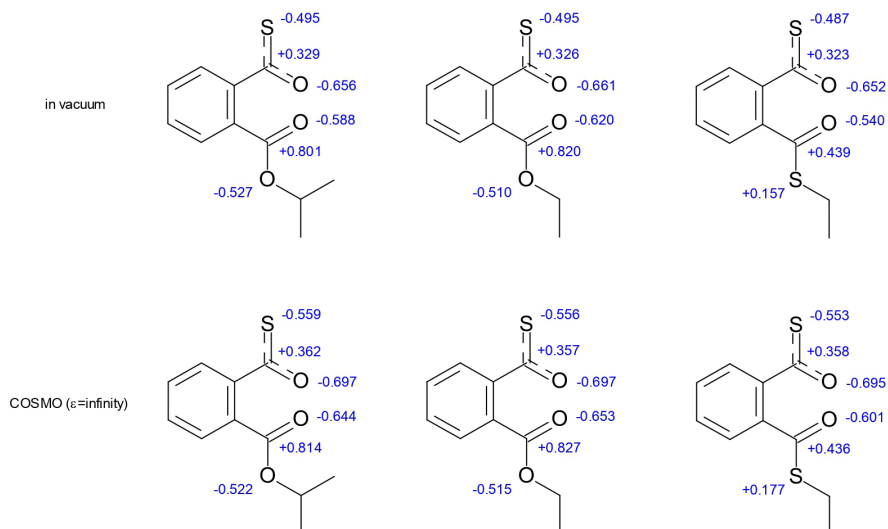
#### Catalytic Cycle



From the resting state **1**, the turnover limiting PO ring opening via a dinuclear transition state yields the preferentially dimeric alkoxide **2**. From previous studies it has been shown, that this species can easily undergo an S/O exchange at the anionic chain end via intermediary cyclization with barriers much lower than for any PO ring opening reaction. In combination with the fact that this rearrangement is exergonic, this means that further reactivity options have to be considered starting from thiolate **3**. One option is addition to PTA, another is reaction with elemental sulfur. From previous studies, both reactions are known to exhibit rather low activation barriers. For the example of a trithiolate product (as an example for several other oligosulfide species), both reactions to **4b** and **4a** are comparably exergonic. The experimental observation that a from thioester chain end (obtained by reaction of a thiolate with PTA) a release of PTA in the presence of sulfur is possible should therefore be a consequence of (a) the respective concentrations and (b) the fact that there is not only the trithiolate but other oligosulfide species in an equilibrium which also means a statistic preference. For the polymer sequence, **4b** represents a dead end, anyway, as the oligosulfides available in the equilibrium with it undergo subsequent PO ring opening much more efficiently. The latter reaction takes place via a zwitterionic mechanism, as the oligosulfides coordinate less strongly to Li<sup>+</sup> and leads to **5**, which is predicted to be a dimer like **2**. Unlike **2**, cannot undergo any rearrangement, thus the alkoxide can practically only perform an addition to PTA, which then concludes the catalytic cycle (**1\***); also this step has already been studied before by us and should proceed easily.

#### Ligand Comparison

NBO population analysis at the M06-2X/def2-TZVPD level. All species are monoanionic.



Whereas the nature of the alkyl group does not have a big influence on the partial charge at any potential donor atom, ester and thioester differ significantly: The donating ability of the carbonyl O is much higher in case of the ester than in case of the thioester.

## Section S7: References

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# Sulfur-containing polyesters from thioanhydride/CS<sub>2</sub>/epoxide ring-opening terpolymerisation: monomer scope and gold-nanoparticle functionalisation<sup>☆</sup>

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## ABSTRACT

Sulfur-containing polymers are receiving increasing attention due to their unique material and chemical properties, yet access to functional variants remains limited. To address this challenge, the ring-opening terpolymerisation (ROTERP) of phthalic thioanhydride (PTA), carbon disulfide (CS<sub>2</sub>), and a range of substituted epoxides was investigated. Polymerisation of linear, branched, aromatic, fluorinated, ether-functionalized, and multi-functional epoxides was achieved, thus providing access to a versatile range of sulfur-rich polymers bearing trithiocarbonate functionalities. Most systems exhibited moderate to high sequence selectivity for an alternating poly(ester-alt-ester-alt-trithiocarbonate) terpolymer structure, with some incorporation of polymer links from the competing ring-opening copolymerisation (ROCOP). The materials demonstrated moderate thermal stability under nitrogen (T<sub>d,5%</sub> up to 314 °C) and tunable glass transition temperatures (T<sub>g</sub> ranging from −20 to 163 °C). The trithiocarbonate groups incorporated along the main chain were employed for grafting the polymer chains to gold nanoparticle surfaces, yielding colloidal stable agglomerates. Furthermore, aldehyde-bearing polymers enabled attachment of organic moieties to the polymer grafted-to the nanoparticles via imine condensation, which could be selectively released under acidic conditions. Our study demonstrates the power of ROTERP as a synthetic platform to access a broad catalogue of functional sulfur-containing polymers and nanomaterials from readily available epoxides.

## 1. Introduction

Sulfur-containing polymers offer distinct properties compared to their all-oxygen analogues [1–7]. These include the ability to coordinate metals, enhanced semi-crystallinity, improved depolymerisability, and superior optical properties. Following early synthetic efforts via polycondensation reactions, various methodologies have recently emerged that offer improved synthetic control. Among these, ring-opening polymerization (ROP) of heterocycles — such as thiolactones, thioesters, and thiiranes — yields homopolymers, including polythioesters, polythiocarbonates, and polythioethers (see Fig. 1(a)) [8–13]. In some cases, the ROP of three- or four-membered heterocycles can be coupled with the insertion of heteroallenes or cyclic anhydrides to generate alternating copolymers, in a process known as ring-opening copolymerization (ROCOP). Sulfur-containing examples include carbon disulfide/epoxide ROCOP to form poly(thiocarbonates) and cyclic

thioanhydride/epoxide ROCOP to produce poly(ester-alt-thioester)s (see Fig. 1(b)) [14–30]. Recently, we demonstrated alternating ring-opening terpolymerization (ROTERP) of ternary monomer mixtures comprising phthalic thioanhydride (PTA), CS<sub>2</sub>, and propylene oxide (PO). Using a simple lithium catalyst—such as lithium benzyloxide (LiOBn)—this process selectively forms poly(ester-alt-ester-alt-trithiocarbonates) with up to 98 % selectivity, rather than the competing poly(ester-alt-thioester) formation from PTA/PO ROCOP (see Fig. 1(c)) [31–33]. However, particularly at lower catalyst loadings, PTA/PO ROCOP is also observed, leading to a more irregular microstructure [34–38]. The poly(ester-alt-ester-alt-trithiocarbonate) links exhibit an unusual regio selectivity, with ester groups adjacent to tertiary carbon centres and trithiocarbonates adjacent to secondary carbon centres [39]. Despite this, the epoxide scope remained limited, and no further applications of these polymers had been investigated. Building on this, the motivation of this work was twofold: Firstly, we identified a series of

<sup>☆</sup> This article is part of a special issue entitled: ‘P- and S-containing polymers’ published in European Polymer Journal.

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other monomer combinations that undergo ROTERP [40–42]. We hypothesized that PTA/CS<sub>2</sub>/epoxide ROTERP should, in principle, provide straightforward access to a wide range of sulfur-containing polymers, leveraging the many epoxides developed for epoxide ROP [43–45]. In testing this hypothesis, we demonstrate that a broad variety of polymer structures—with tuneable thermal properties and functionalities—are easily accessible via ROTERP. Secondly, we aimed to make use of the dual functionality of trithiocarbonate moieties incorporated in the polymer backbone on one hand and additional functional groups that are introduced with the oxirane monomer on the other for the formation of hybrid nanomaterials. We hypothesized that the trithiocarbonate groups enable straightforward anchorage of the synthesized polymer molecules to gold nanoparticle surfaces (Fig. 1(d)), while aldehyde groups in the oxirane monomer would offer the possibility for dynamic covalent chemistry, enabling the controlled release of a cargo from the nanoparticulate support. Acid-promoted release of an organic dye from the colloidal gold species and concomitant restoration of its fluorescence served as a model scenario to test this possibility in this promising type of hybrid nanomaterials proving that ROTERP polymers can be applied in the functionalization of gold nanoparticles.

## 2. Results and discussion

To investigate whether PTA/CS<sub>2</sub>/epoxide ROTERP is compatible with different epoxides and how sequence selectivity and polymer properties are affected, we employed a range of epoxides (see Fig. 2) under unified ROTERP conditions. For baseline comparison, butylene

oxide (BO) and propylene oxide (PO)—used in our previous study—were also examined, albeit under different loading than previously investigated [31].

Performing CS<sub>2</sub>/PTA/BO ROTERP (Table 1, run #1) using 1 eq. lithium benzyloxide (LiOBn, generated in situ from Li[N(SiMe<sub>3</sub>)<sub>2</sub>] and BnOH), 500 eq. BO, 200 eq. PTA, and 500 eq. CS<sub>2</sub> at 80 °C for 2 h resulted in 70 % PTA conversion. The polymer was isolated via precipitation from DCM/MeOH, and its microstructure, apparent molar mass and molar-mass distribution, and the thermal properties were evaluated (Fig. 3). The <sup>1</sup>H NMR spectrum (Fig. 3(a)) confirms that the polymeric product consists primarily of poly(ester-*alt*-ester-*alt*-trithiocarbonate) links from the ROTERP process. These are indicated by two aryl CH resonances from a symmetrically substituted aromatic unit at 7.60 and 7.45 ppm, connected to the tertiary CH at 5.27 ppm; the CH<sub>2</sub> group appears between 3.60 and 3.85 ppm. The CH resonance correlates to quaternary aryl ester signals at 133 ppm in the <sup>1</sup>H–<sup>13</sup>C HMBC, while the CH<sub>2</sub> resonances correlate to trithiocarbonate groups (see ESI Figure S 8). Additionally, the <sup>1</sup>H NMR spectrum reveals the presence of thioester groups from co-occurring ROCOP, visible as minor aryl signals from unsymmetrically substituted aromatic units and CH<sub>2</sub> resonances at 3.01 ppm, which correlate to quaternary thioester resonances at 191 ppm in the <sup>1</sup>H–<sup>13</sup>C HMBC spectrum. The sequence selectivity of the ROTERP process versus co-occurring ROCOP, as determined per <sup>1</sup>H NMR (see ESI Section S2), is 86 %. The estimated uncertainty of these values is ±5 % based on repeated integrations of independent spectra and signal overlap, as common for NMR methods.

Fig. 4(a) illustrates the proposed propagation mechanism for

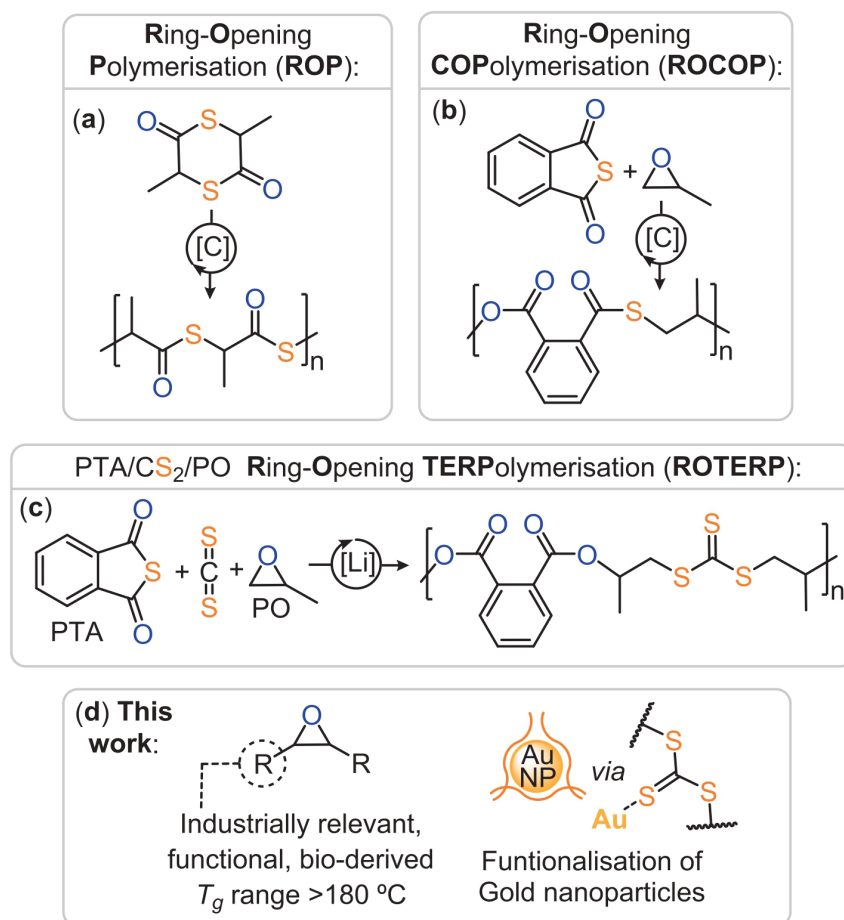


Fig. 1. Comparison of sulfur containing (a) ROP, (b) ROCOP and (c) ROTERP. (d) Outline of the current study.

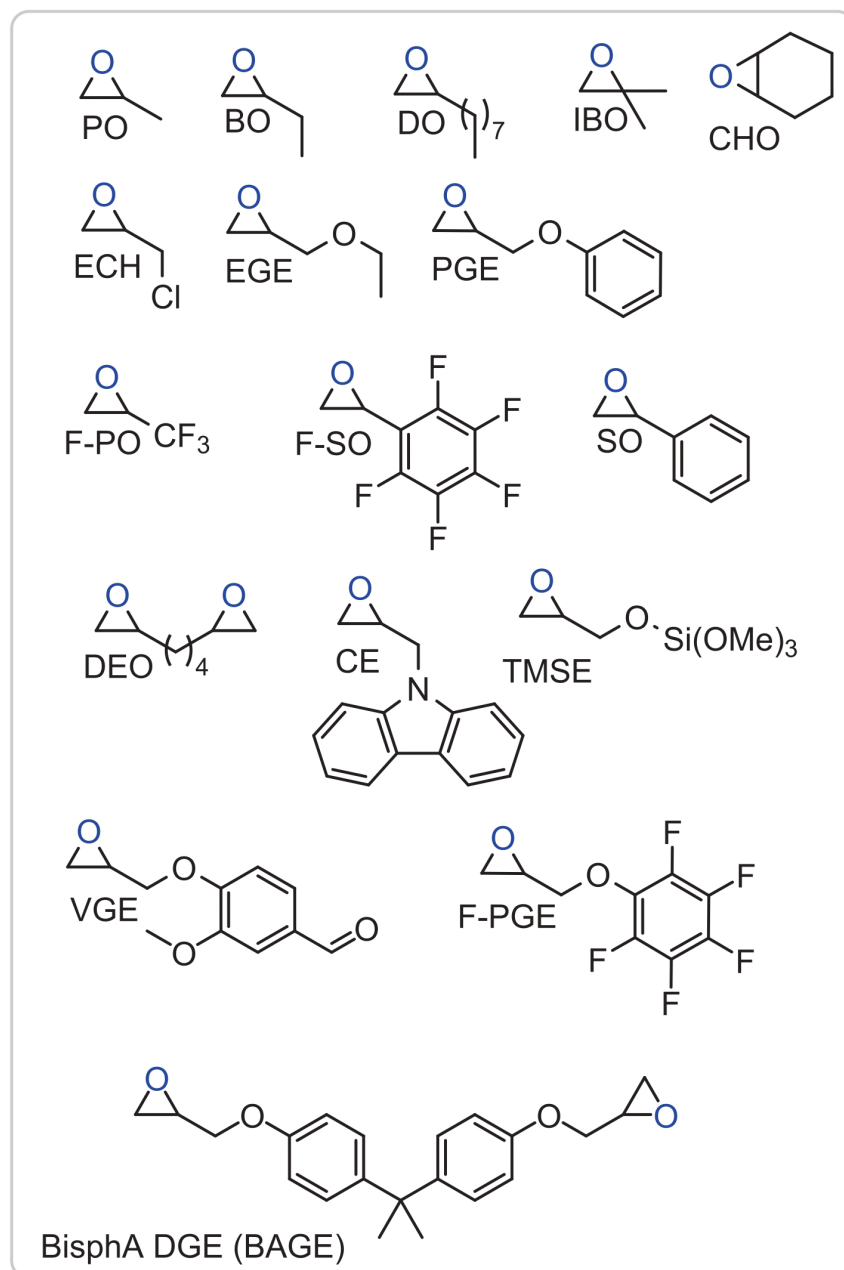


Fig. 2. Epoxides employed in this study.

ROTERP, while Fig. 4(b) shows the competing ROCOP pathway. Minor amounts (2 % relative to epoxide consumption) of cyclic dithiocarbonate by-products were also detected, consistent with the side pathway illustrated in Fig. 4(c).

Gel permeation chromatography (GPC) analysis of the polymer reveals an apparent weight-averaged molar mass of  $M_w = 58$  kg/mol (polystyrene calibration) and a polydispersity of  $D = 1.8$ . This polydispersity is well above the expected value for a controlled chain-growth polymerization, and accordingly, the molecular weight distribution is unsymmetric. This suggests the occurrence of side reactions such as chain transfer, chain-end coupling, and transesterification, which are commonly observed during sulfur-containing ROCOP [14]. Previous investigations on PTA/CS<sub>2</sub>/epoxide ROTERP revealed that the polydispersities remained comparatively broad regardless of concentration,

catalyst loading, or temperature [31]. Although the molecular weight increased linearly with conversion, resulting in some weight control, the polydispersity broadened with conversion. For a detailed mechanistic analysis, the reader is referred to our original contributions [31–33].

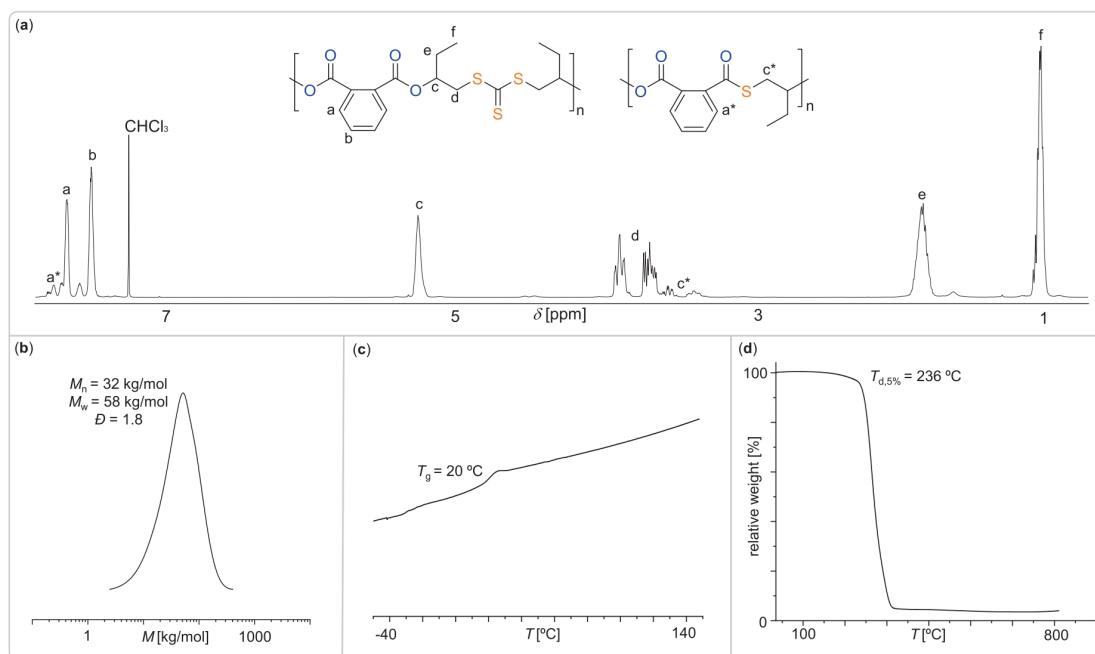
Differential scanning calorimetry (DSC) shows the material is amorphous, with a glass transition temperature ( $T_g$ ) of 20 °C. Thermogravimetric analysis reveals a decomposition onset temperature ( $T_{d,5\%}$ ) of 236 °C. These results serve as a reference for the other epoxides investigated.

Switching to epoxides with other aliphatic chains (Table 1, runs #2 and #3) significantly affects thermal properties. Moving from PO to BO and decyl oxide (DO) leads to a decrease in  $T_g$  to 20 °C and –20 °C, respectively. As expected, sequence selectivity and molar masses (normalized to conversion) remain comparable due to the chemical

**Table 1**

Polymerizations investigated in this study.

| Run <sup>a</sup> | Epoxide           | time   | Conv. [%] <sup>b</sup> | Polymer select. [%] <sup>c</sup> | Sequence select. [%] <sup>d</sup> | $M_w$ [kg/mol] <sup>d</sup> | $D^d$ | $T_g$ [°C] <sup>e</sup> | $T_{d(5\%)}^f$ [°C] <sup>f</sup> |
|------------------|-------------------|--------|------------------------|----------------------------------|-----------------------------------|-----------------------------|-------|-------------------------|----------------------------------|
| #1               | BO                | 3 h    | 70                     | 98                               | 86                                | 58                          | 1.8   | 20                      | 236                              |
| #2               | PO                | 2 h    | 86                     | 95                               | 87                                | 80                          | 2.1   | 48                      | 230                              |
| #3               | DO                | 19 h   | 78                     | 97                               | 83                                | 64                          | 2     | −20                     | 258                              |
| #4               | IBO               | 18 h   | 82                     | 79                               | 94                                | 58                          | 1.8   | 23                      | 209                              |
| #5               | CHO               | 72 h   | 20                     | 96                               | 75                                | 7                           | 1.8   | 115                     | 233                              |
| #6               | SO <sup>g</sup>   | 336 h  | 30                     | 85                               | n. d.                             | 3                           | 1.5   | 37                      | 211                              |
| #7               | PGE               | 20 h   | 99                     | 79                               | 84                                | 25                          | 1.9   | 37                      | 250                              |
| #8               | EGE               | 25 h   | 92                     | 97                               | 79                                | 26                          | 1.6   | 9                       | 241                              |
| #9               | ECH               | 15 h   | 90                     | 92                               | 91                                | 24                          | 1.9   | 54                      | 209                              |
| #10              | TMSE <sup>h</sup> | 45 min | 84                     | 89                               | 88                                | n. d.                       | n. d. | −15                     | 255                              |
| #11              | VGE               | 22 h   | 82                     | 92                               | 53                                | 11                          | 1.7   | 81                      | 256                              |
| #12              | CE <sup>g</sup>   | 16 h   | 75                     | 70                               | n. d.                             | 35                          | 1.3   | 136                     | 269                              |
| #13              | F-PO              | 20 h   | 88                     | 56                               | 91                                | 25                          | 1.6   | 62                      | 314                              |
| #14              | F-PGE             | 5 h    | 83                     | 93                               | 87                                | 43                          | 1.2   | 40                      | 255                              |
| #15              | F-SO <sup>g</sup> | 384 h  | 40                     | 90                               | n. d.                             | 7                           | 1.3   | 90                      | 249                              |

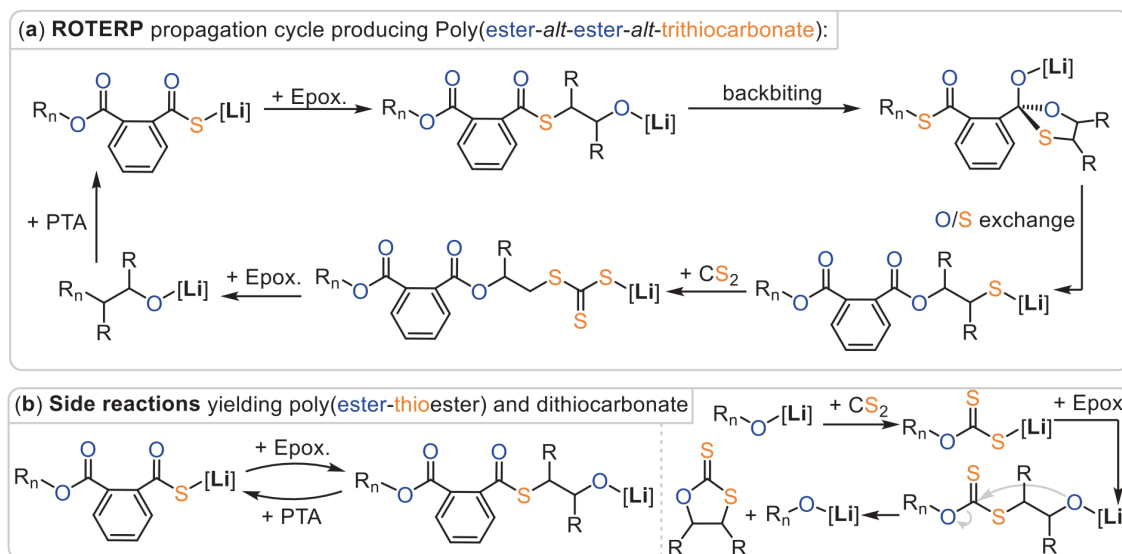
<sup>a</sup> ROTERP conducted at 80 °C and with a loading of 1 eq. LiOBn: 500 eq. Epoxide: 200 eq. PTA: 500 eq. CS<sub>2</sub>.<sup>b</sup> Relative peak integrals of aromatic signals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of the crude reaction mixture corresponding to polymer resonances.<sup>c</sup> Relative peak integrals of the CH signals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of the crude reaction mixture corresponding to polymer resonances.<sup>d</sup> Relative peak integrals of the CH<sub>2</sub> signals in the normalised <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of polymer resonances corresponding to ROTERP links. <sup>d</sup>Determined by GPC (gel permeation chromatography) measurements conducted in THF on a system calibrated using narrowly dispersed polystyrene standards.<sup>e</sup> Determined by differential scanning calorimetry (DSC) from a second heating curve at 10 K/min.<sup>f</sup> Determined by thermogravimetric analysis (TGA).<sup>g</sup> Complete determination of selectivity not possible due to overlapping signals.<sup>h</sup> Cross-linking from hydrolysis of −Si(OMe)<sub>3</sub> groups preventing GPC.**Fig. 3.** (a) <sup>1</sup>H NMR (b) GPC, (c) DSC and (d) TGA data of precipitated polymer corresponding to table 1 run #1.

similarity of the monomers.

We next explored disubstituted epoxides, focusing on 1,2-dimethyl epoxide (isobutylene oxide, IBO; run #4). Under analogous conditions, ROTERP yielded 82 % PTA conversion after 18 h, affording a polymer with 94 % sequence selectivity—higher than its mono-substituted counterpart, PO. According to the ROTERP mechanism (Fig. 3), this suggests that the alkoxide intermediate formed from IBO ring-opening facilitates O/S exchange via back-biting, consistent with prior reports in sulfur-containing ROCOP [17]. However, increased

formation of cyclic dithiocarbonate by-products reduced overall polymer selectivity to 79 %. GPC analysis shows  $M_w = 58$  kg/mol ( $D = 1.8$ ). As the epoxide contains no stereocenter, which could render the resulting polymer atactic, it shows a semi-crystalline behavior with a  $T_g$  of 23 °C, melting temperature  $T_m$  of 110 °C (see ESI Figure S 23), similar to recent polymers obtained from IBO, and a thermal decomposition onset at 209 °C [46].

Cyclohexene oxide (CHO, run #5) was also included in the monomer scope due to its potential to yield polymers with improved thermal



**Fig. 4.** (a) PTA/ $CS_2$ /Epoxide ROTERP propagation mechanism. During each cycle, the degree of polymerization indicated by the subscript  $n$  increases. (b) Co-occurring side reactions.

properties, owing to its bicyclic structure. Consistent with this, ROTERP with CHO gave a high  $T_g$  of 115 °C and a decomposition onset at 233 °C. However, the polymerization efficiency was notably reduced, achieving only 20 % PTA conversion after 72 h. GPC confirms the formation of shorter polymers ( $M_w = 7$  kg/mol,  $D = 1.8$ ), potentially due to a higher concentration of diol impurities—an often-encountered issue with CHO in ROCOP [47]. Attempts to obtain higher weight materials by adapting the loading failed, which implies some limitation of the ROTERP process. Sequence selectivity also dropped to 75 %, presumably due to steric hindrance from the rigid cyclohexyl ring interfering with O/S exchange via backbiting.

Next, we turned to styrene oxide (SO, entry #6), a challenging epoxide in ROCOP. Due to SO's aromatic substituent rendering the CH position more prone to nucleophilic attack, ring-opening typically occurs at both the  $CH_2$  and CH positions, resulting in a loss of regioselectivity [48]. In our case, slow polymerization occurred, reaching only 30 % PTA conversion after 14 days.  $^1H$  NMR spectroscopy confirms regio-unselective polymerization, showing multiple broad and overlapping resonances. Due to this lack of regioselectivity, structural determination of sequence selectivity wasn't possible. 2D NMR analysis confirms the formation of some ROTERP terpolymer links, with proton signals in the 3.00–3.10 ppm range correlating to trithiocarbonate groups at around 220 ppm. Nevertheless, significant thioester formation is observed in the  $^{13}C$  NMR, indicating poor sequence selectivity. GPC analysis shows a low apparent molar mass ( $M_w = 3$  kg/mol,  $D = 1.5$ ), suggesting poor polymerization control, likely due to transesterification side reactions. DSC reveals the material is amorphous with a  $T_g = 37$  °C and a decomposition onset at  $T_{d,5\%} = 211$  °C.

Phenyl glycidyl ether (PGE, run #7) achieved 99 % PTA conversion after 20 h, yielding a polymer with 79 % polymer selectivity and 84 % sequence selectivity. The polymer has an apparent  $M_w = 25$  kg/mol ( $D = 1.9$ ),  $T_g = 37$  °C, and  $T_{d,5\%} = 250$  °C. Its aliphatic analogue, ethyl glycidyl ether (EGE, run #8), improved polymer selectivity to 97 %, albeit at the cost of reduced sequence selectivity (79 %). The resulting amorphous polymer had an  $M_w = 26$  kg/mol ( $D = 1.6$ ),  $T_g = 9$  °C, and  $T_{d,5\%} = 241$  °C. These results show that glycidyl ethers—of which a wide variety of versions with functional substituents exist (see below)—are well tolerated in the ROTERP process.

Glycidyl ethers are synthesized from epichlorohydrin (ECH, run #9), an epoxide with widespread industrial relevance. ECH reached 90 %

PTA conversion after 15 h, with 92 % polymer selectivity and 91 % sequence selectivity, producing a polymer with  $M_w = 24$  kg/mol ( $D = 1.9$ ). DSC analysis tentatively supports the selectivity, showing a distinct, unbroadened  $T_g$  at 54 °C, with no additional transitions indicative of branching or cross-linking. This is somewhat surprising, as the electrophilic  $RCH_2Cl$  group in ECH and its polymers could be expected to undergo  $S_N2$  attack by the nucleophilic sulfur chain ends—an issue observed in related polymerizations [49].  $^1H$  NMR reveals minor sequence errors from co-occurring ROCOP, particularly signals between 3.55 and 3.47 ppm that correlate with a thioester carbon at 193 ppm in the HMBC. Furthermore, the presence of  $RCH_2Cl$  groups is confirmed via HSQC correlation of the  $CH_2$  resonance at 3.79 ppm with a 45 ppm signal, typical of halogen-adjacent carbons. No polymer links from side reactions of the chain end with the  $RCH_2Cl$  groups could be observed.

Next, we investigated functional glycidyl ethers, beginning with (3-glycidyloxypropyl)trimethoxysilane (TMSE, run #10), which bears silyl functionality. After 45 min, the reaction viscosity increased drastically, halting stirring. Crude  $^1H$  NMR analysis indicated 84 % PTA conversion, 89 % polymer selectivity, and 88 % sequence selectivity. The resulting material had a  $T_g = -15$  °C and  $T_{d,5\%} = 255$  °C. Moisture from ambient humidity slowly hydrolyzes the methoxy groups to silanols ( $-Si-OH$ ), which undergo further condensation to form  $-Si-O-Si-$  linkages, creating an insoluble network [50]. Consequently, GPC analysis was not conducted to avoid instrument damage. However, the opportunity for crosslinking after ROTERP was leveraged to form shape-defined sulfur-containing silicones. A freshly precipitated polymer (from acidified methanol) was cast in a cylindrical mold and left under benchtop conditions for 3 days, followed by further storage in a humidified chamber (a desiccator containing water) and subsequent drying. The result was a cylindrical and brittle object. Gel fractions in DCM and THF, excellent solvents for the parent linear polymer, are 99 % confirming crosslinking. This procedure increased the  $T_g$  from  $-15$  °C to  $-8$  °C, and  $T_{d,5\%}$  from 255 °C to 271 °C.

We then turned to vanillin glycidyl ether (VGE, run #11), synthesized from vanillin and epichlorohydrin. Although VGE is solid at room temperature, the ROTERP reaction temperature (80 °C) is above its melting point, enabling homogeneous polymerization. VGE reached 82 % PTA conversion after 22 h, producing 92 % polymer selectivity but a reduced sequence selectivity of 53 %. The  $^1H$  NMR spectrum confirms that the aldehyde group remains intact, with a  $-CHO$  proton resonance



at 9.66 ppm. Despite moderate sequence control, the polymer displays favorable thermal properties ( $T_g = 81^\circ\text{C}$ ,  $T_{d,5\%} = 256^\circ\text{C}$ ). However, its relatively low molar mass ( $M_w = 11\text{ kg/mol}$ ) suggests limited control, likely due to side reactions such as transesterification [51].

Next, we investigated a functionalized carbazole epoxide (CE, run #12). Polymerization with PTA and  $\text{CS}_2$  for 16 h gave 75 % PTA conversion and 70 % polymer selectivity. The isolated polymer had an  $M_w = 35\text{ kg/mol}$ ,  $D = 1.3$ , and exhibited an exceptional  $T_g = 163^\circ\text{C}$  ( $T_{d,5\%} = 269^\circ\text{C}$ ), which may be attributed to  $\pi$ - $\pi$  interactions between carbazole units in the solid state.

Fluorinated monomers were also tested to evaluate their impact on polymer sequence and properties, particularly since fluorination is known to enhance thermal stability [52]. However, fluorinated ROCOP polymers remain scarcely explored [53–55]. 1,1,1-Trifluoro-2,3-epoxypropane (F-PO, run #13) was employed and reached 88 % PTA conversion, with a polymer selectivity of 56 %, and a molar mass of  $M_w = 25\text{ kg/mol}$  ( $D = 1.6$ ). DSC showed a  $T_g$  of  $62^\circ\text{C}$ , while TGA recorded a  $T_{d,5\%}$  of  $314^\circ\text{C}$ —the highest thermal stability among all tested monomers. Compared to the non-fluorinated PO-based polymer, this reflects an increase of over  $80^\circ\text{C}$  in thermal stability, highlighting the substantial effect of fluorination while maintaining catalytic performance and sequence selectivity. Phenylglycidylether with a  $\text{C}_6\text{F}_5$  moiety (2,3-epoxypropyl pentafluorophenyl ether, F-PGE, run #14) reached 83 % PTA conversion after 5 h, with 93 % polymer selectivity and 87 % sequence selectivity. GPC analysis revealed a high  $M_w$  of  $43\text{ kg/mol}$ , nearly double that of the non-fluorinated PGE under similar conditions. This increase may be attributed to inverse electron demand  $\pi$ - $\pi$  stacking interactions involving the fluorinated aromatic ring, a phenomenon previously reported in ROCOP and potentially applicable here [54]. In contrast, thermal properties were only slightly improved: DSC revealed a  $T_g = 40^\circ\text{C}$ , and TGA showed  $T_{d,5\%} = 255^\circ\text{C}$ , comparable to PGE. Fluorinated styrene oxide (2-(perfluorophenyl)oxirane, F-SO, run #15) showed poor reactivity, reaching only 10 % PTA conversion after 15 days. Similar to non-fluorinated SO, regioselectivity was not controlled due to regio-random epoxide ring-opening, making precise assessment of sequence selectivity difficult. GPC showed a  $M_w$  of  $7\text{ kg/mol}$ . The polymer exhibited  $T_g = 90^\circ\text{C}$  and  $T_{d,5\%} = 249^\circ\text{C}$ , both notably higher than the non-fluorinated counterpart. However, due to differences in molar mass, these thermal improvements cannot be unambiguously attributed to fluorination.

Finally, we explored difunctional bis-epoxides — an aliphatic version (DEO) and aromatic bisphenol A diglycidyl ether (BAGE) — to determine whether ROTERP could directly yield crosslinked networks. Each system was prepared using 1 equiv. LiOBn, 300 equiv. epoxide, 200 equiv. PTA, and 500 equiv.  $\text{CS}_2$ , with epoxide loading adjusted for the bifunctionality to encourage more uniform crosslinking. DEO yielded a soft, solid material within 1 h. After repeated purification via extraction, DSC revealed a  $T_g = -10^\circ\text{C}$ , and TGA a  $T_{d,5\%} = 230^\circ\text{C}$ . BAGE-based polymer formed a stiffer material with a  $T_g = 84^\circ\text{C}$  and a  $T_d = 270^\circ\text{C}$ . However, as expected, neither material was soluble or thermally processable due to the crosslinked nature.

The ROTERP process introduces trithiocarbonate groups, which—due to the chemically soft lone pairs of sulfur—can interact with metals [56,57]. Moreover, it enables the incorporation of various functional epoxides into sulfur-containing polymers, presenting opportunities to tether these functionalities onto metal surfaces. To demonstrate this, gold nanoparticles (AuNPs) were functionalized with polymer ligands using a grafting-to approach, exploiting the affinity of trithiocarbonate groups for gold-nanoparticle surfaces (see ESI Section S 4) [58,59].

The polymer derived from vanillin glycidyl ether (VGE, run #11) was selected due to the presence of aldehyde groups on the vanillin moiety, which can participate in imine condensation. Prior to surface grafting, imine condensation was carried out between Rhodamine 110 and the polymer. This dye was selected as it can act as a fluorescent marker due to the fact that AuNPs are known to quench the fluorescence of nearby

dye molecules in a distance-dependent manner [60,61].

Dynamic light scattering (DLS) measurements showed a modest increase in the hydrodynamic diameter of the AuNPs from 17 nm to 29 nm immediately after polymer grafting. This suggests the formation of a polymer shell via “wrapping” by the VGE-derived ROTERP terpolymer, which contains multiple trithiocarbonate groups along its main chain, as previously demonstrated for comparable systems [62]. After purification by centrifugation and re-dispersion, a further increase in hydrodynamic size to 139 nm was observed, indicating the formation of small nanoparticle agglomerates. Consistent with this, visible extinction spectroscopy revealed a pronounced red-shift of the plasmon resonance (see Fig. 5). This behavior is attributed to plasmon coupling interactions within the agglomerates which form during the performed purification of nanohybrids by centrifugation/re-dispersion [63]. This is likely a result of limited surface stabilization due to a relatively small polymer molar mass, “looped” multidentate binding to the nanoparticle surface, or a combination of both, leading to a comparably thin polymer shell (compare with DLS results above). However, extinction spectra recorded at various time points after purification showed no further shifts in the plasmon peak, indicating that the aggregation process did not proceed further, and a stable colloidal dispersion was obtained.

Imine functionalities are hydrolytically labile, enabling the potential for acid-triggered dye release. This was evaluated by analyzing the extinction spectra of the supernatant collected from functionalized AuNP dispersions after acid treatment. Upon the addition of HCl, extinction signals corresponding to Rhodamine were observed in the supernatant. Quantitative analysis based on dye extinction yielded an estimated released dye concentration of  $0.7\text{ }\mu\text{M}$ . This corresponds to approximately 0.2 molecules of Rhodamine 110 chloride per  $\text{nm}^2$  of nanoparticle surface area, calculated using a calibration curve obtained in the same solvent system.

Consistent with the known quenching effect of AuNPs, no fluorescence was observed in the dye-polymer-AuNP conjugate. However, fluorescence was restored upon acid addition, confirming dye release (see Fig. 6). As a control, AuNPs functionalized with thiol-terminated polystyrene pre-treated with Rhodamine in the same way showed no detectable dye release under identical acidic conditions. This demonstrates the system's unique capability to function as an efficient, pH-responsive nanoprobe.

### 3. Conclusions and Outlook

In conclusion, this study demonstrates the broad applicability of ring-opening terpolymerisation (ROTERP) for the synthesis of functional sulfur-containing polymers using a diverse range of epoxides. The method provides access to polymers containing poly(ester-*alt*-ester-*alt*-trithiocarbonate) linkages with tunable thermal and structural properties. From an environmental standpoint, the present synthetic route

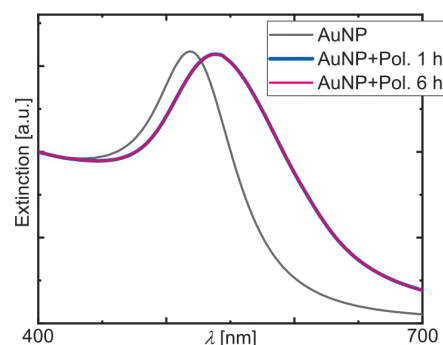
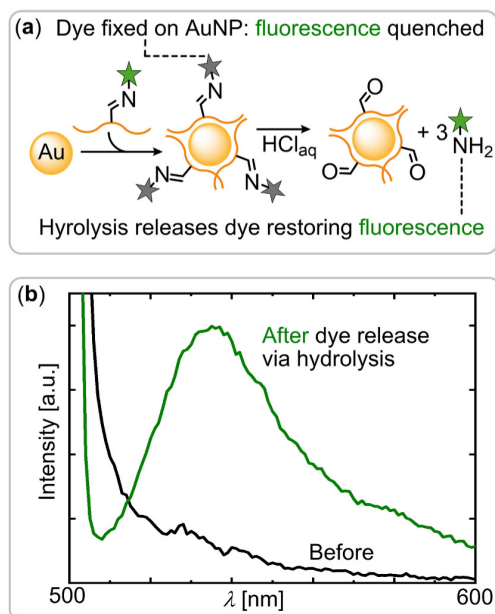


Fig. 5. Visible extinction spectra of citrate capped AuNPs (black trace) and polymer-functionalized AuNPs after 1 and 6 h (coloured traces) in a THF/DMF solvent mixture.



**Fig. 6.** (a) AuNP functionalisation and dye release methodology. (b) Fluorescence spectra of the AuNP solutions with polymer prior to and following acid addition.

cannot be classified as “green.” The use of  $\text{CS}_2$  and (halogenated) epoxides limits its sustainability. Nevertheless, the modularity of the ROTERP process and the wide commercial availability of its monomers make it a flexible and accessible platform for developing sulfur-containing polymers. However, side reactions are common and substantially impede the controllability of the methodology, particularly with respect to molecular weight predictability and polydispersity. These limitations are more pronounced for certain epoxides, resulting in only modest molecular weights under practical conditions. Importantly, the incorporation of sulfur centers enables downstream applications such as gold nanoparticle surface functionalization with built-in pH-responsive dye release. Overall, ROTERP represents a powerful and modular tool for designing advanced polymeric and nanomaterial systems with tailored functionalities.

#### 4. Safety considerations

Both carbon disulfide and epoxides (especially ECH) are highly hazardous. These reagents are volatile, flammable, neurotoxic, sensitizing, and suspected carcinogens. All operations involving these reagents were conducted in a well-ventilated fume hood using appropriate personal protective gear. Reaction vessels were kept sealed under inert atmosphere as long as possible to minimize vapor exposure. Liquid and solid residues were quenched under basic conditions and collected in appropriate waste streams according to institutional hazardous-waste regulations.

Alex Plajer and Christian Rossner report financial support was provided by Chemical Industry Fund. Alex Plajer reports financial support was provided by German Research Foundation. Alex Plajer reports financial support was provided by Daimler and Benz Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

Cesare Gallizioli: Investigation, Writing – original draft, Writing –

review & editing. Marina Sebastian: Investigation, Writing – original draft, Writing – review & editing. Malte Cornelsen: Investigation. Christian Rossner: Conceptualization, Investigation, Resources, Supervision, Writing – original draft, Writing – review & editing. Alex J. Plajer: Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

We thank the “Fonds der Chemischen Industrie” (Liebig fellowships to CR and AJP) and the “Daimler and Benz Foundation” (personal scholarship for A. J. P) as well as the “Deutsche Forschungsgemeinschaft” (project number 542928411, CRC 1585 project number 492723217 for subproject SP01) for financial support. Andreas Fery is thanked for helpful discussions. Juan Guevara and Nina Nestmann are thanked for experimental support.

#### Data availability

Data will be made available on request.

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**Supporting information**

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## Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. NMR spectra were recorded by using Jeol JNMECA 400II, Bruker Advance 300 and 500 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are referenced to the residual proton resonance of the deuterated solvents.  $\text{CS}_2$  and epoxides were dried over calcium hydride at room temperature for 3 days followed by distillation under argon atmosphere.  $\text{BnOH}$  was dried over 4Å molecular sieves and degassed. Phthalic thioanhydride (PTA) was synthesized according to the literature procedure and then purified by recrystallisation from  $\text{CHCl}_3$  and two sublimations under dynamic vacuum at  $90^\circ\text{C}$  and was stored inside an argon filled glovebox prior to use.<sup>[1]</sup> VGE (vanillin monoglycidyl ether) and 9-(Oxiran-2-ylmethyl)-9H-carbazole (CE) were prepared following previously reported procedures.<sup>[2],[3]</sup>

All other reagents were used as received if not stated otherwise. All reagents were stored and used inside an Ar filled glovebox.

Size exclusion chromatography (SEC) was performed using a Waters 515 HPLC pump and THF as eluent at a flow rate of 0.5 mL/min. A volume of 100  $\mu\text{L}$  of polymer solution (1-2 mg/mL) was injected with a 707 Waters autosampler into a column setup comprising a guard column (MesoPore Guard 5 x 0.75 cm, particle size 3  $\mu\text{m}$ ). Polymer size distribution was monitored with a Waters 414 refractive index detector. Narrow distributed polystyrene standards were used for calibration and 1,2-dichlorobenzene as internal reference. Each polymer sample was dissolved in HPLC-grade THF (2 mg/mL) and filtered through a 0.45  $\mu\text{m}$  porous filter frit prior to analysis.

TGA data was measured using a Netzsch TG 209. DSC was measured on a Netzsch 204 F1 "Phoenix" at 10 K/min heating rate.

Extinction spectroscopy was performed using a Cary 5000 photospectrometer in respective solution using glass cuvettes (optical path length 10mm). Baseline correction was performed by subtracting the spectrum of the pure solvent.

Hydrodynamic diameter and dispersity of the nanoparticles were measured using a dynamic light scattering instrument (Anton Paar Litesizer 500) equipped with a laser diode operating at 658 nm. Measurements were performed in backscattering mode, i.e. at a scattering angle of  $175^\circ$ .

TEM imaging was performed on a Zeiss Libra-120 TEM instrument at an acceleration voltage of 120 kV, and on a Zeiss Libra-200 at an acceleration voltage of 200 kV. Scattered electrons were blocked with an objective aperture in the focal plane of the objective lens. One drop of the nanoparticle (NP) colloidal solution was applied onto carbon-coated copper grids and dried in air.

Fluorescence measurements were performed using an Agilent Cary Eclipse spectrofluorometer. Samples were excited at 496 nm, and emission spectra were recorded over the range of 500–600 nm using a slit width of 5 nm.

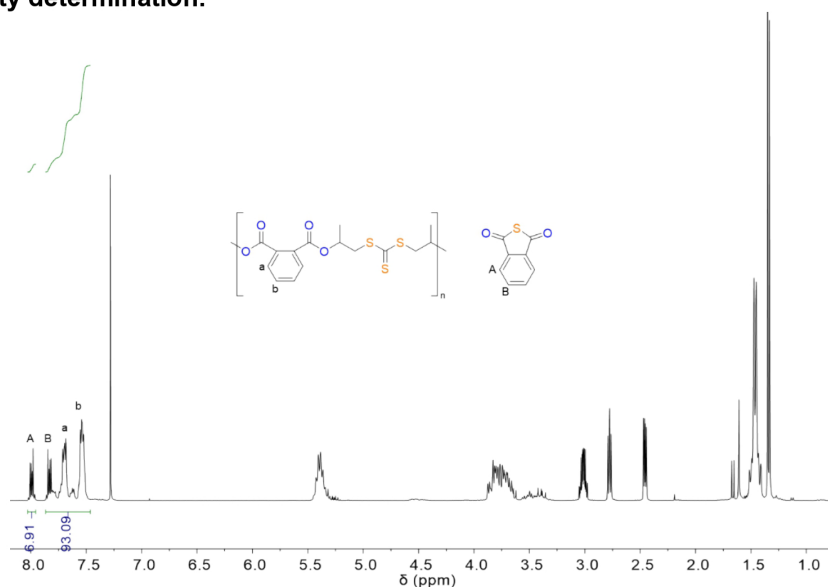
For experiments involving gold nanoparticles, all glassware was thoroughly cleaned with aqua regia and subsequently rinsed multiple times with Milli-Q water prior to use.

## Section S2: Polymerisation procedure

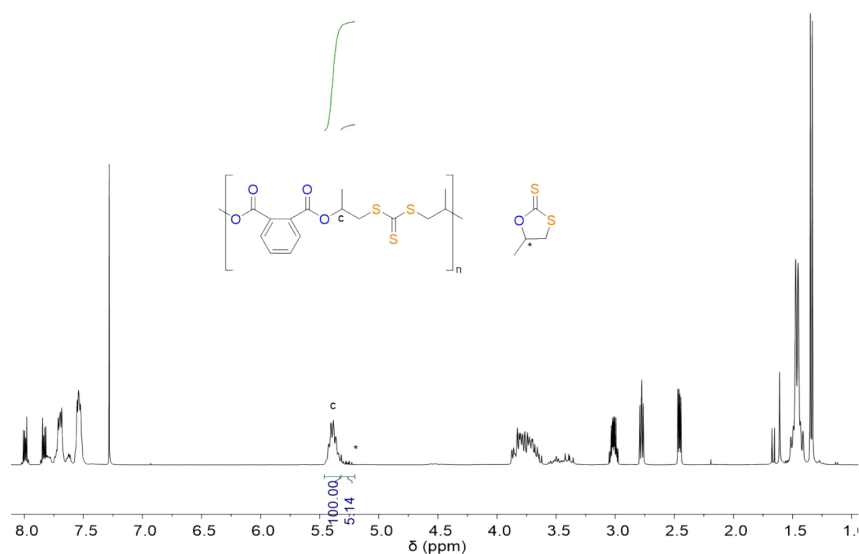
### General polymerisation protocol:

Inside an argon-filled glovebox, LiHMDS and BnOH were dissolved in the epoxide and the mixture was transferred to an oven dried vial equipped with an oven dried stirrer bar. PTA was added followed by CS<sub>2</sub>, and the vial was sealed with a melamine cap containing a Teflon inlay, brought outside the glovebox, and placed in a pre-heated aluminum block at the specified temperature for the specified time. To ensure reproducibility, we opted to run the polymerisation at 30°C as “room temperature” representing room temperature in the summer. At the end point of the reaction, the polymer was isolated by dilution in DCM (5 mL) and successive addition of the polymerisation mixture to 40 mL of MeOH resulting in the precipitation of the polymer which was isolated by centrifugation. This was followed by additional precipitation from DCM/MeOH for some samples.

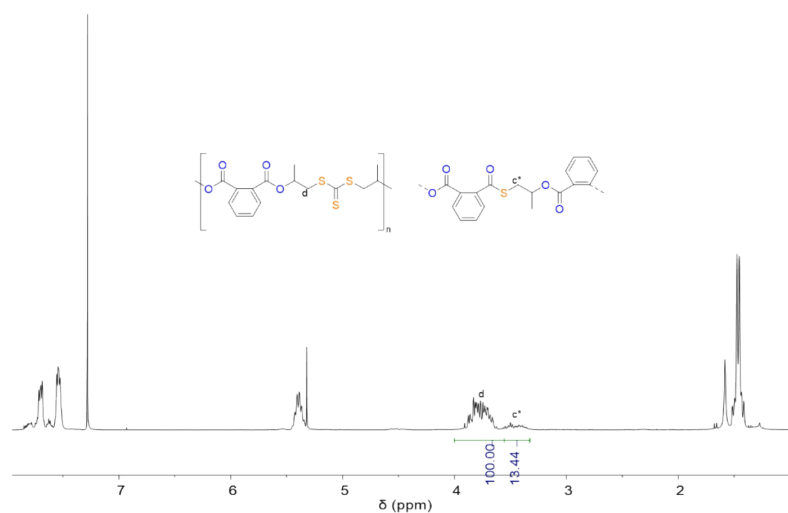
### Selectivity determination:



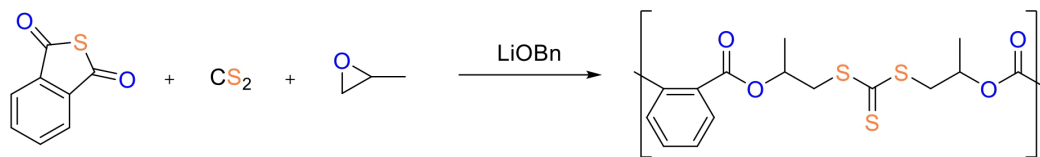
Monomer conversion was calculated with the integrative ratio between the aromatic integrals that are part of the polymer chain and the signals corresponding to unreacted PTA in the crude mixture. The entire aromatic region was integrated and set to 100. With this normalization the PTA signal at ca. 8 ppm was integrated, and the value was doubled to consider the second signal that is overlapping with polymer aromatic moieties to determine the overall fraction of unconsumed PTA.



To determine polymer selectivity, the integrative ratio between the signals stemming from the tertiary CH signal polymer chain and the tertiary CH signal corresponding to the cyclic dithiocarbonate byproducts was analyzed. The area that is covered by both the signals is normalized as 100 followed by integration of the signal corresponding to the cyclic byproduct to obtain the product fractions.



Polymer linkage selectivity was calculated considering the ratio of the CH<sub>2</sub> signals stemming from ROTERP and ROCOP as shown above. The total area corresponding to CH<sub>2</sub> signals was integrated and normalized as 100. With this normalization, the signal stemming from ROCOP (here labeled as C\*) was integrated to obtain the respective fraction of the two sequences. Instances in which these signals were not clearly discernable are presented as n.d. in the polymerization table. Although one ROTERP linkage comprises two CH<sub>2</sub> groups while one ROCOP link comprises one CH<sub>2</sub> group, this selectivity determination takes into account that for a ROTERP link also twice as many insertion processes have to occur selectively.

Section S3: PTA/CS<sub>2</sub>/PO ROTERP

Scheme S 1: controlled synthesis of a poly(ester-alt-trithiocarbonate) from thioanhydride, carbon disulfide and propylene oxide.

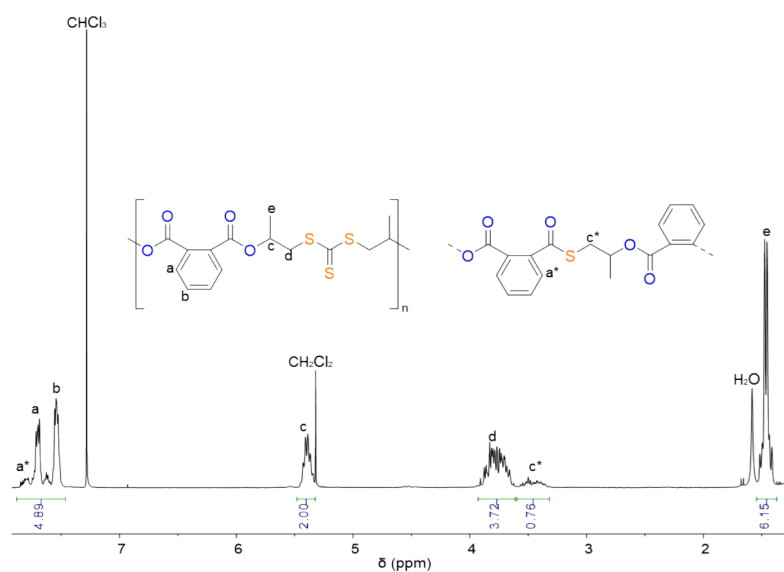


Figure S 1: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #1.

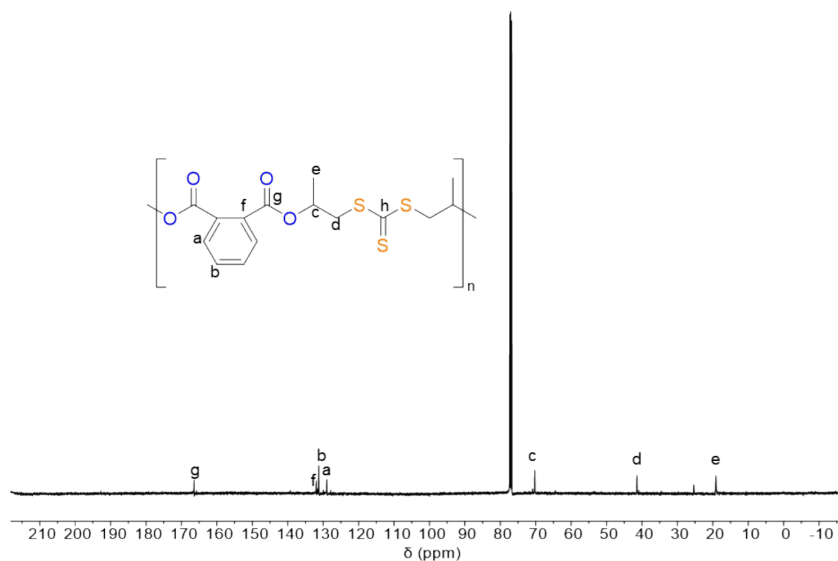


Figure S 2: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #1.

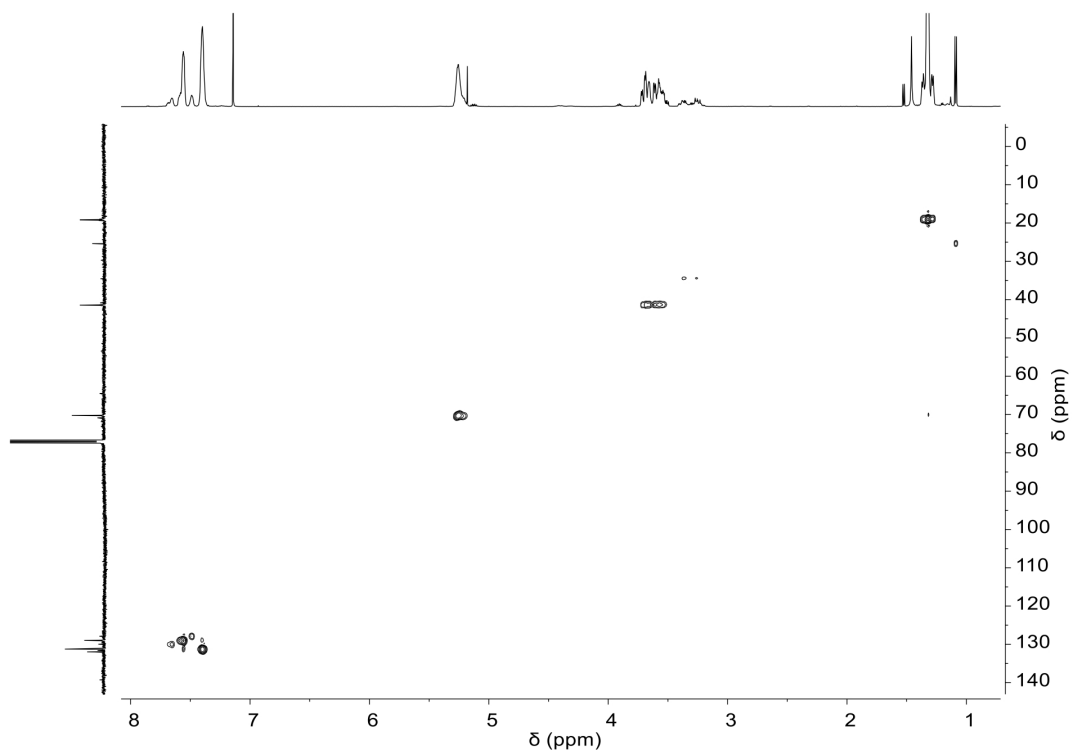


Figure S 3:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #1.

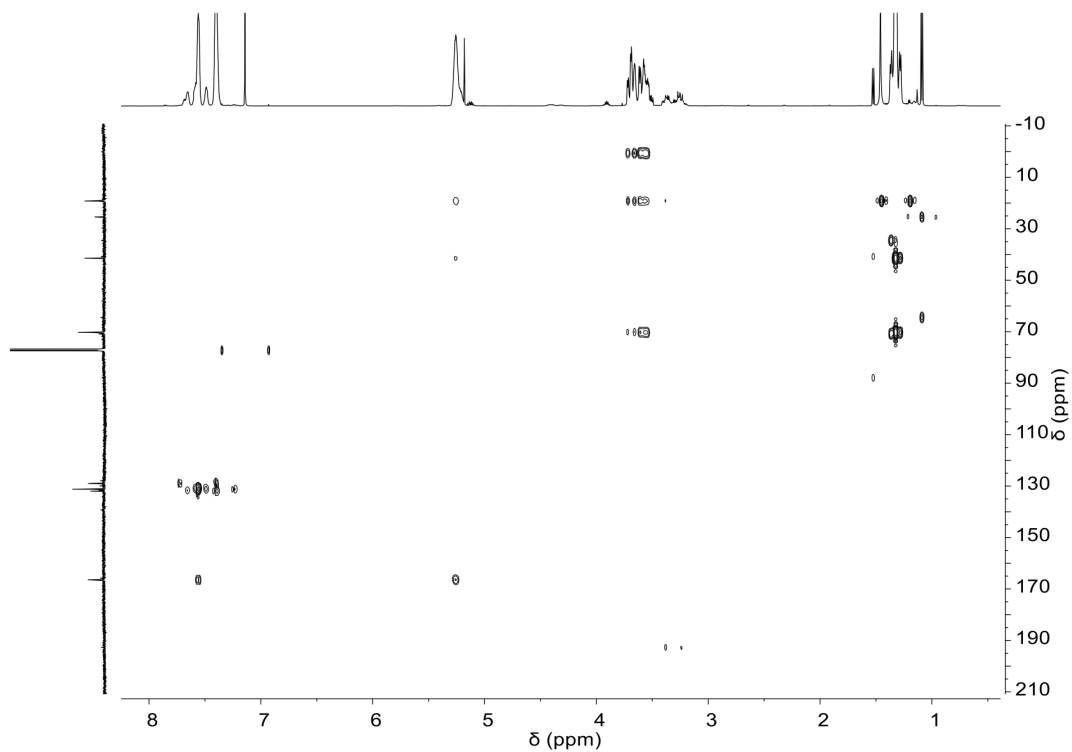


Figure S 4:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #1.

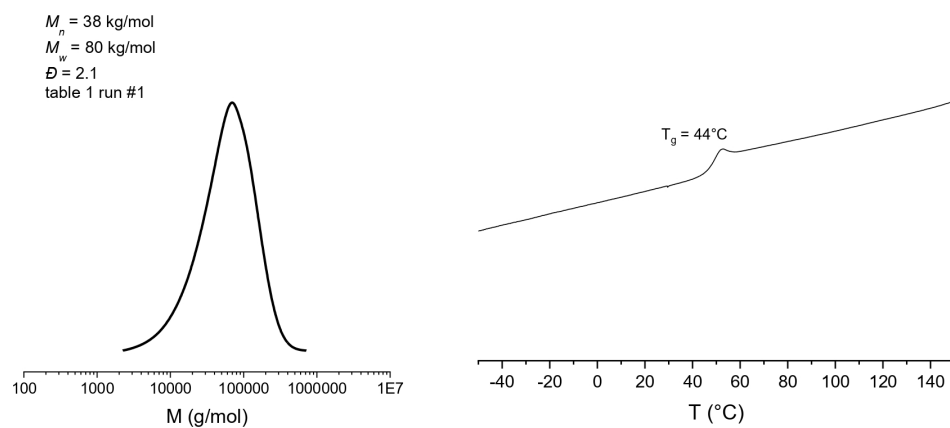


Figure S 5: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #1.

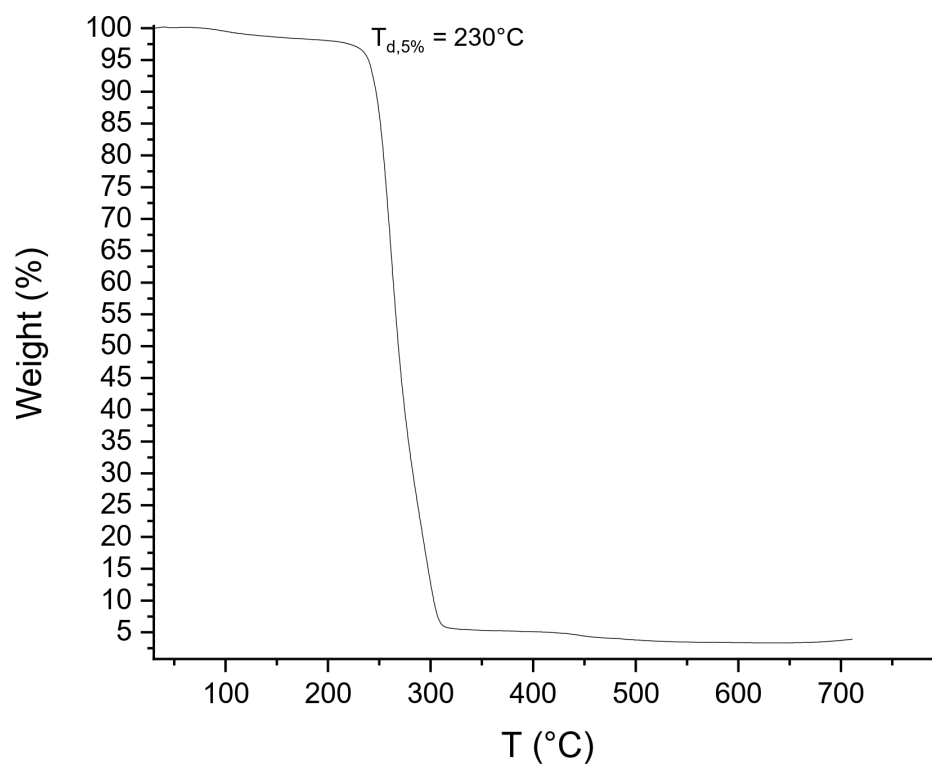


Figure S 6: TGA data of the precipitated polymer corresponding to table 1 run #1.

Monomer scoping was conducted with the same polymerisation methodology described in **Section S2**.

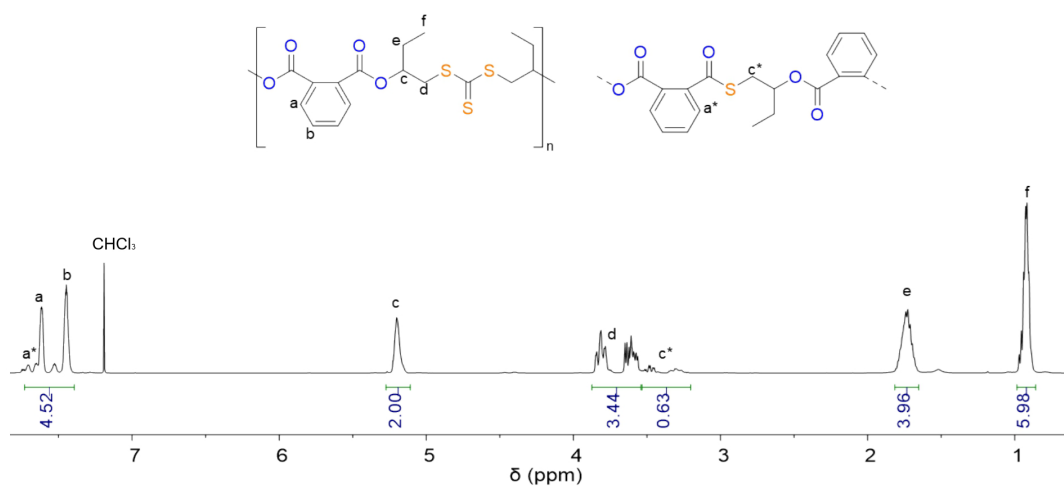


Figure S 7:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #2.

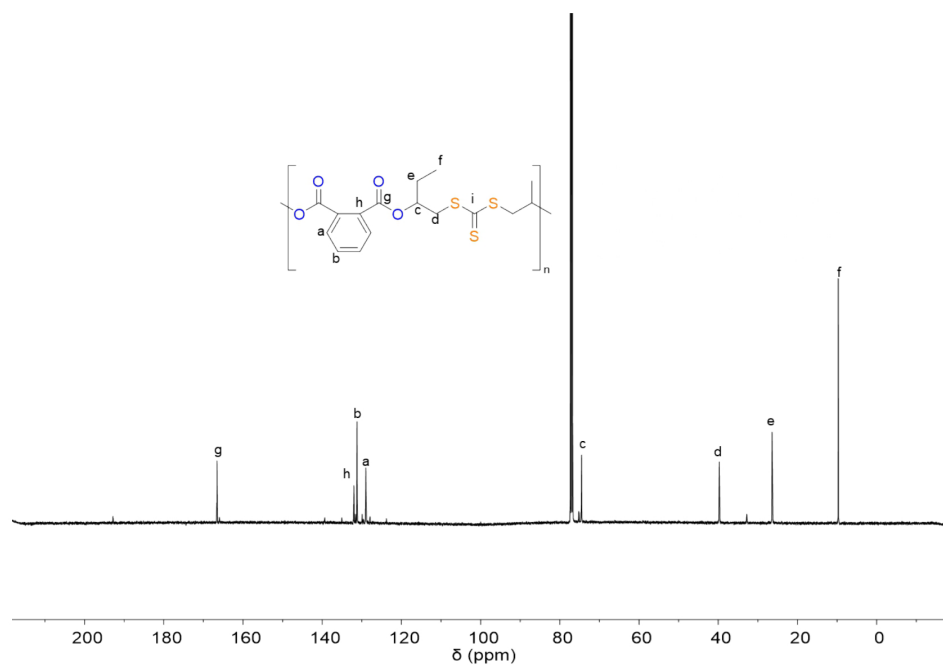


Figure S 8:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #2.



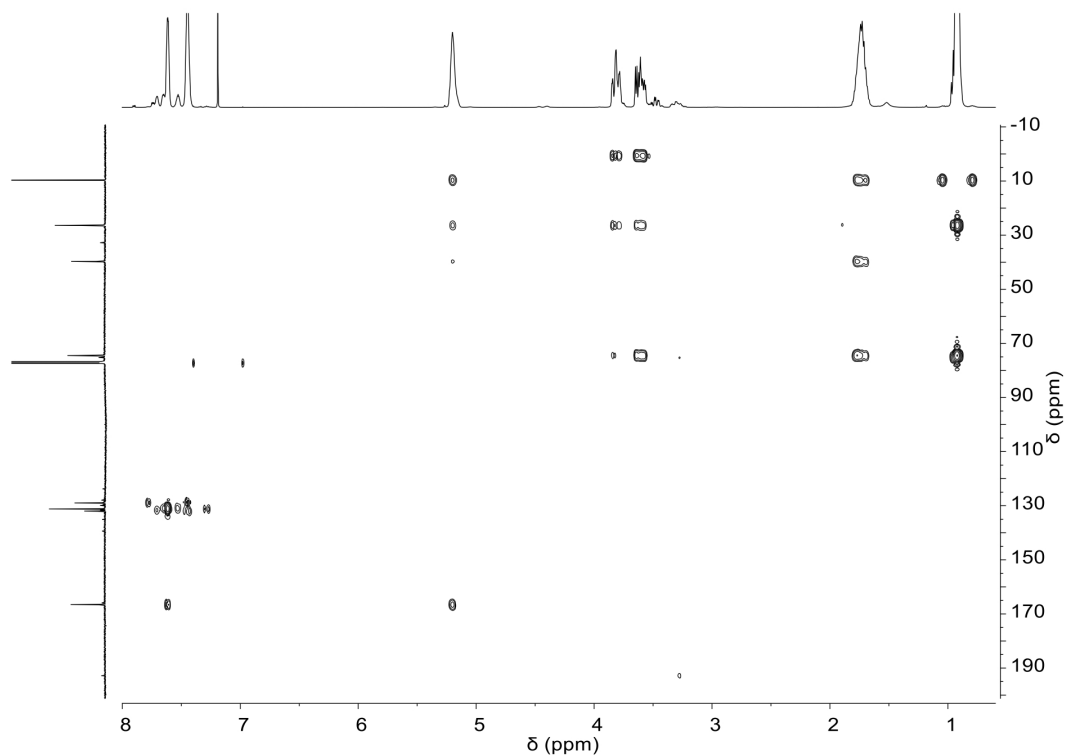


Figure S 9:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #2.

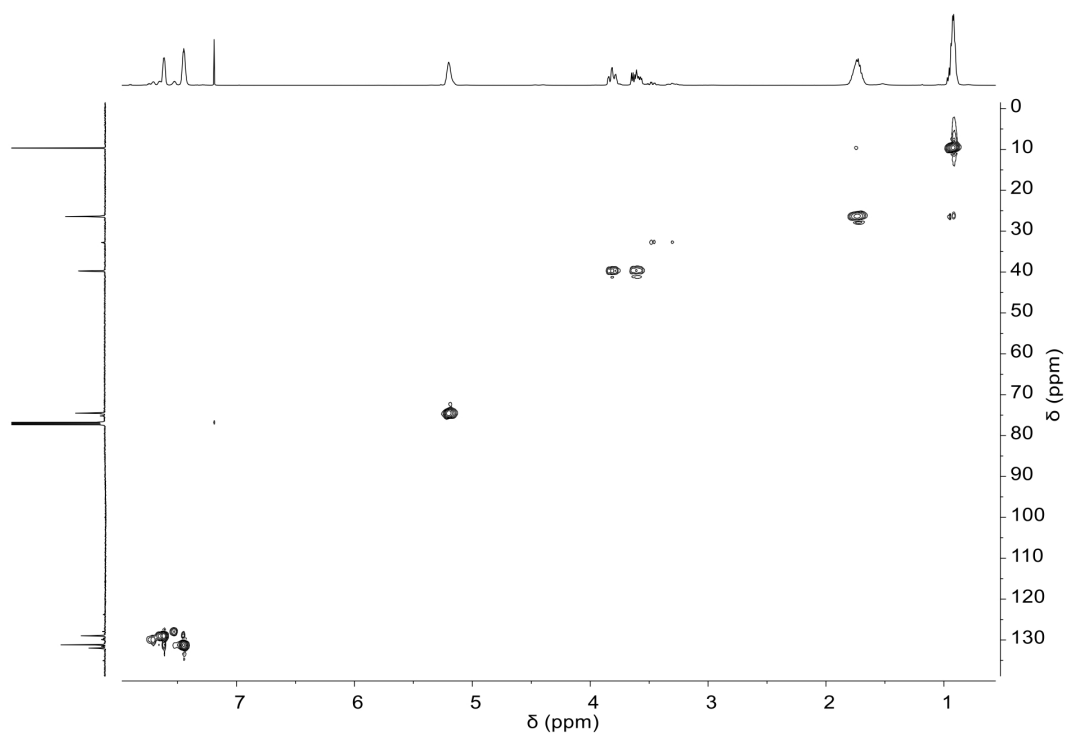


Figure S 10:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #2.

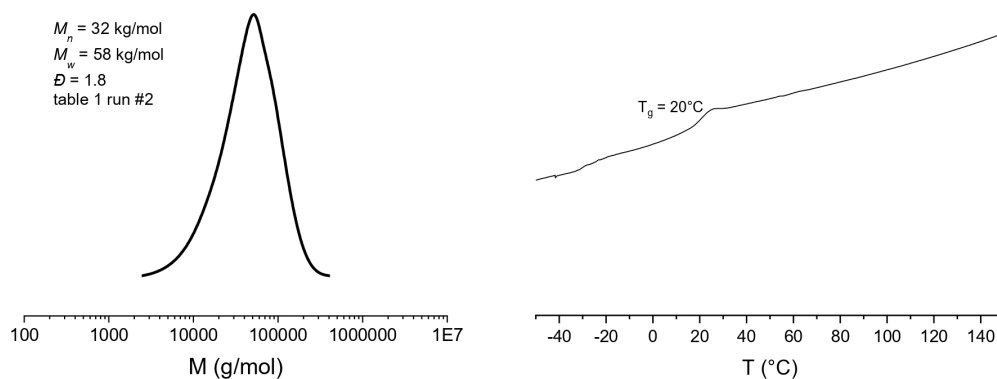


Figure S 11: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #2.

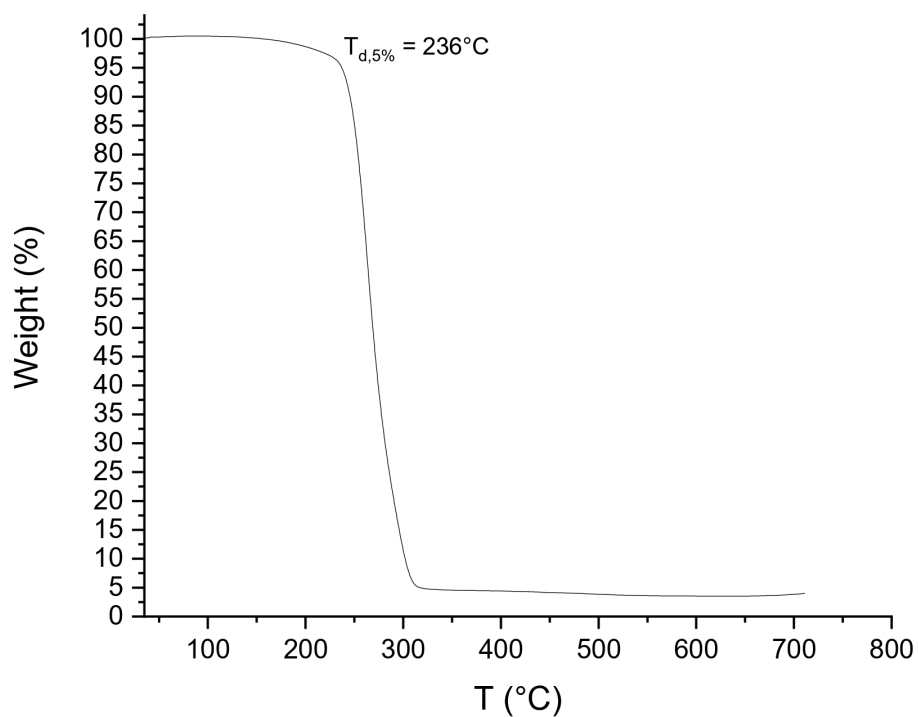


Figure S 12: TGA data of the precipitated polymer corresponding to table 1 run #2.

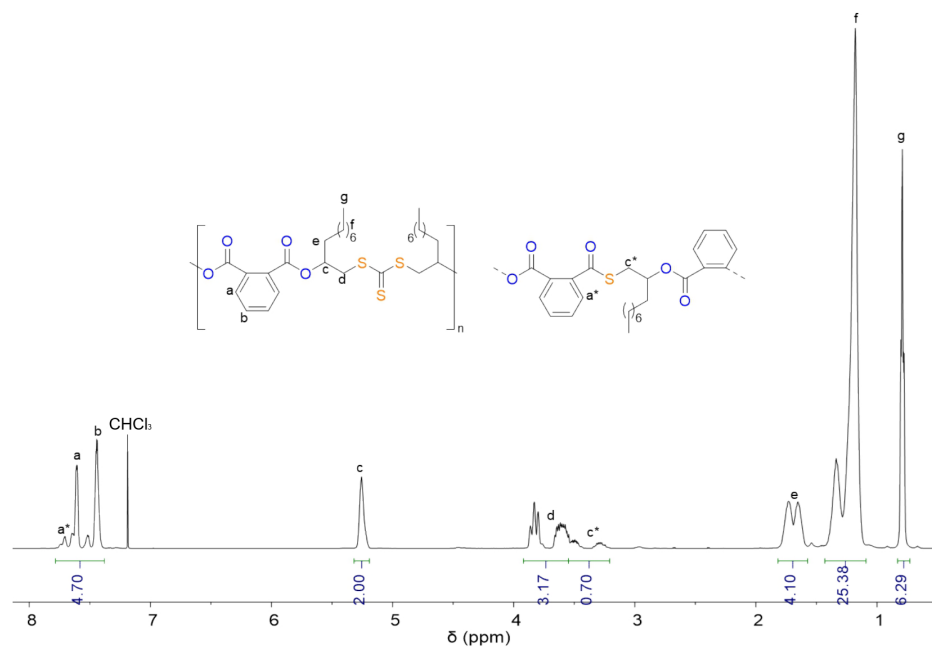


Figure S 13:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #3.

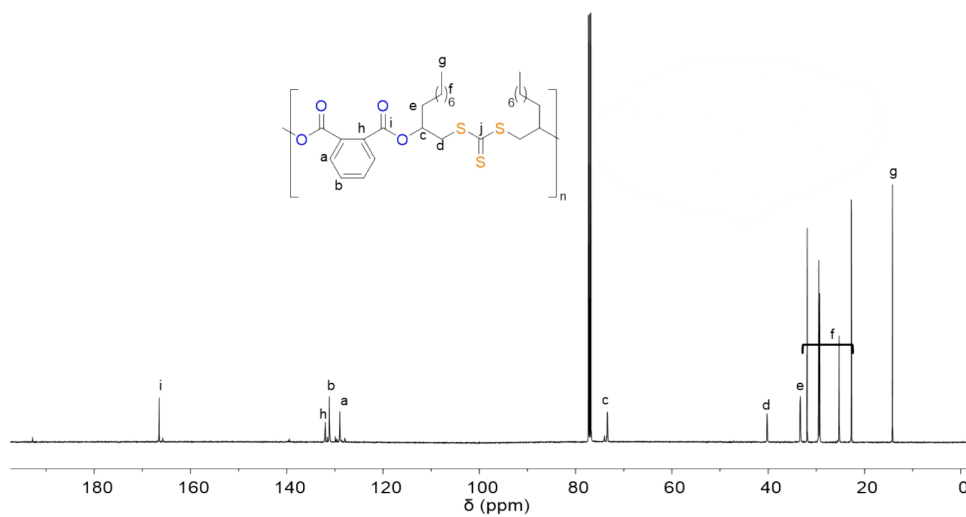


Figure S 14:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #3.

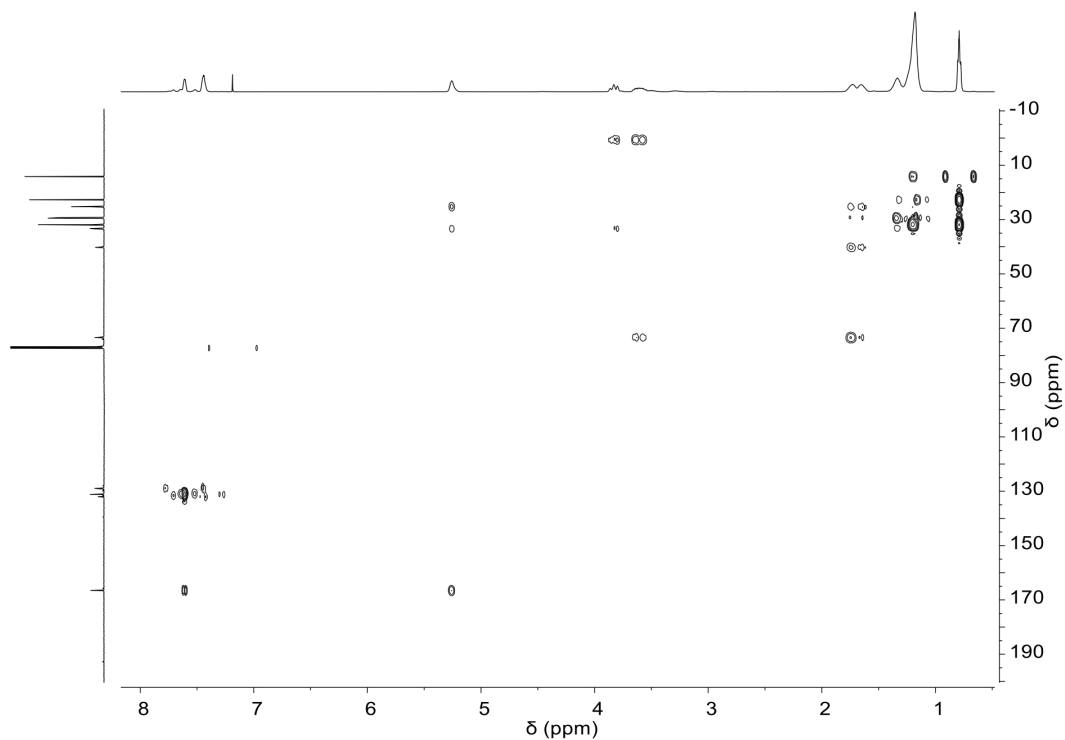


Figure S 15:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #3.

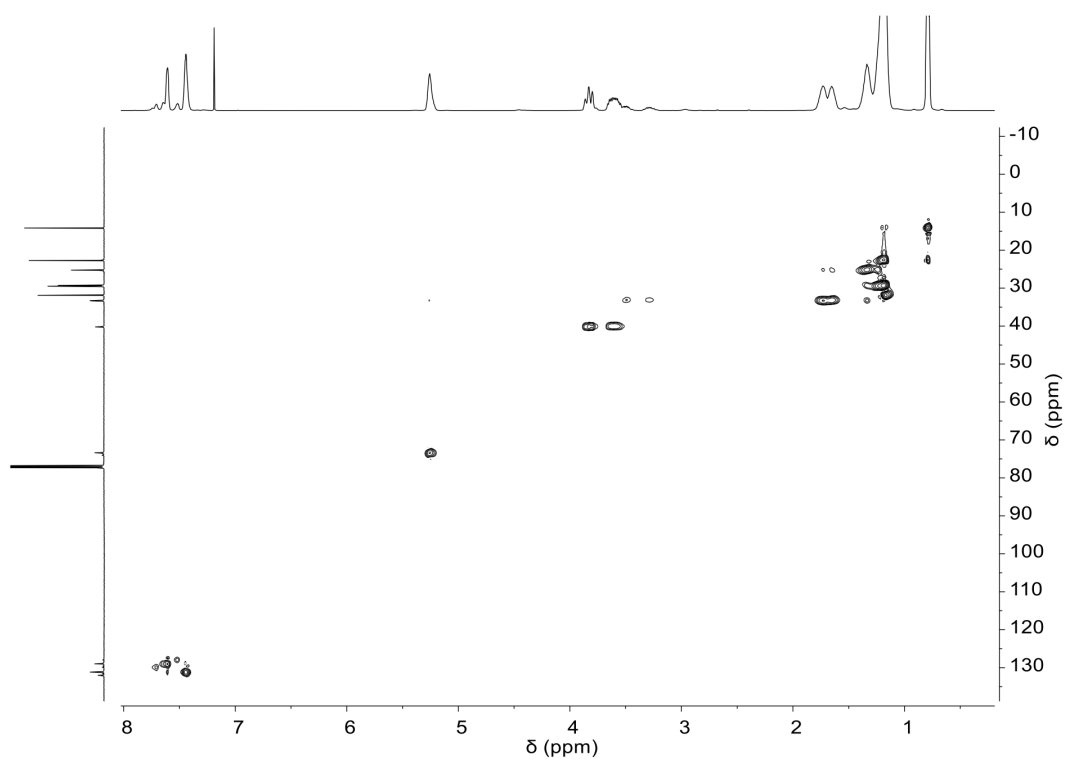


Figure S 16:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #3.

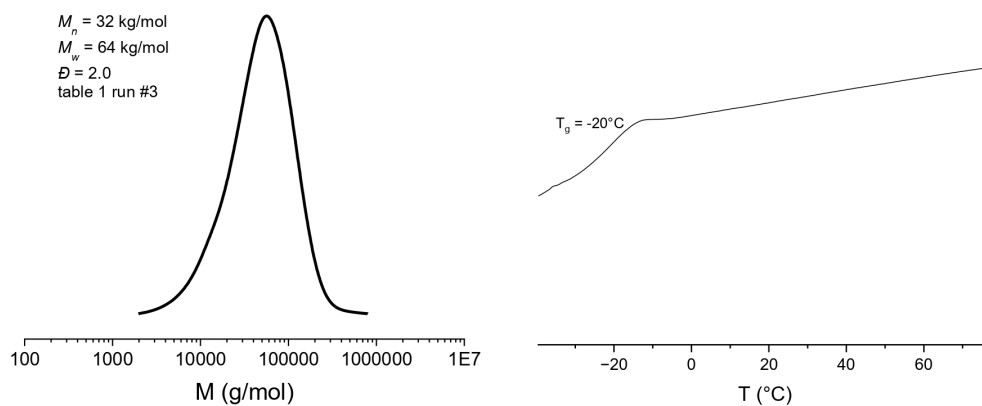


Figure S 17: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #3.

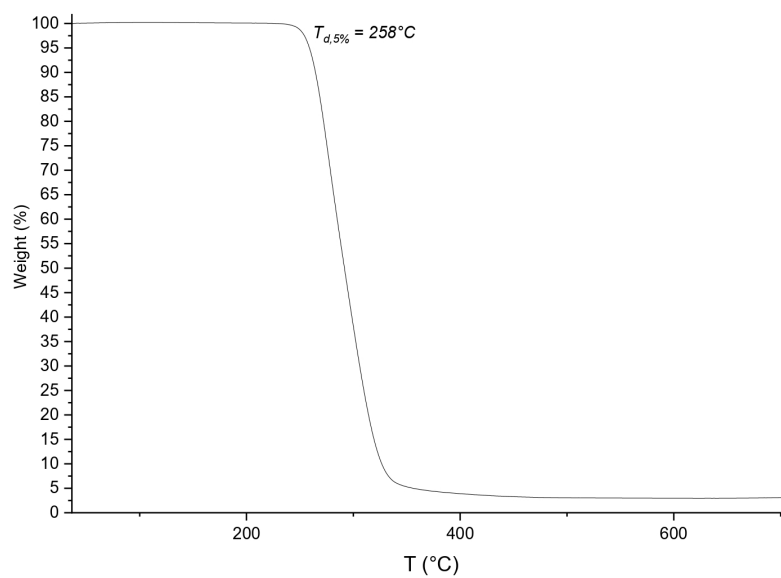


Figure S 18: TGA data of the precipitated polymer corresponding to table 1 run #3.

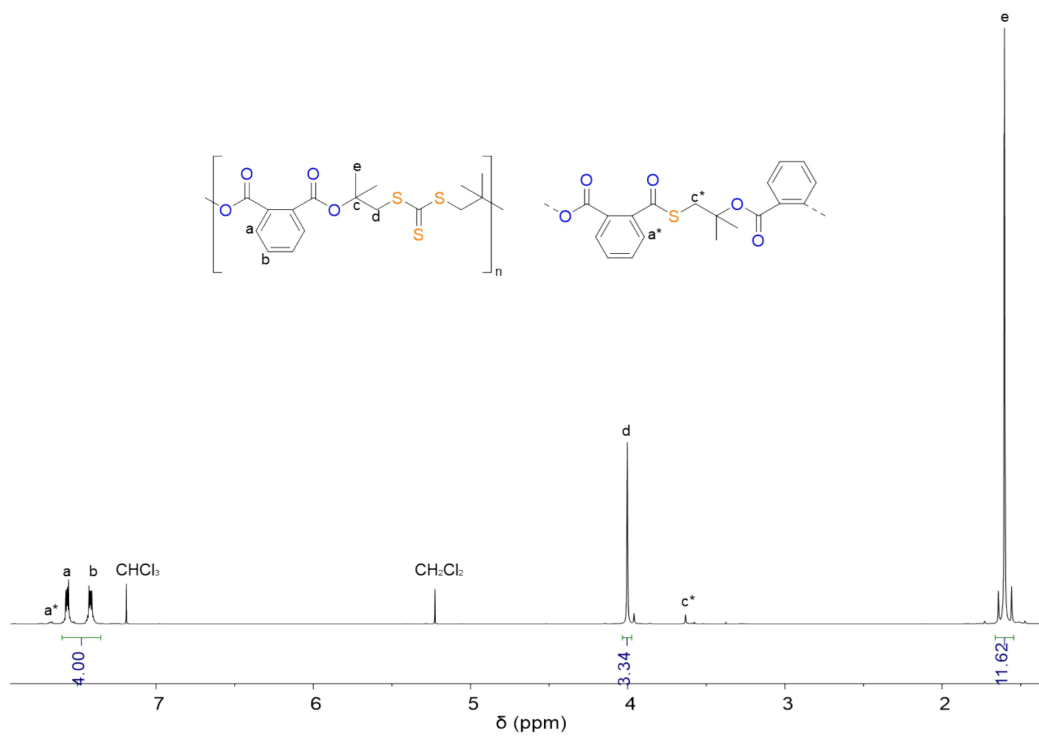


Figure S 19: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #4.

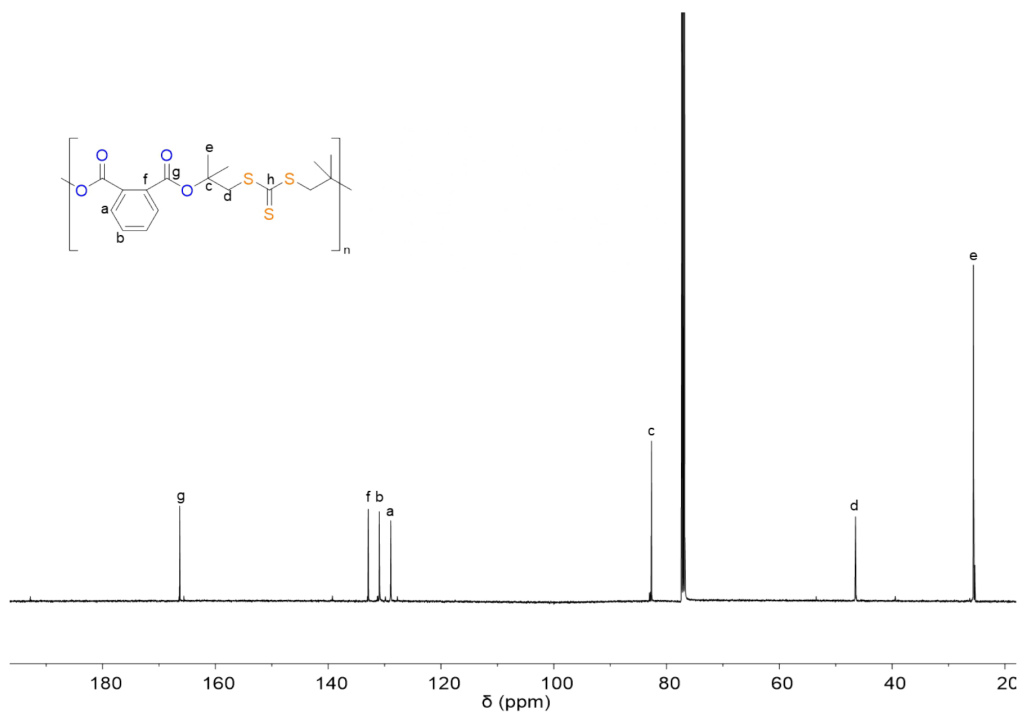


Figure S 20: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #4.

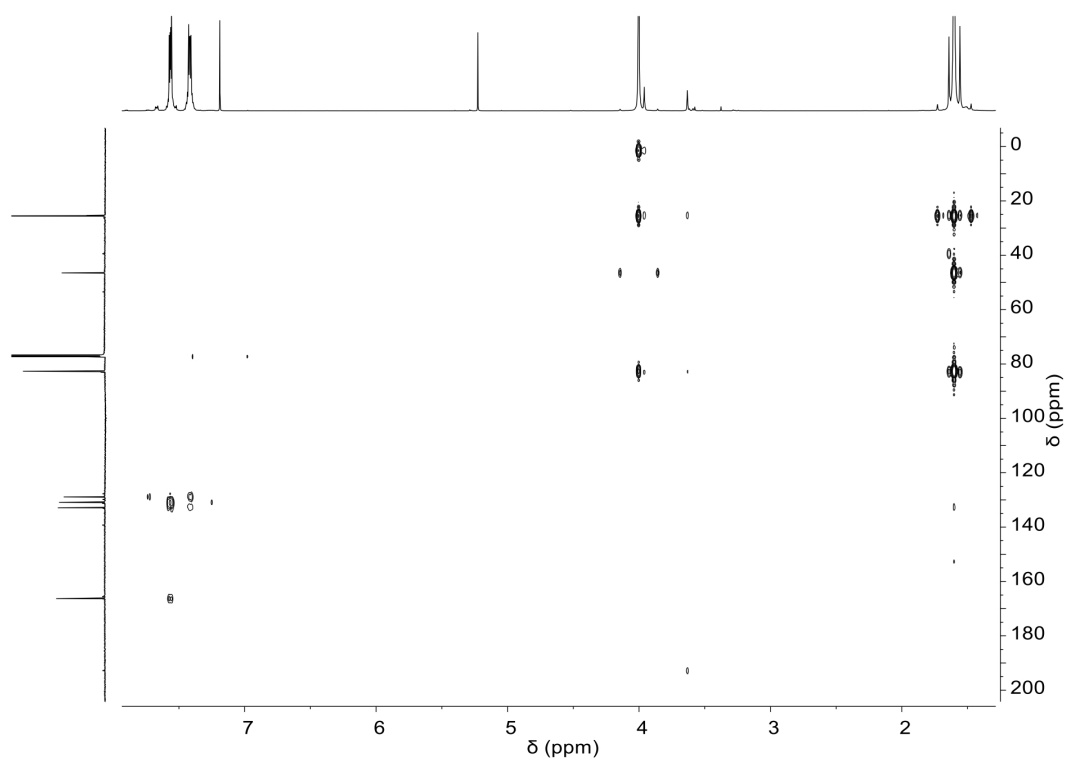


Figure S 21:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #4.

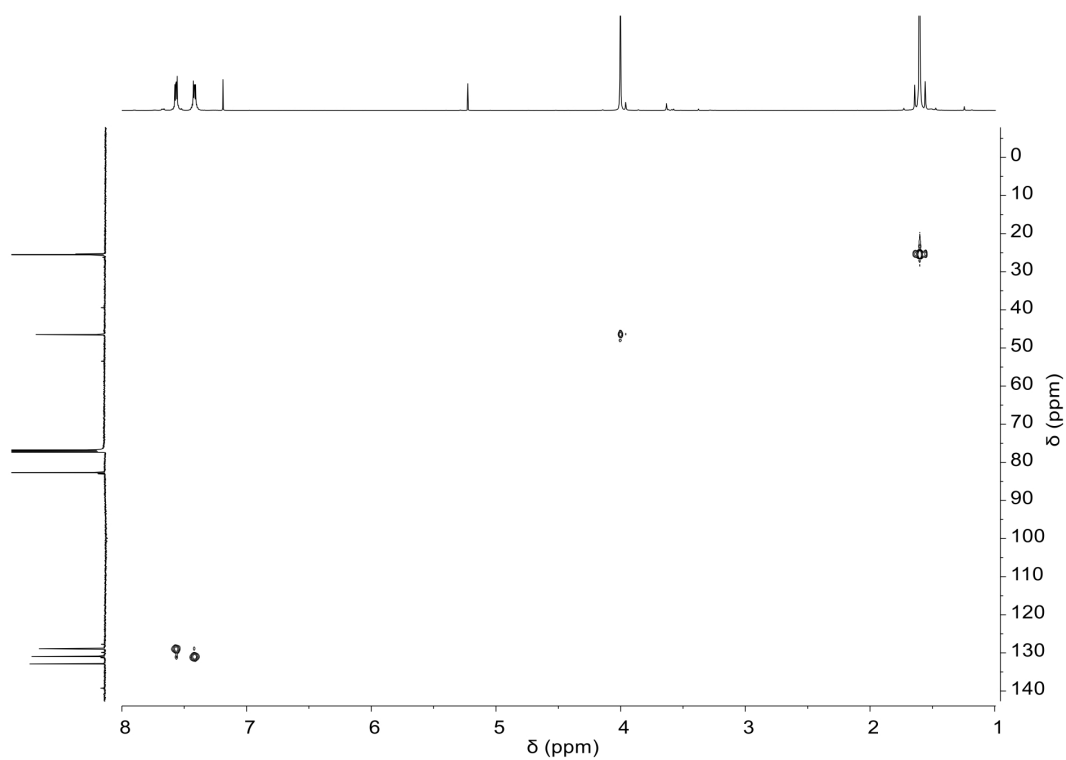


Figure S 22:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #4.

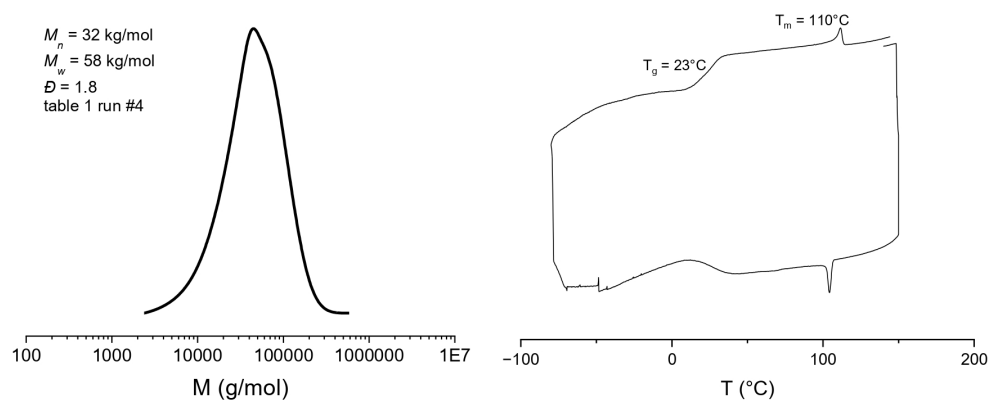


Figure S 23: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #4.

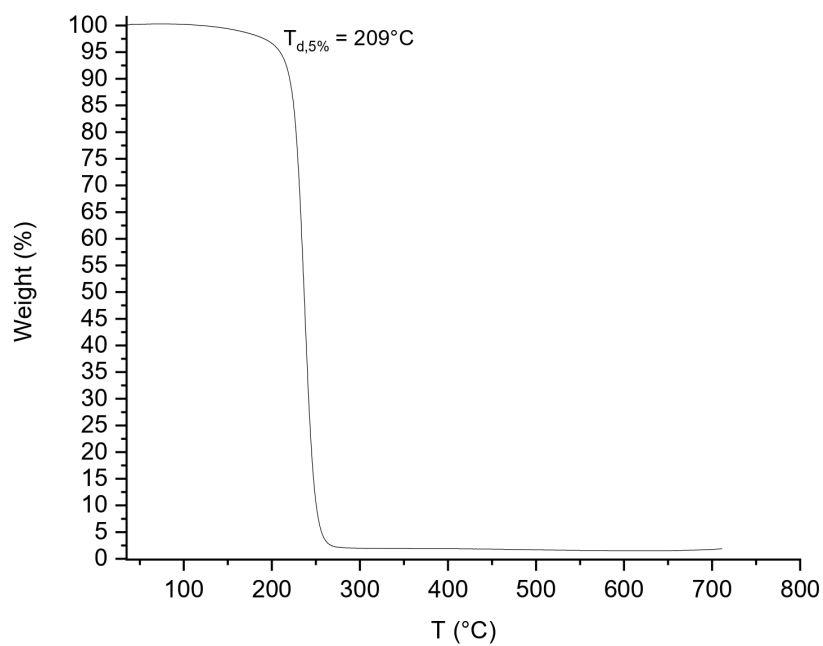


Figure S 24: TGA data of the precipitated polymer corresponding to table 1 run #4.



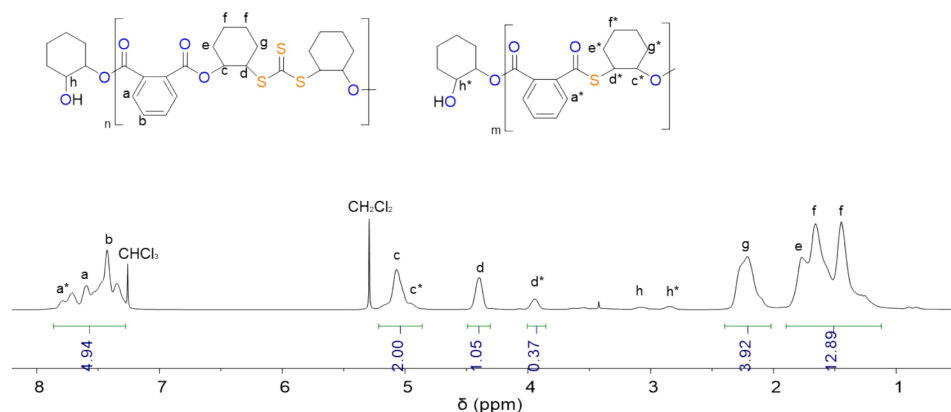


Figure S 25:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #5.

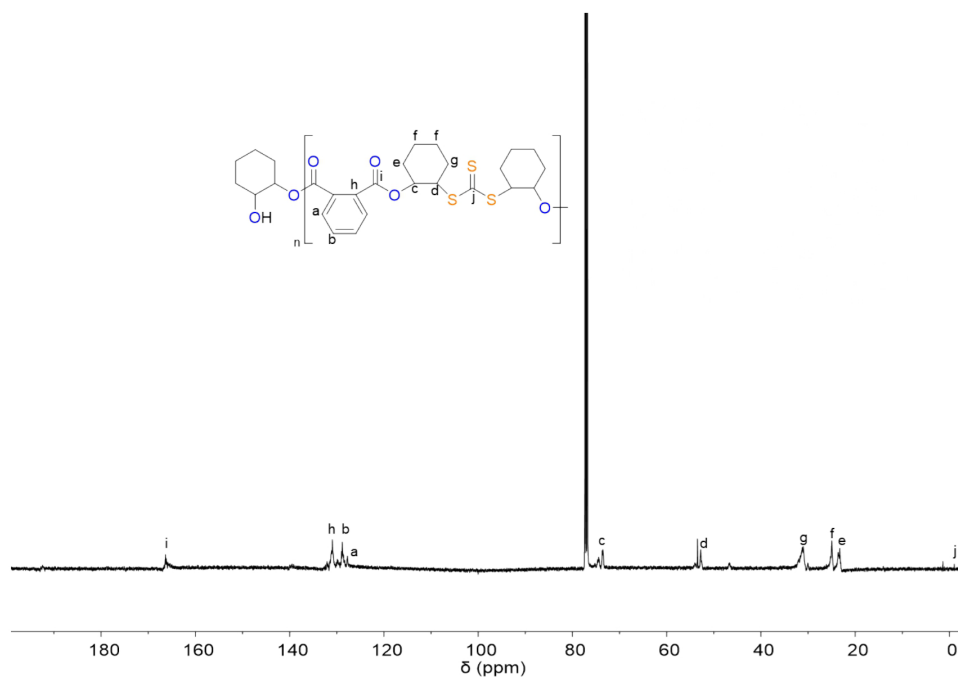


Figure S 26:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #5.

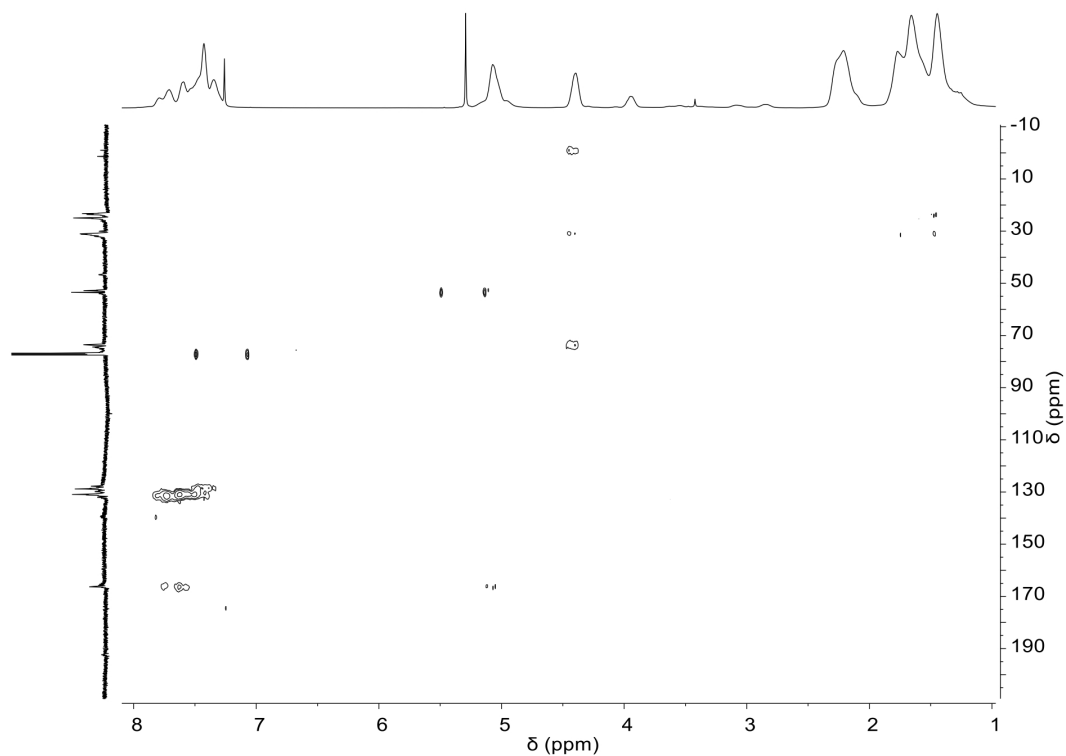


Figure S 27:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #5.

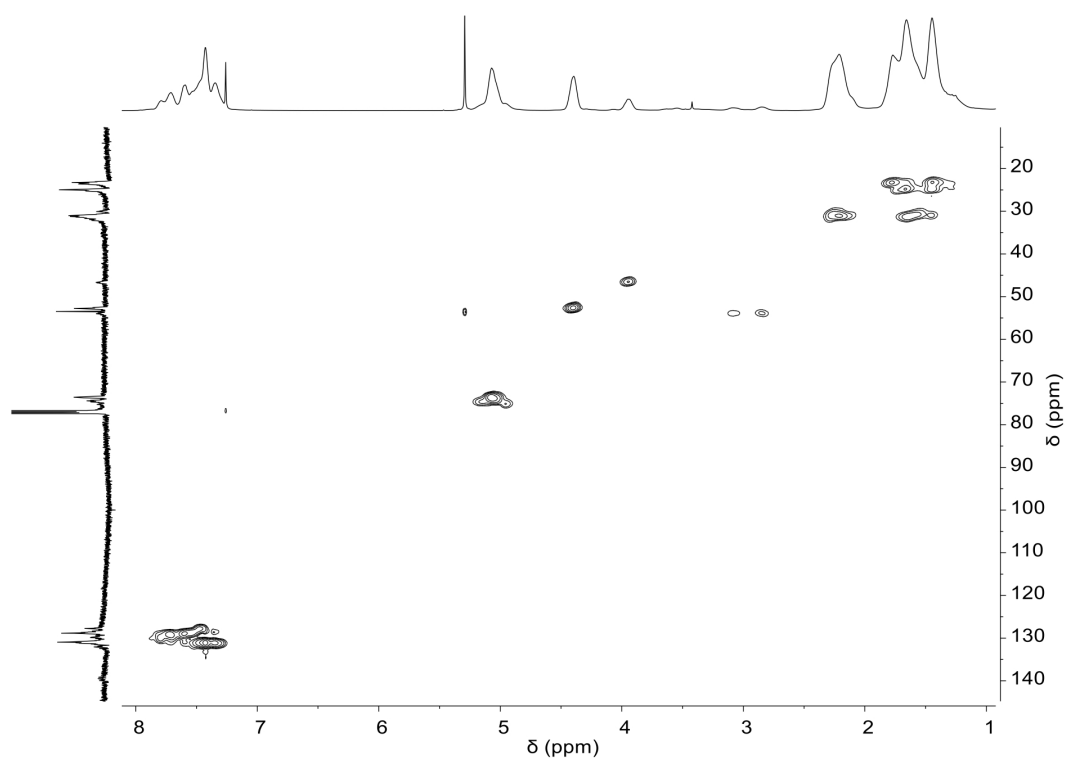


Figure S 28:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #5.

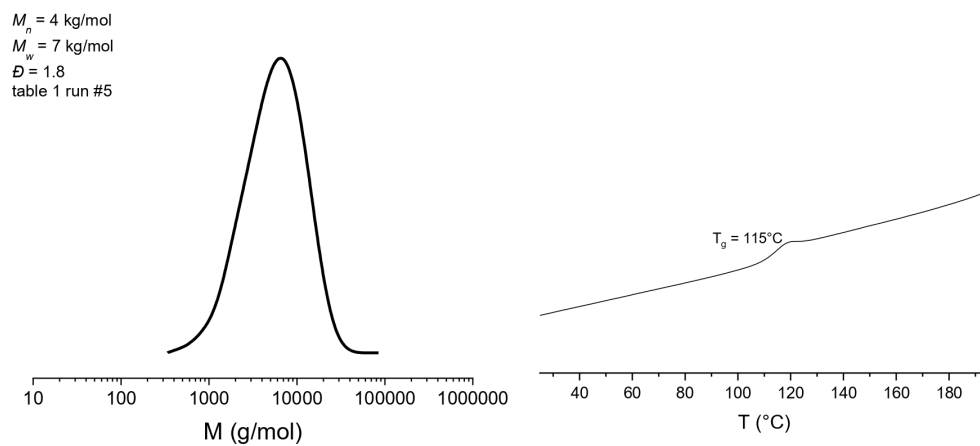


Figure S 29: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #5.

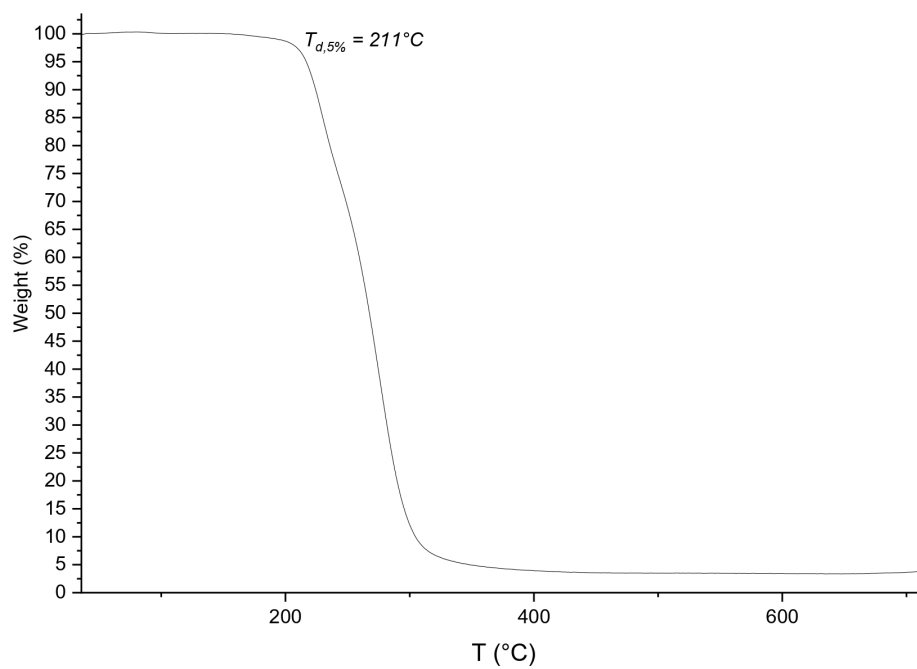


Figure S 30: TGA data of the precipitated polymer corresponding to table 1 run #5.

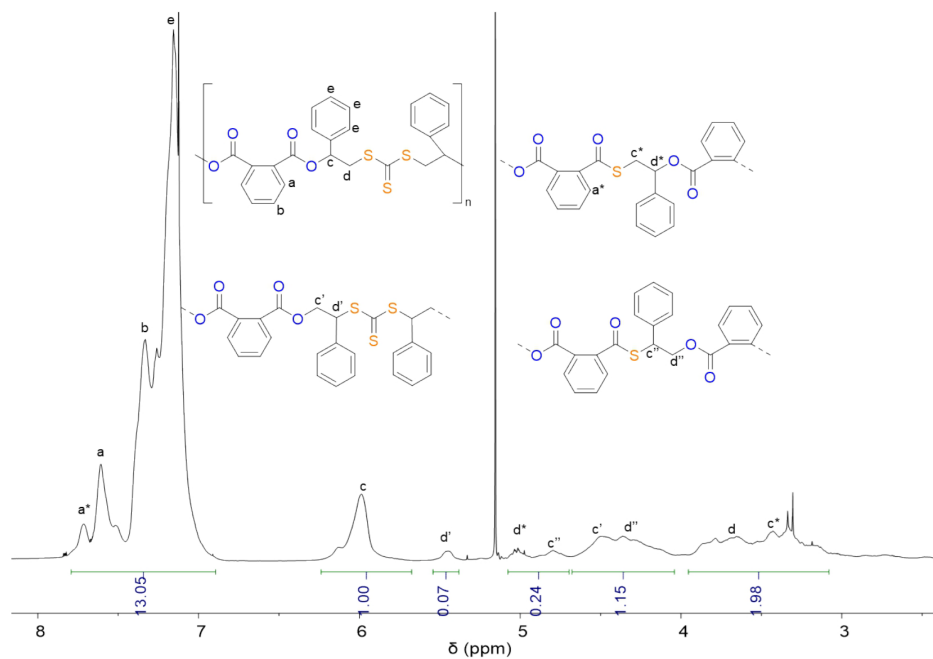


Figure S 31:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #6.

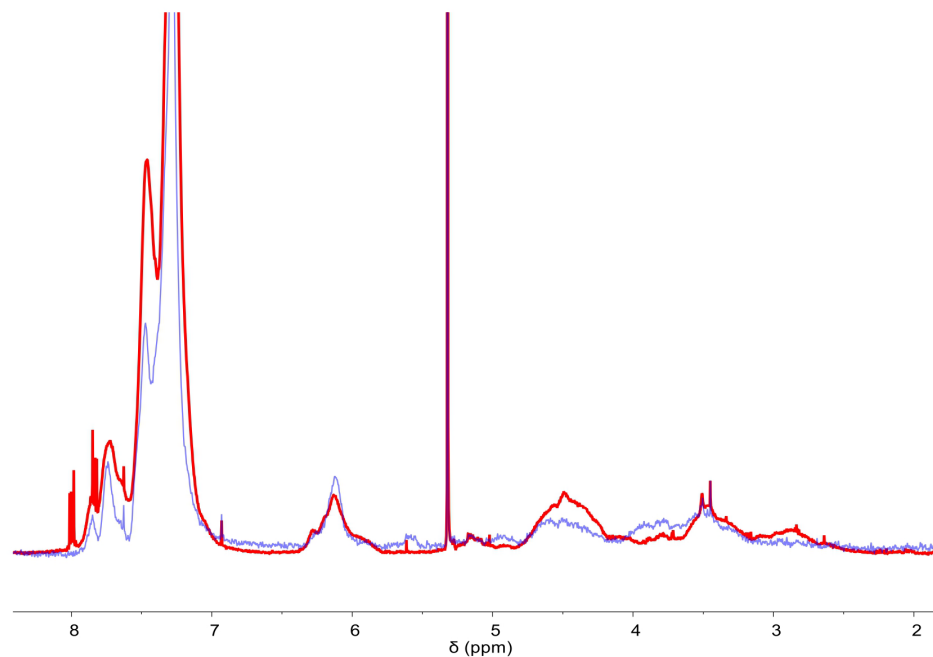


Figure S 32: superimposed  $^1\text{H}$ -NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #6 (blue) and the precipitated polymer obtained from the copolymerization of SO and PTA (red).

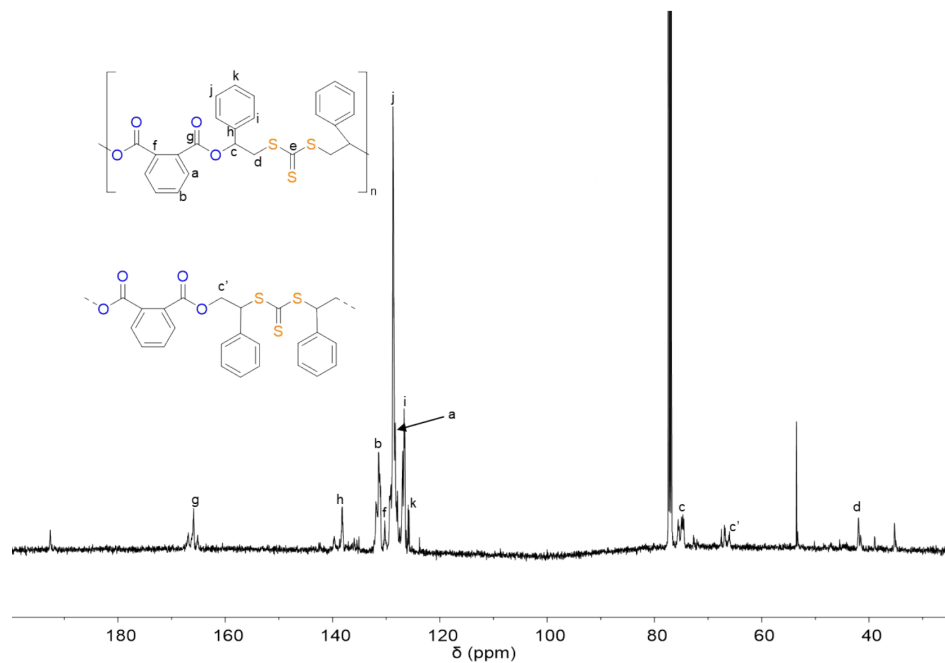


Figure S 33:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #6.

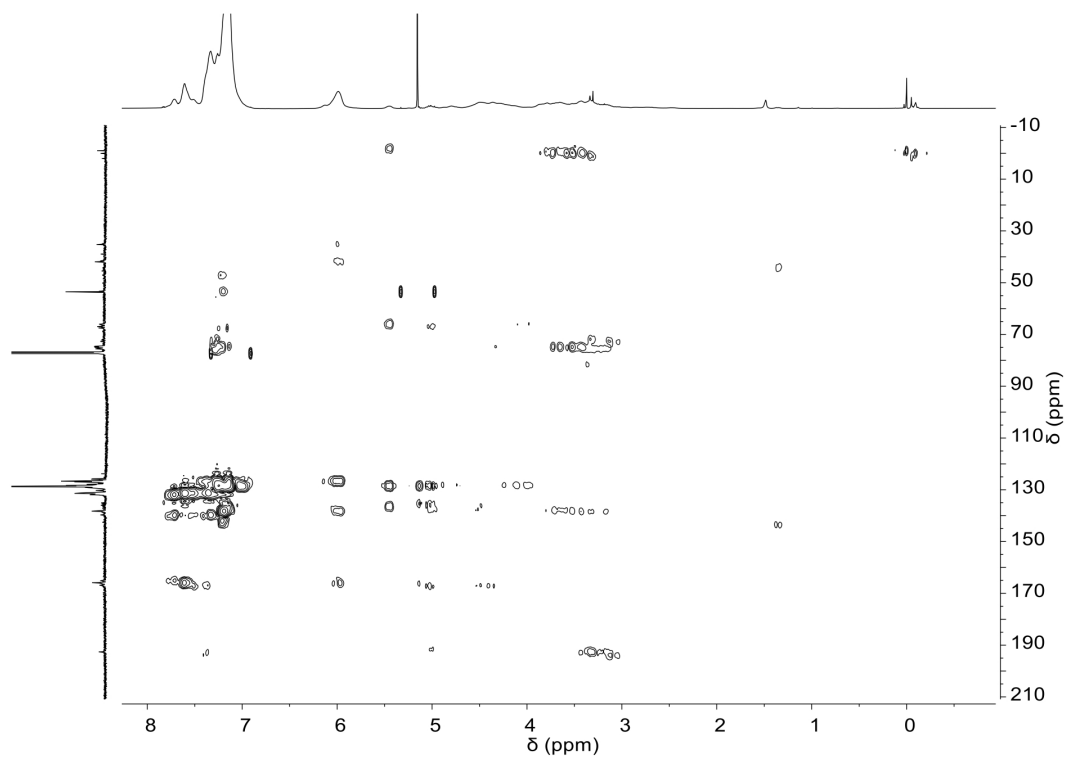


Figure S 34:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #6.

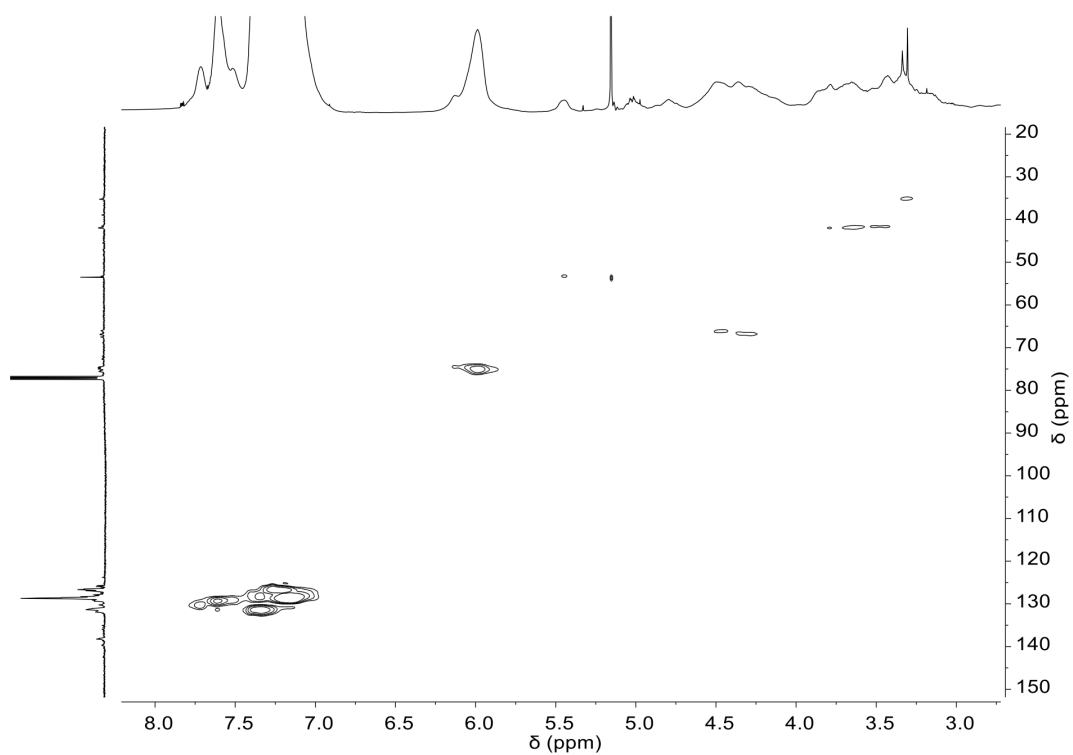


Figure S 35:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #6.

$M_n = 2 \text{ kg/mol}$   
 $M_w = 3 \text{ kg/mol}$   
 $\mathcal{D} = 1.5$   
 table 1 run #6

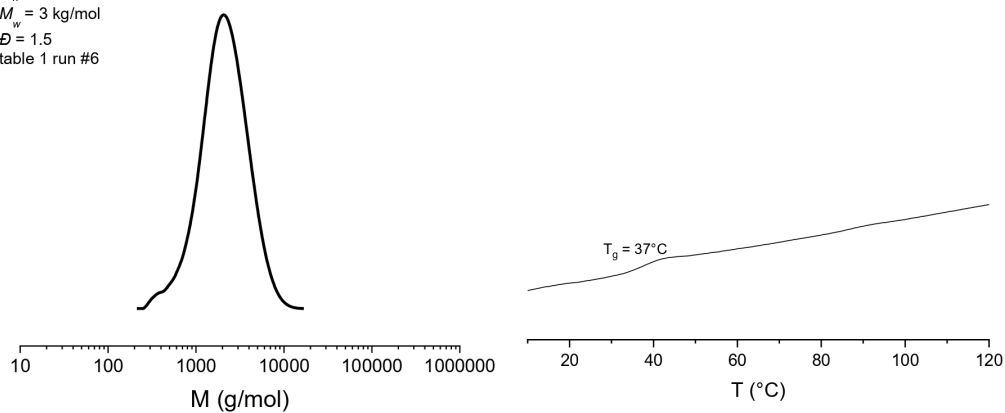


Figure S 36: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #6.

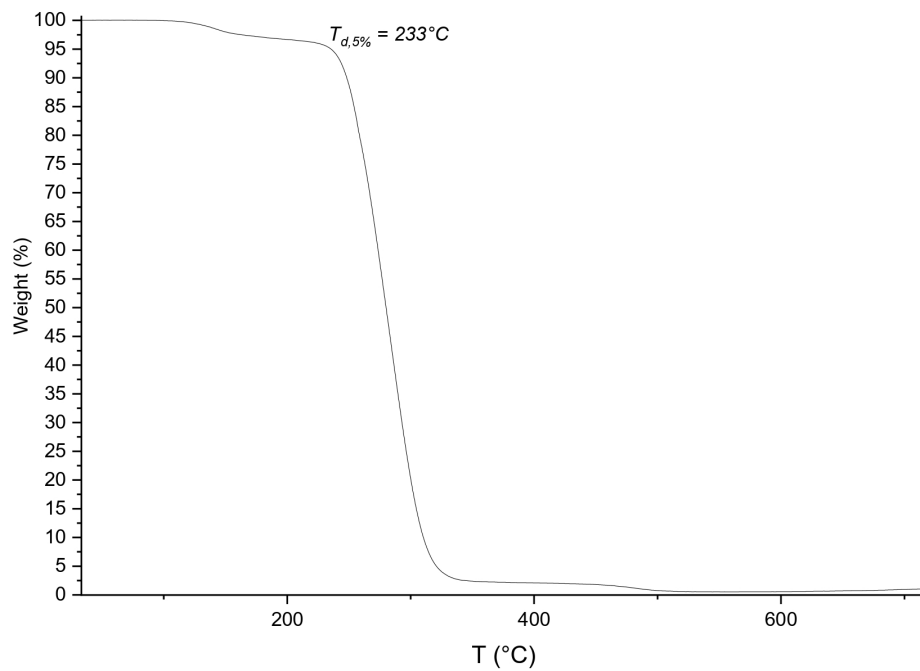


Figure S 37: TGA data of the precipitated polymer corresponding to table 1 run #6.

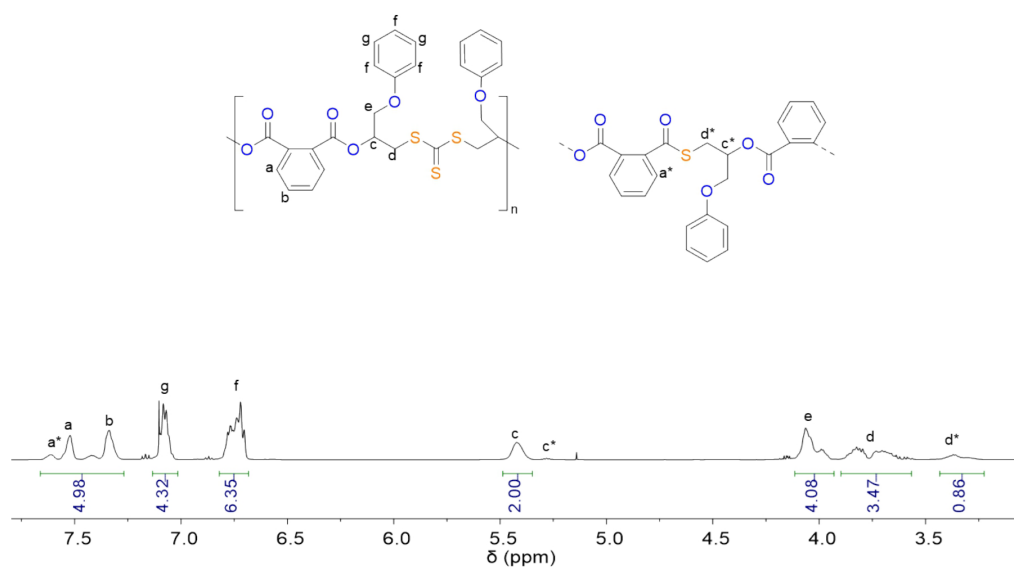


Figure S 38: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #7.

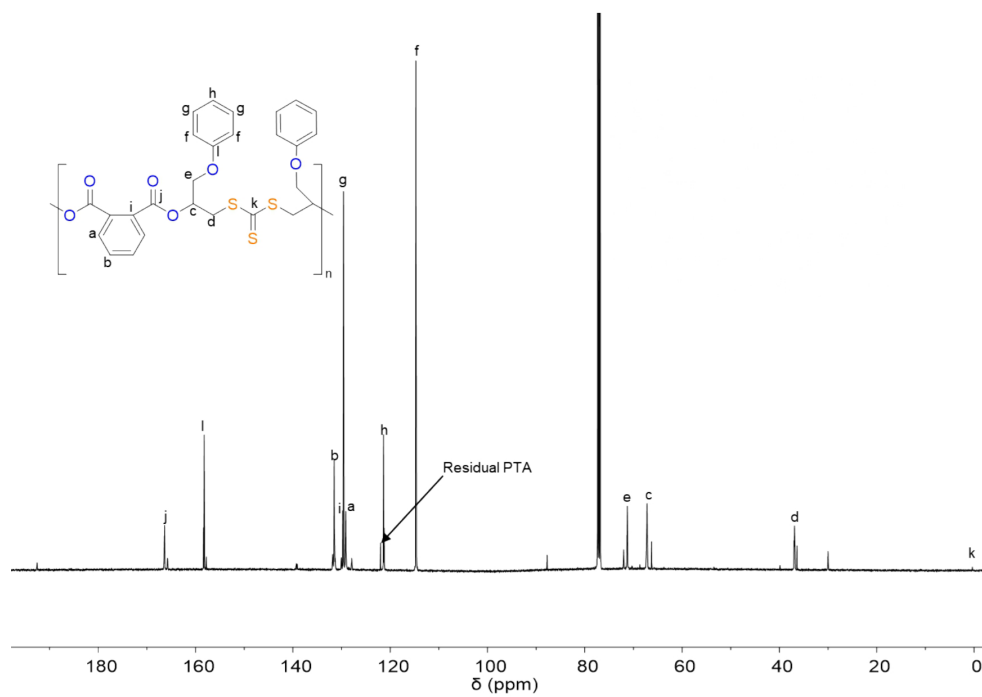


Figure S 39:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #7.

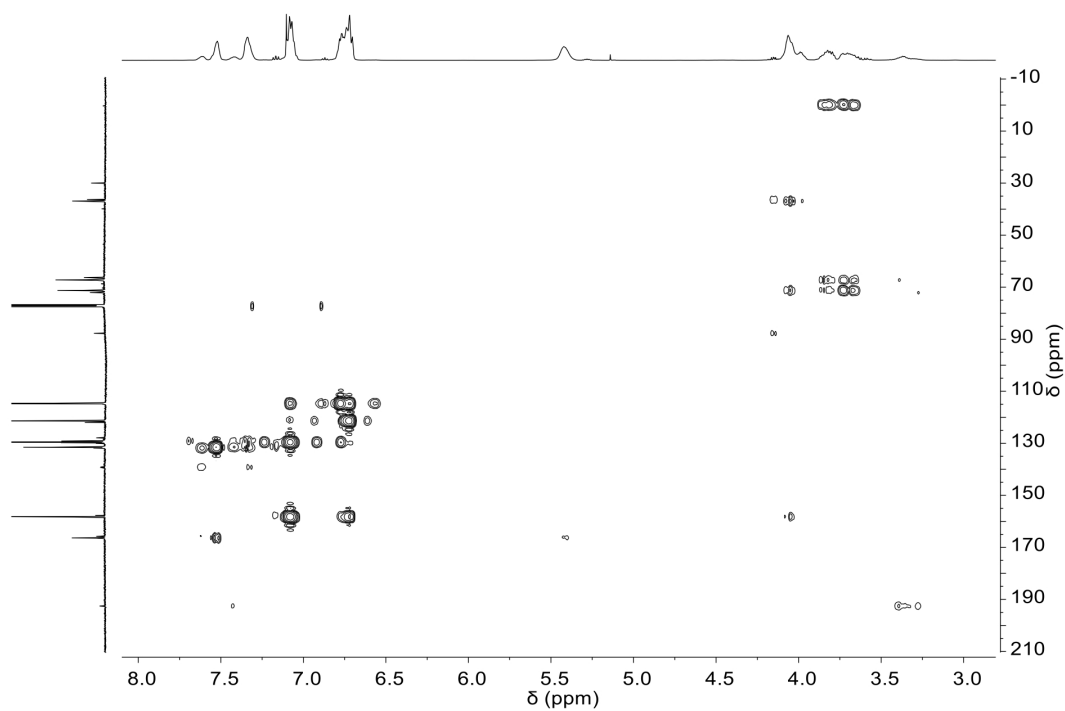


Figure S 40:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #7.



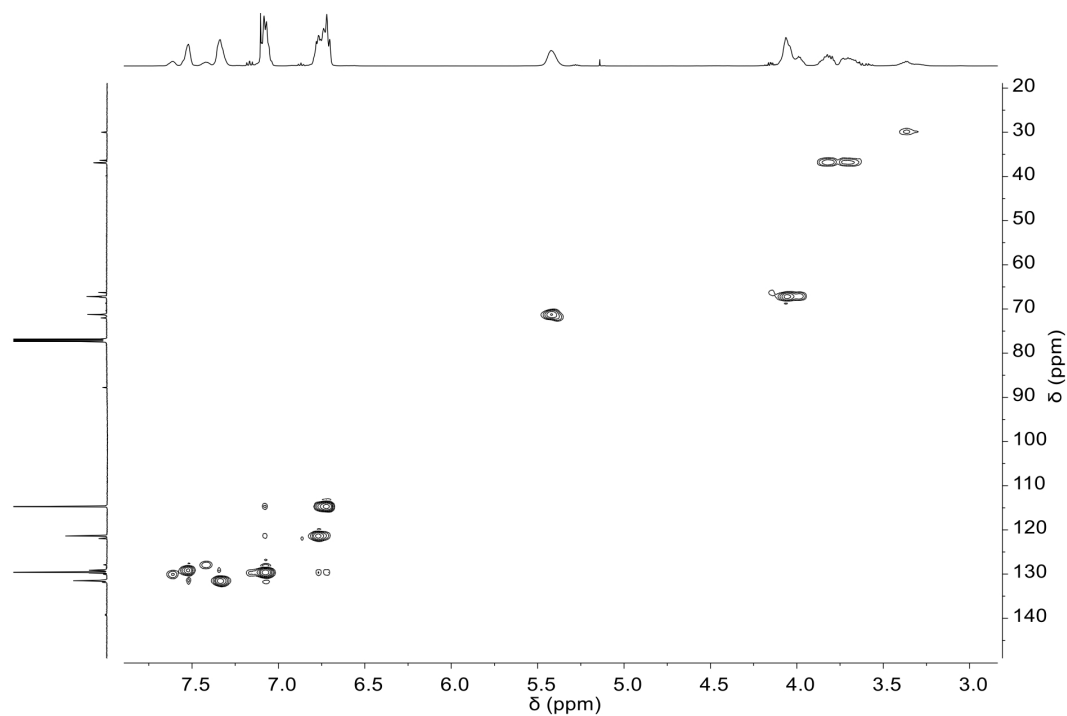


Figure S 41:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #7.

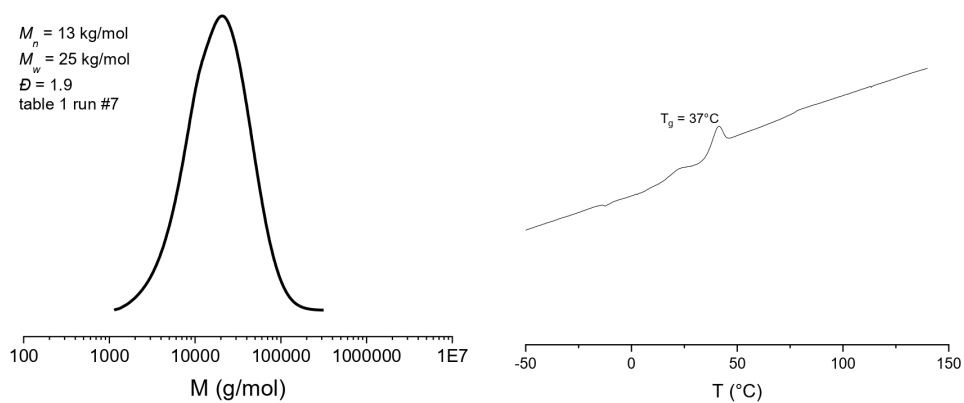


Figure S 42: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #7.

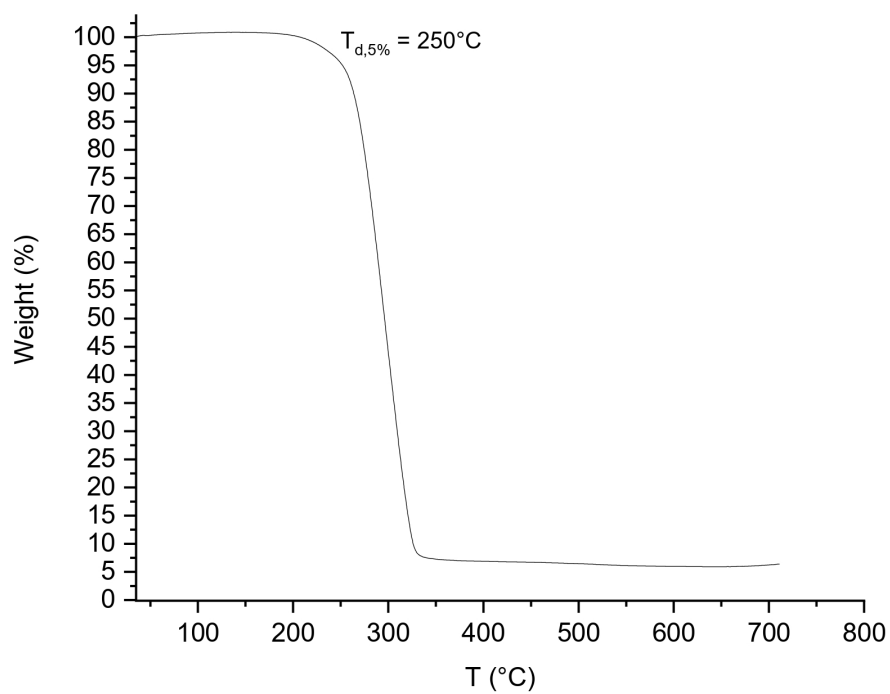


Figure S 43: TGA data of the precipitated polymer corresponding to table 1 run #7.

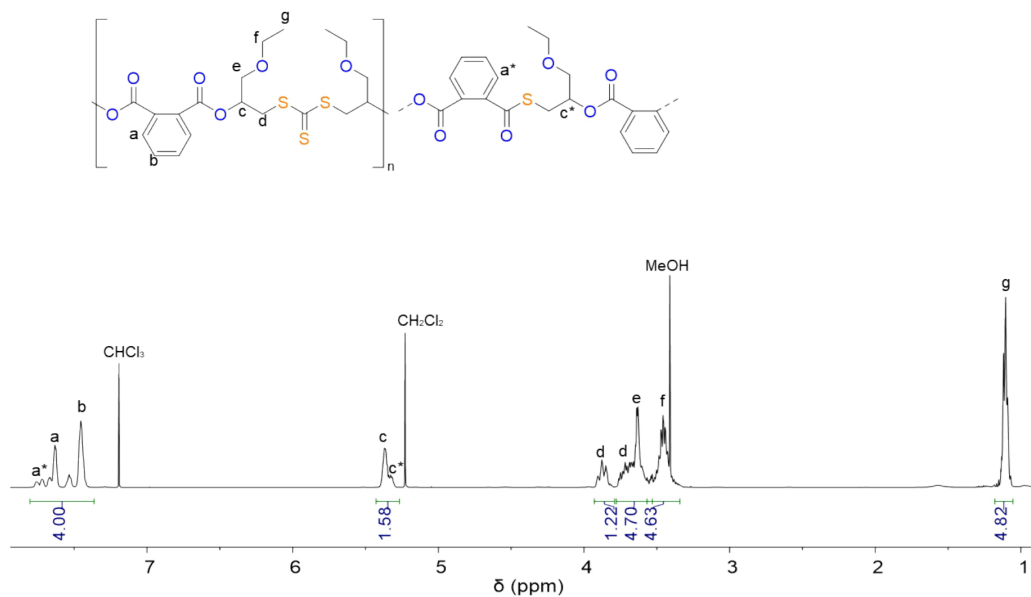


Figure S 44:  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to table 1 run #8.

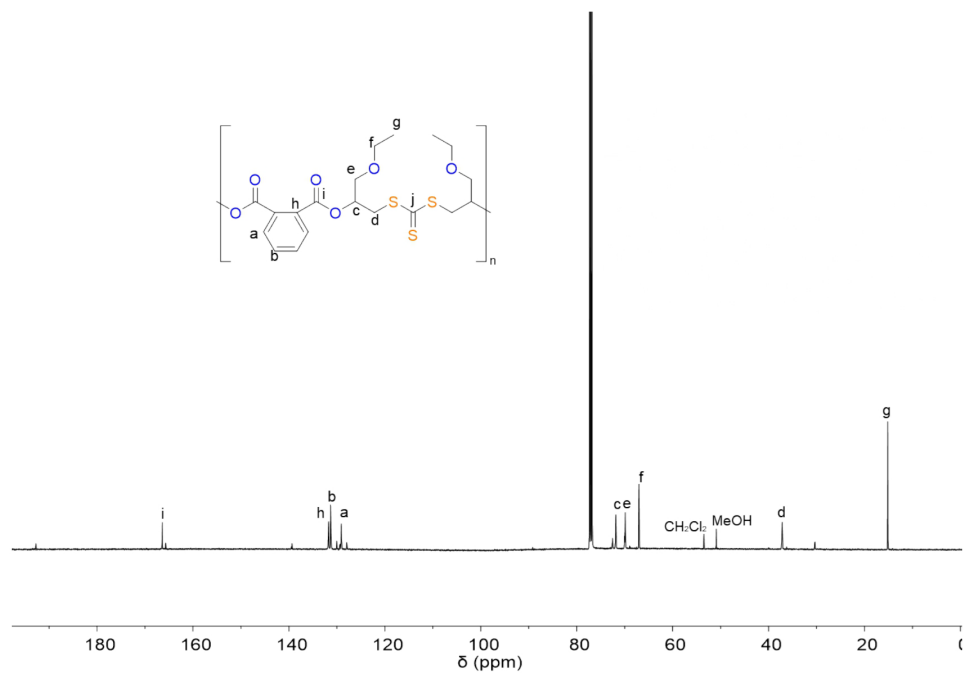


Figure S 45:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #8.

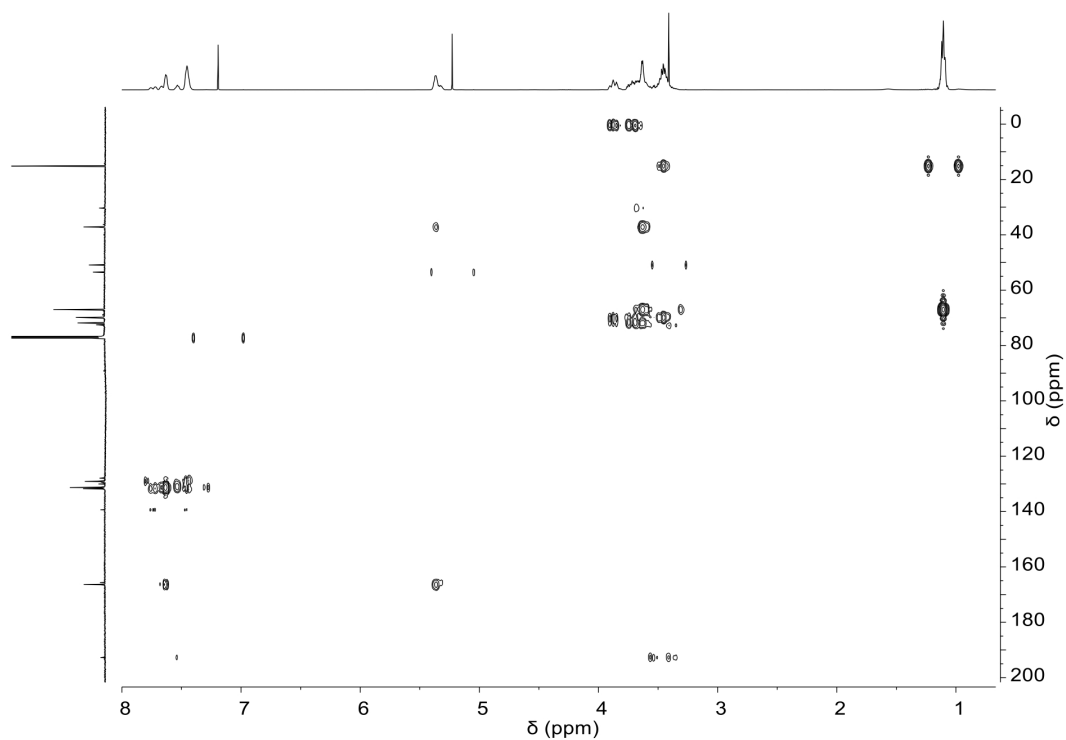


Figure S 46:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #8.

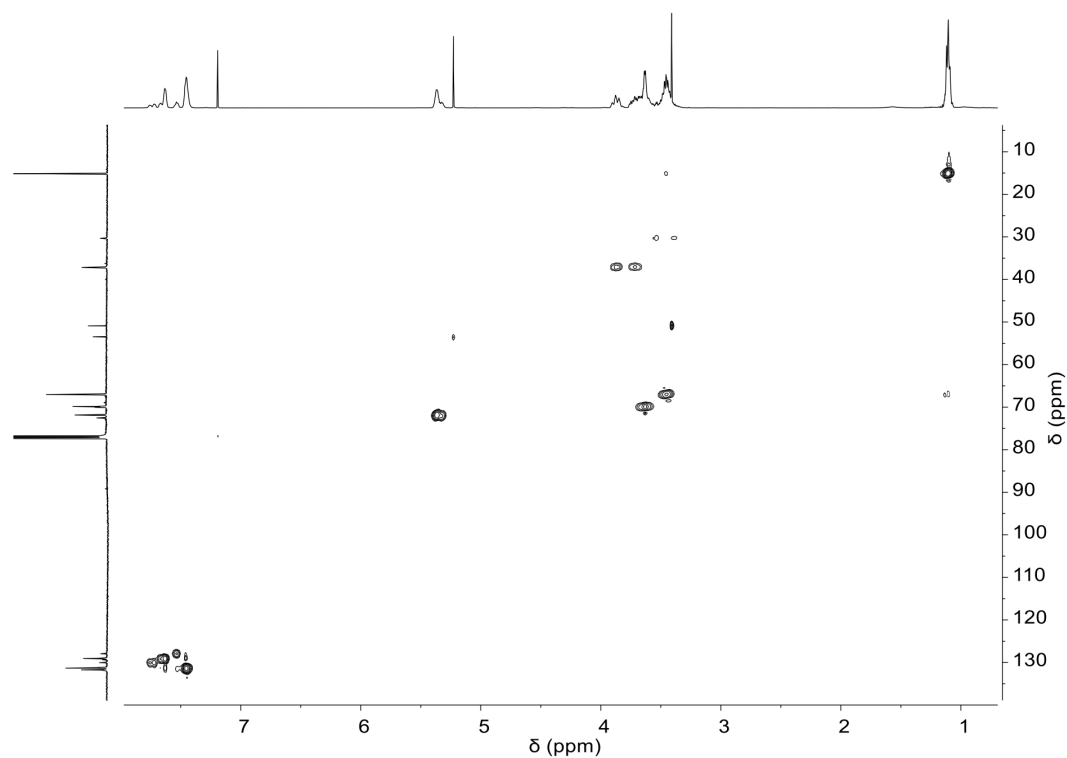


Figure S 47:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #8.

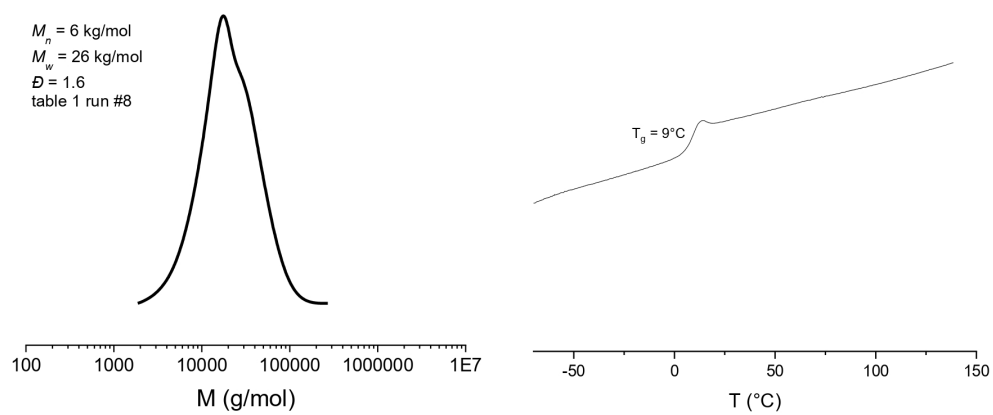


Figure S 48: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #8.

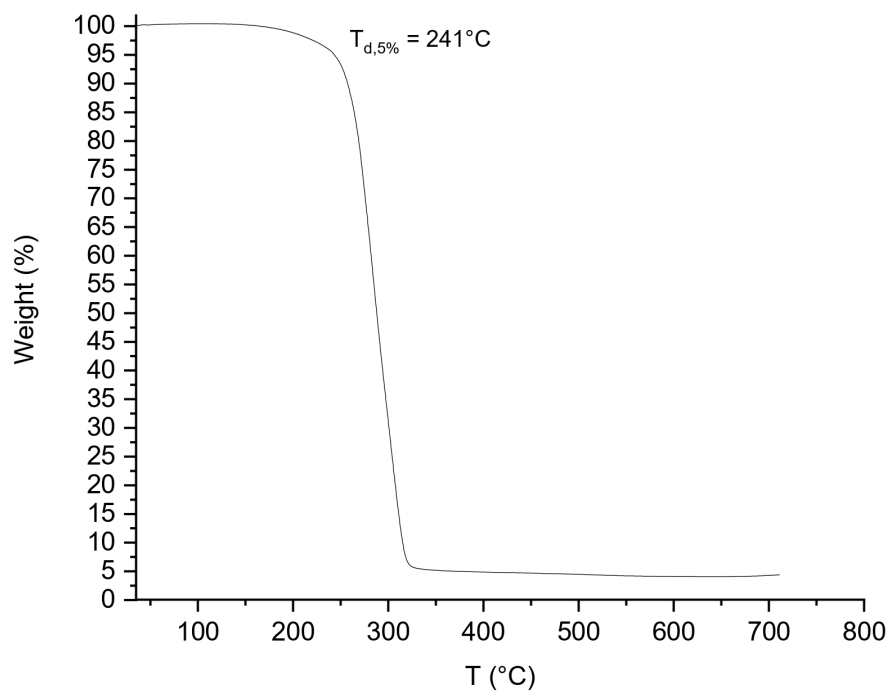


Figure S 49: TGA data of the precipitated polymer corresponding to table 1 run #8.

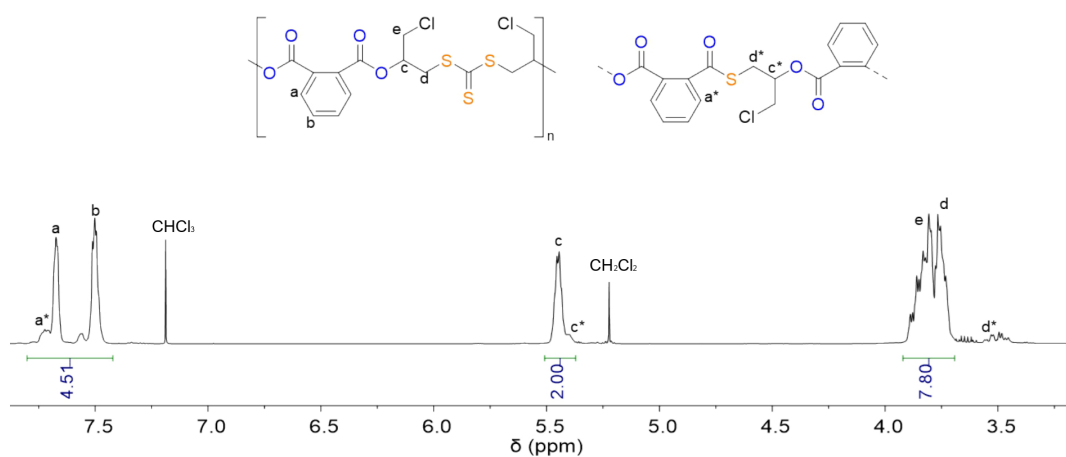


Figure S 50: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the crude mixture (top) and precipitated polymer corresponding to table 1 run #9.

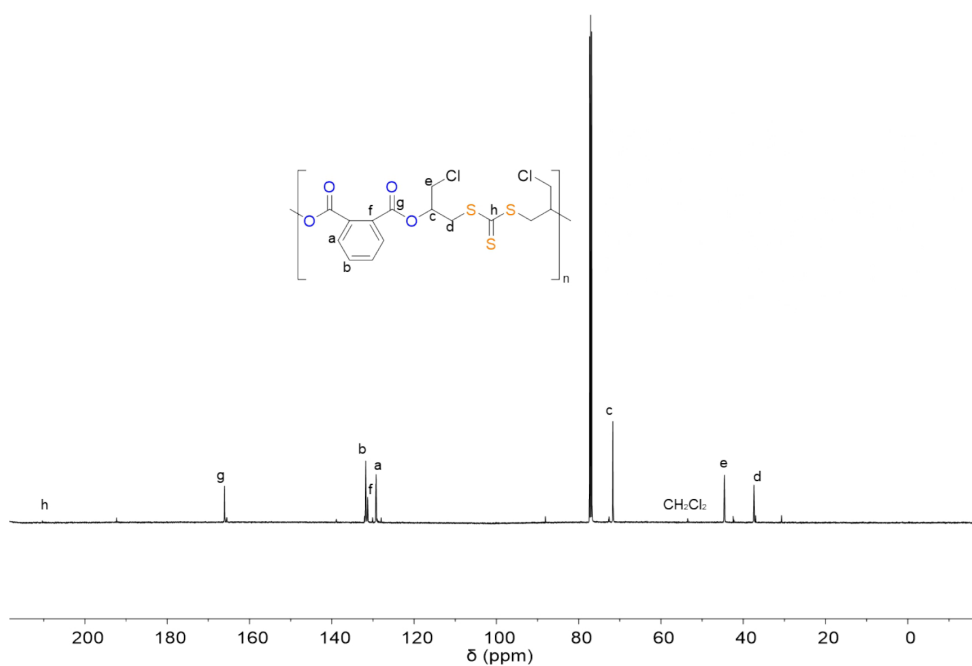


Figure S 51: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #9.

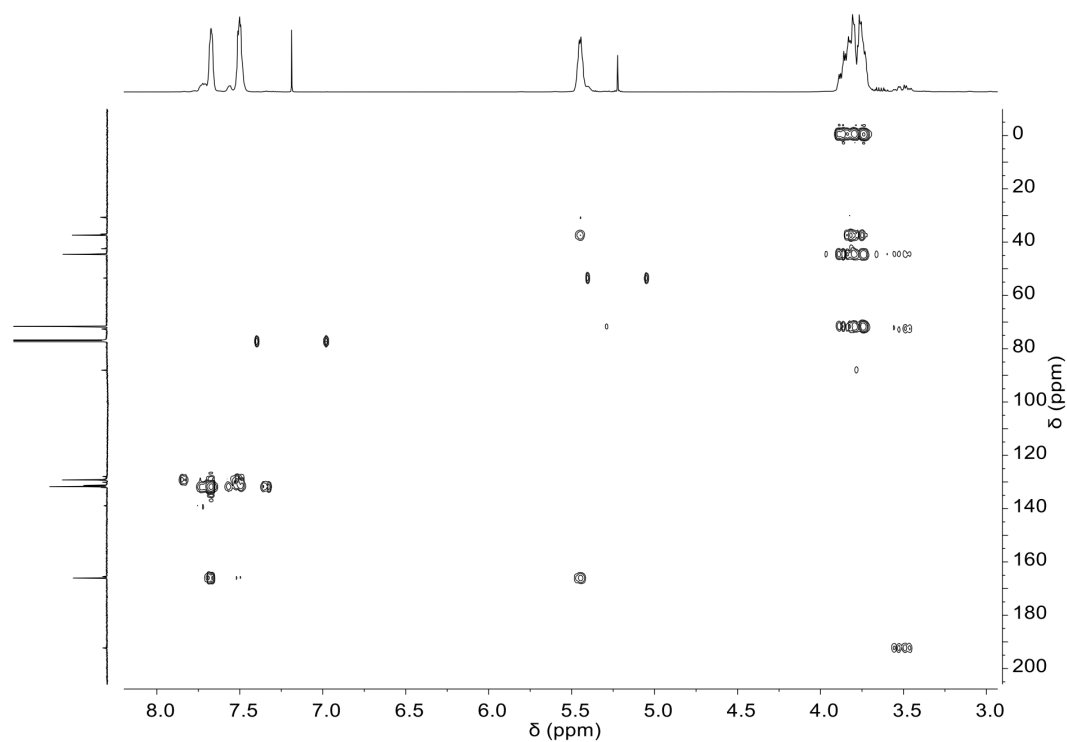


Figure S 52:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #9.

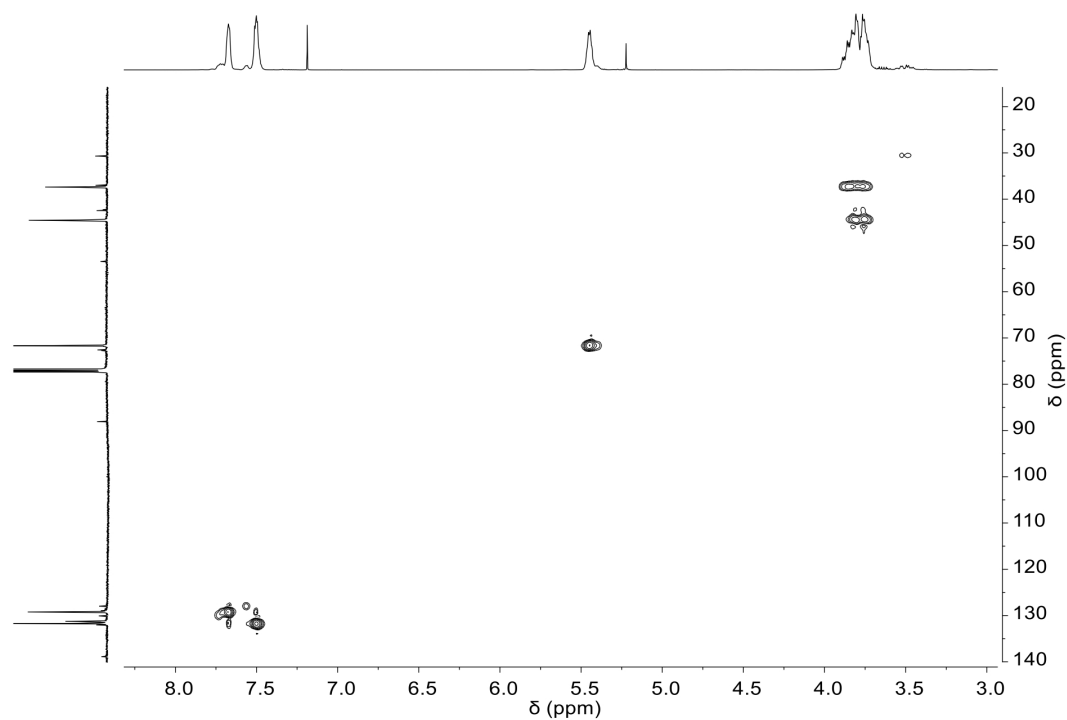


Figure S 53:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #9.

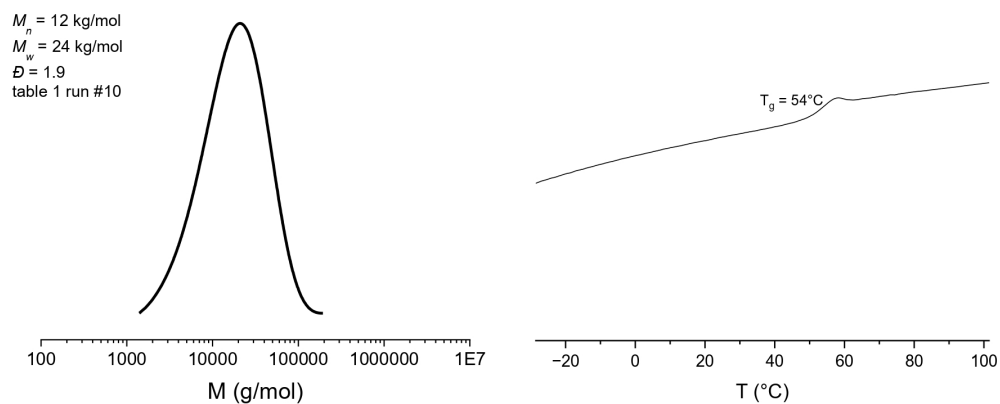


Figure S 54: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #9.

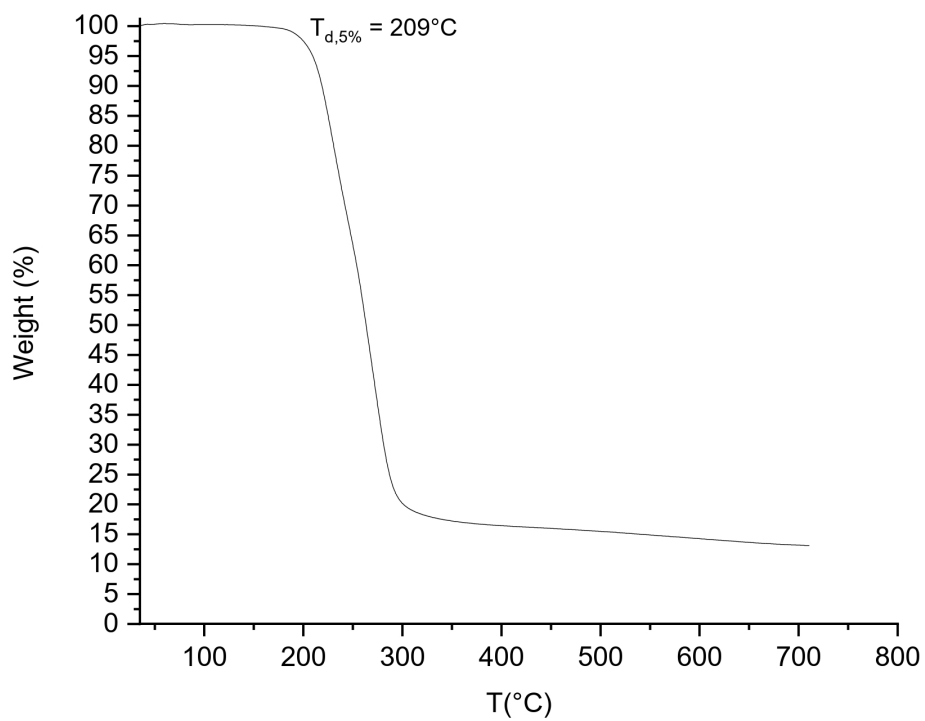


Figure S 55: TGA data of the precipitated polymer corresponding to table 1 run #9.



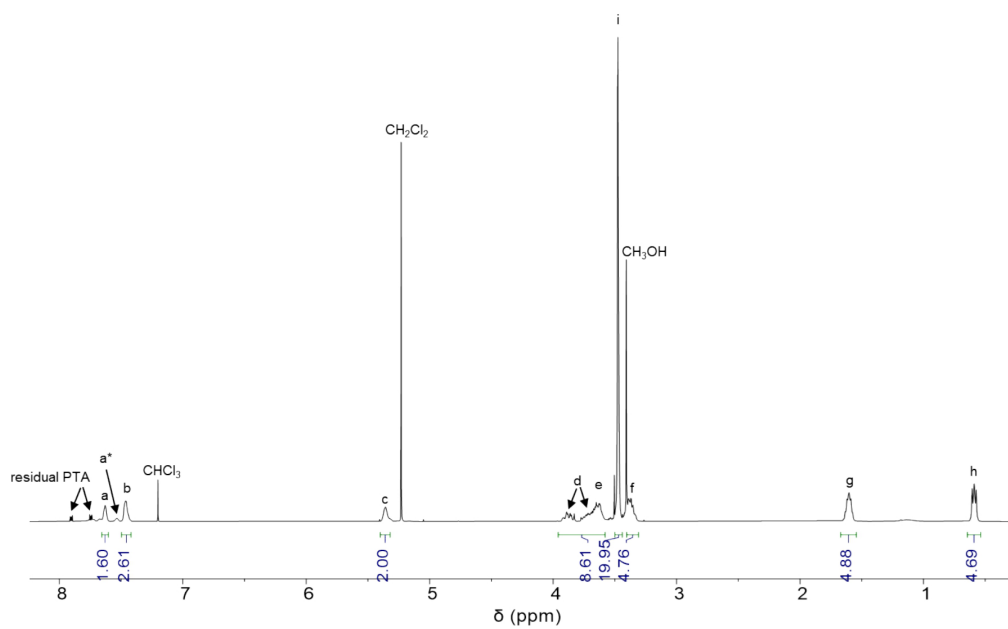


Figure S 56:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25°C) of the crude mixture (top) and precipitated polymer corresponding to table 1 run #10.

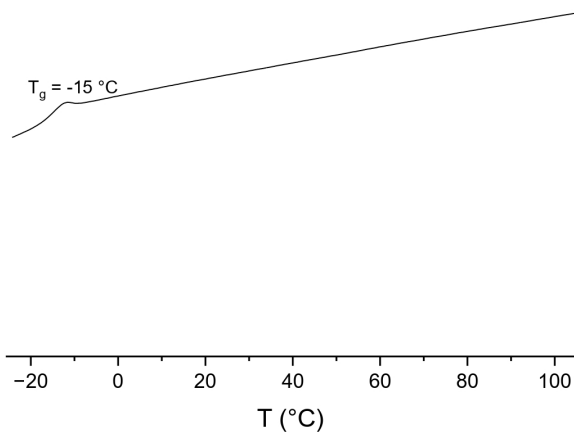


Figure S 57: DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #10.

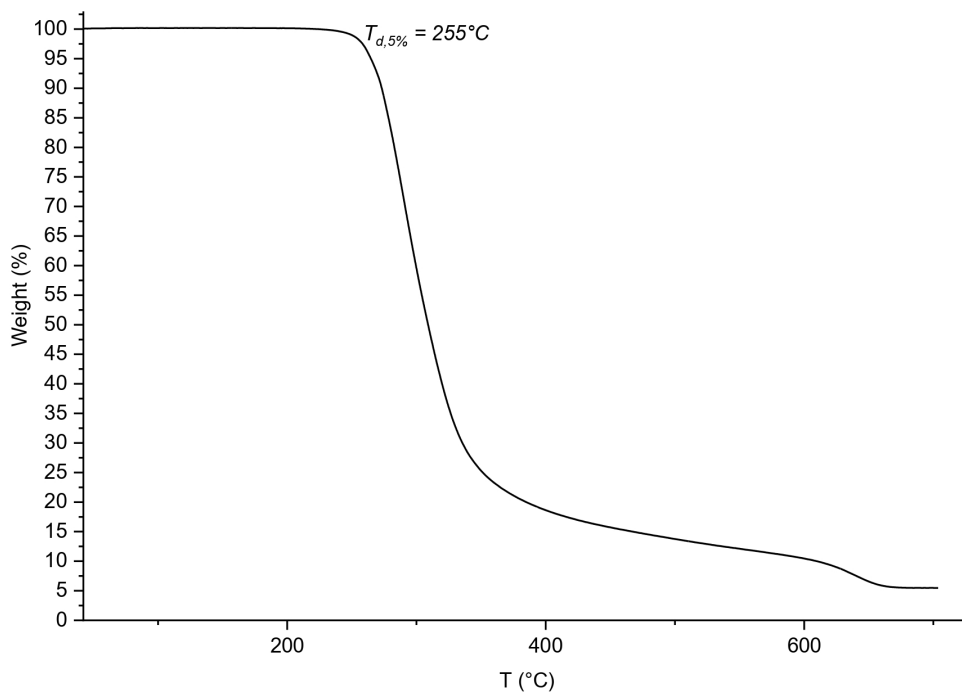


Figure S 58: TGA data of the precipitated polymer corresponding to table 1 run #10.

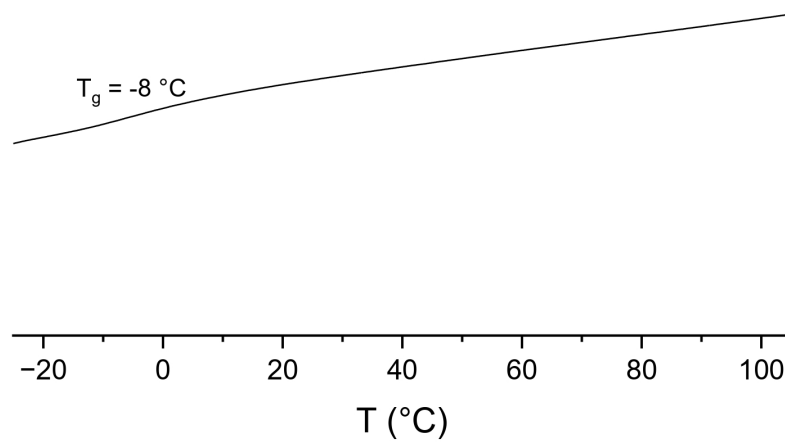


Figure S 59: DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #10 after cross linking.

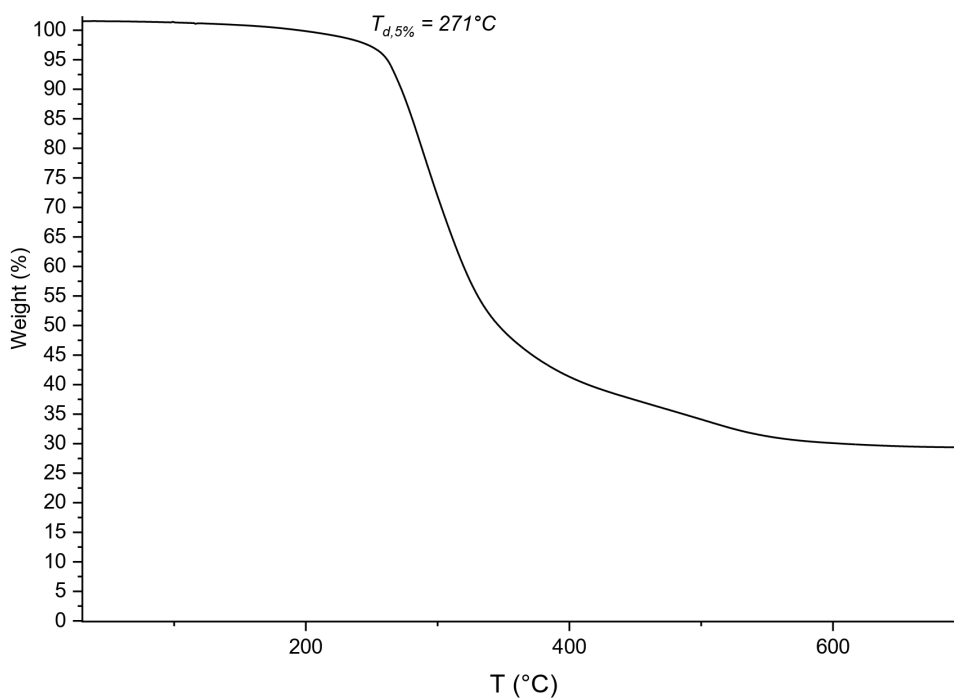


Figure S 60: TGA data of the precipitated polymer corresponding to table 1 run #10 after cross linking.

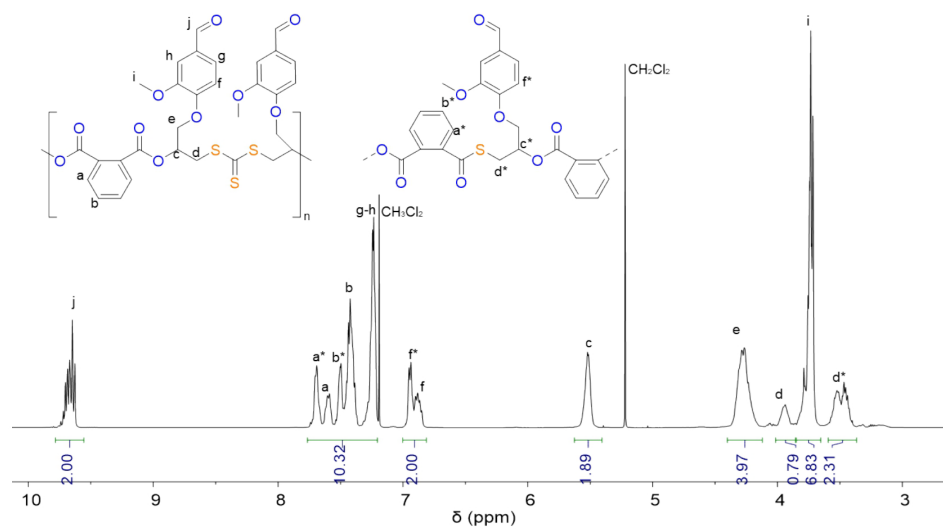


Figure S 61:  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to table 1 run #11.

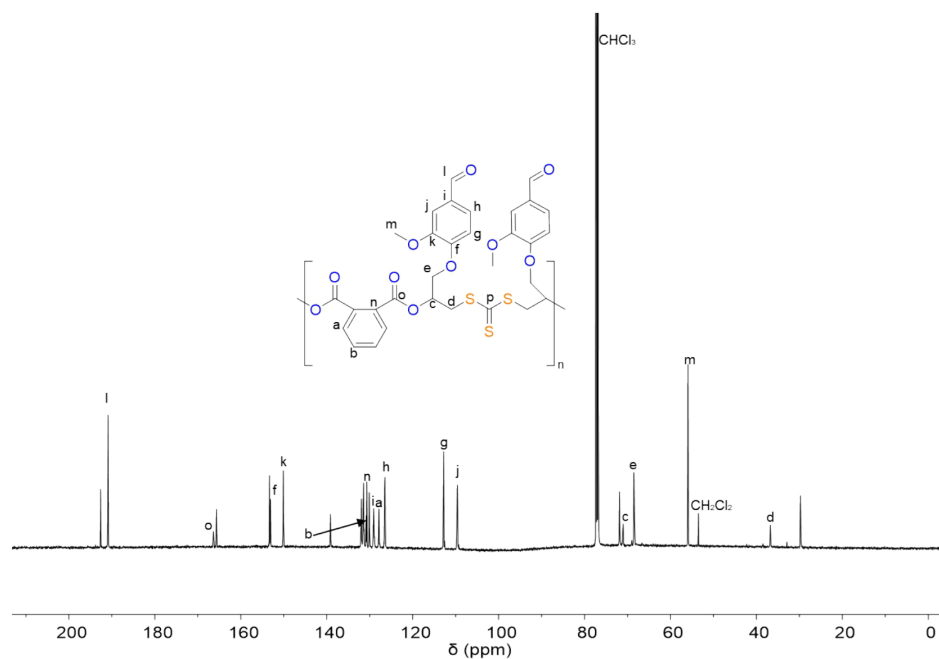


Figure S 62:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #11.

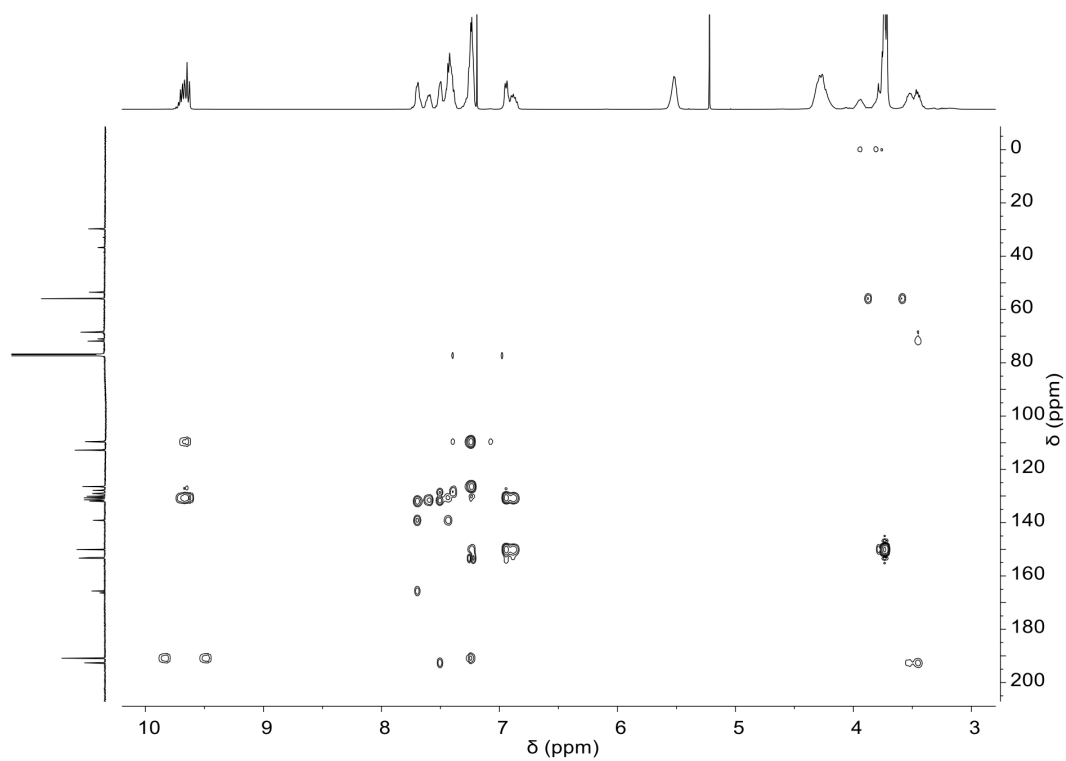


Figure S 63:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #11.

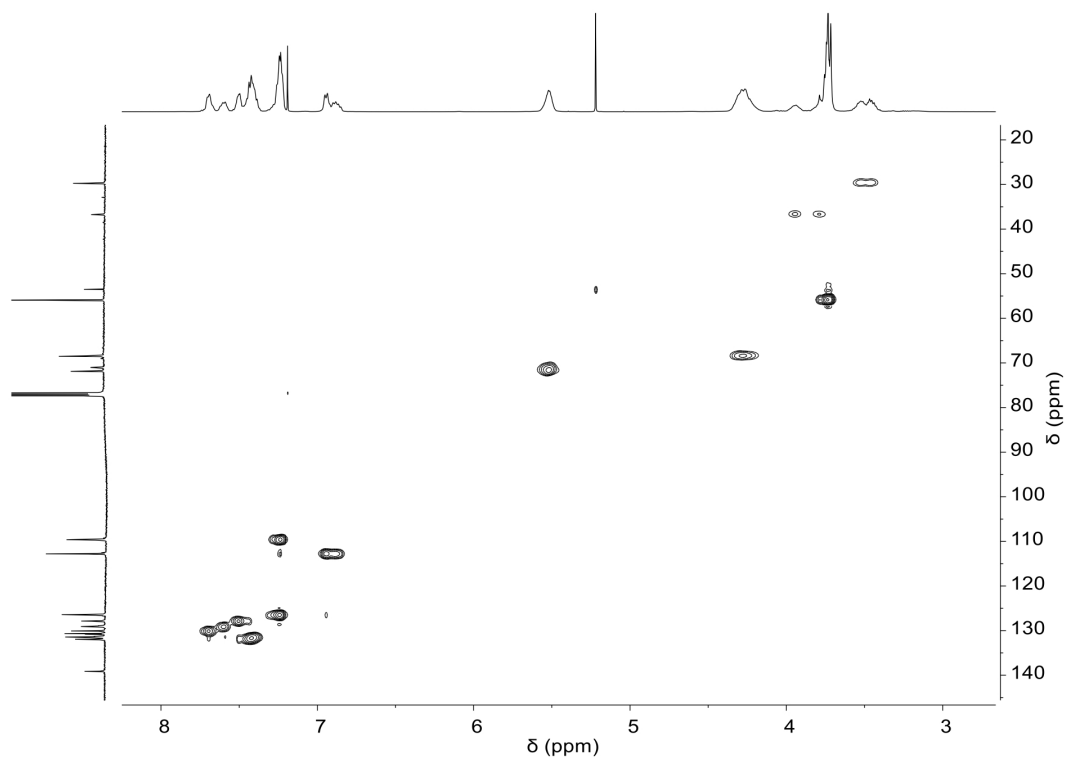


Figure S 64:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #11.

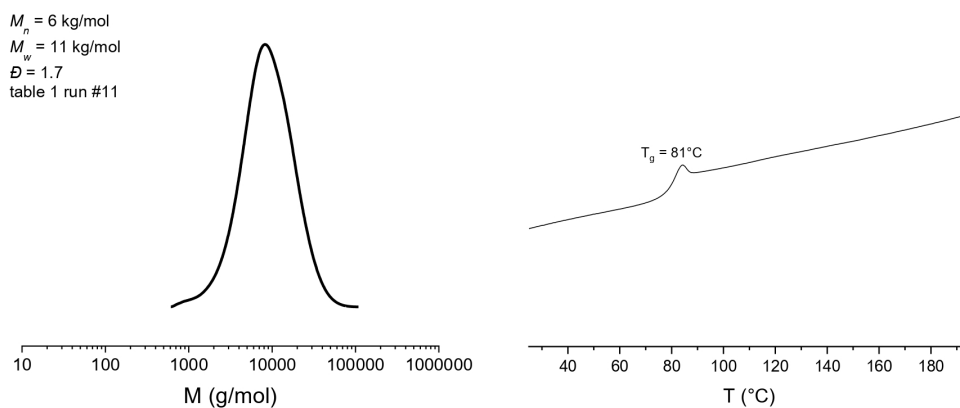


Figure S 65: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #11.

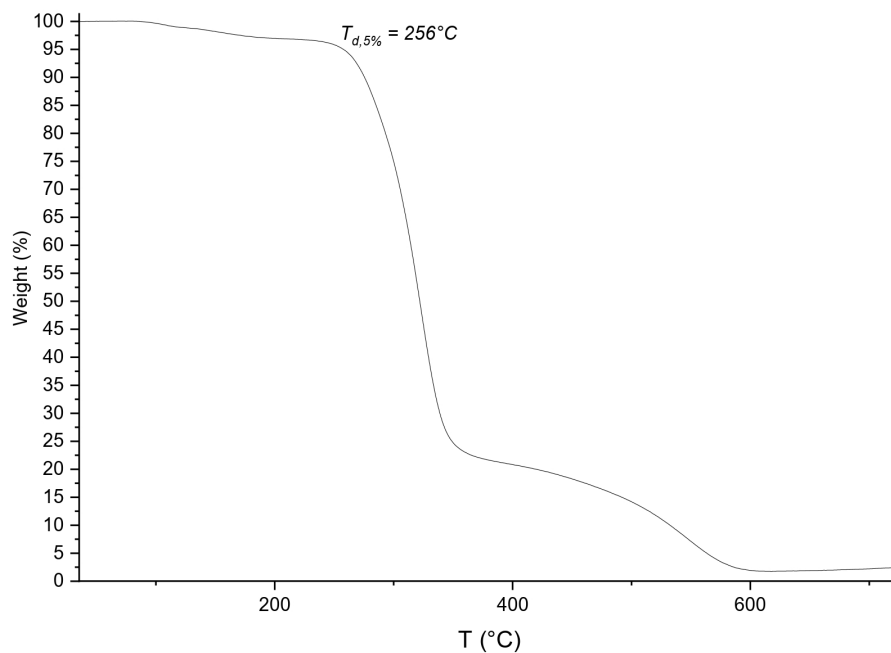


Figure S 66: TGA data of the precipitated polymer corresponding to table 1 run #11.

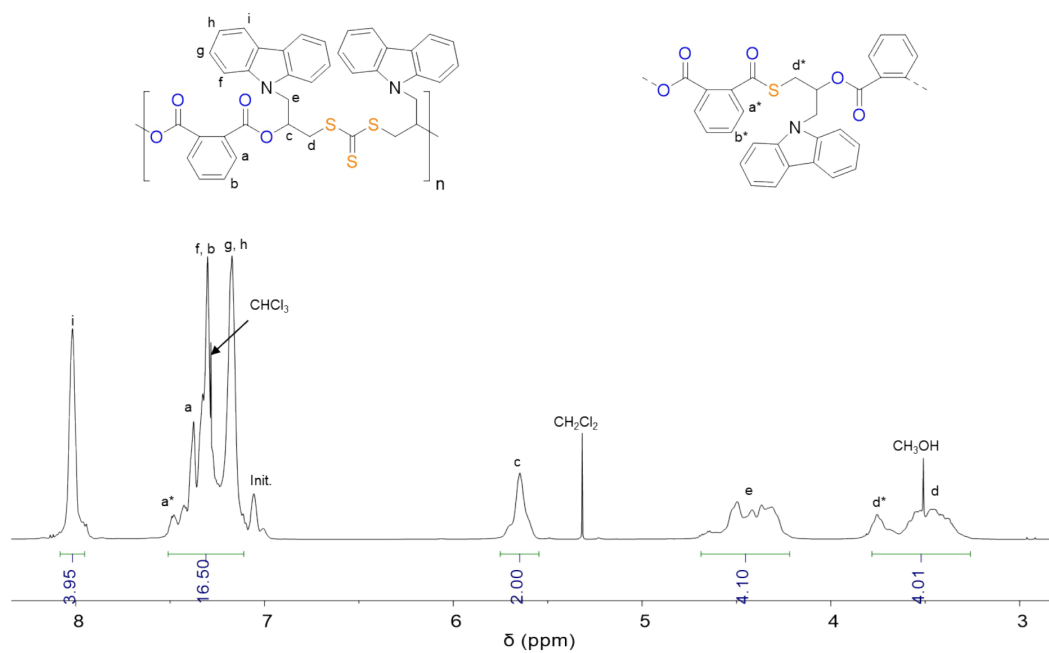


Figure S 67:  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to table 1 run #12.

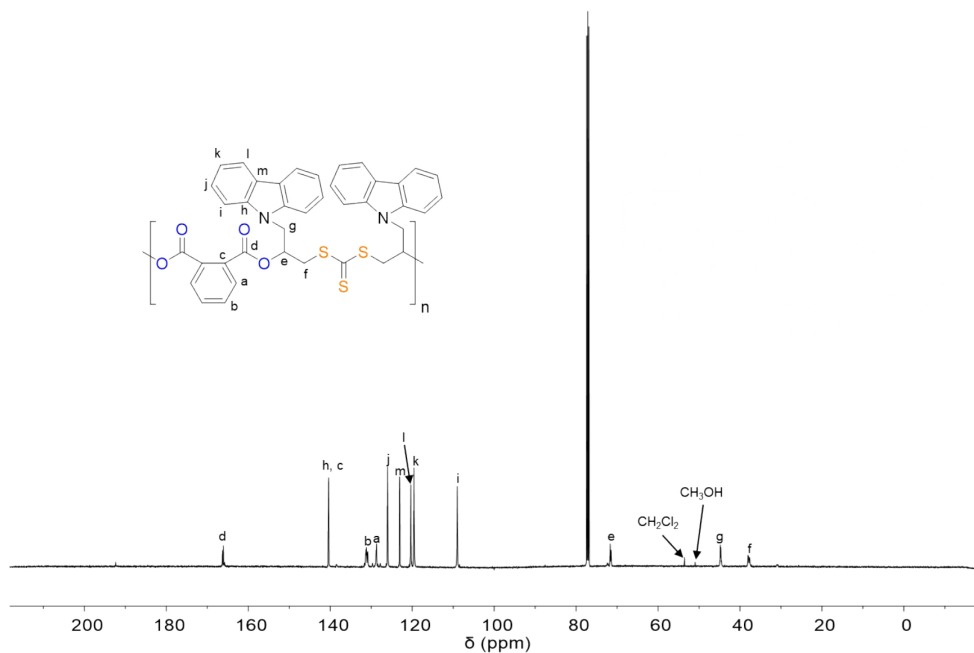


Figure S 68:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #12.

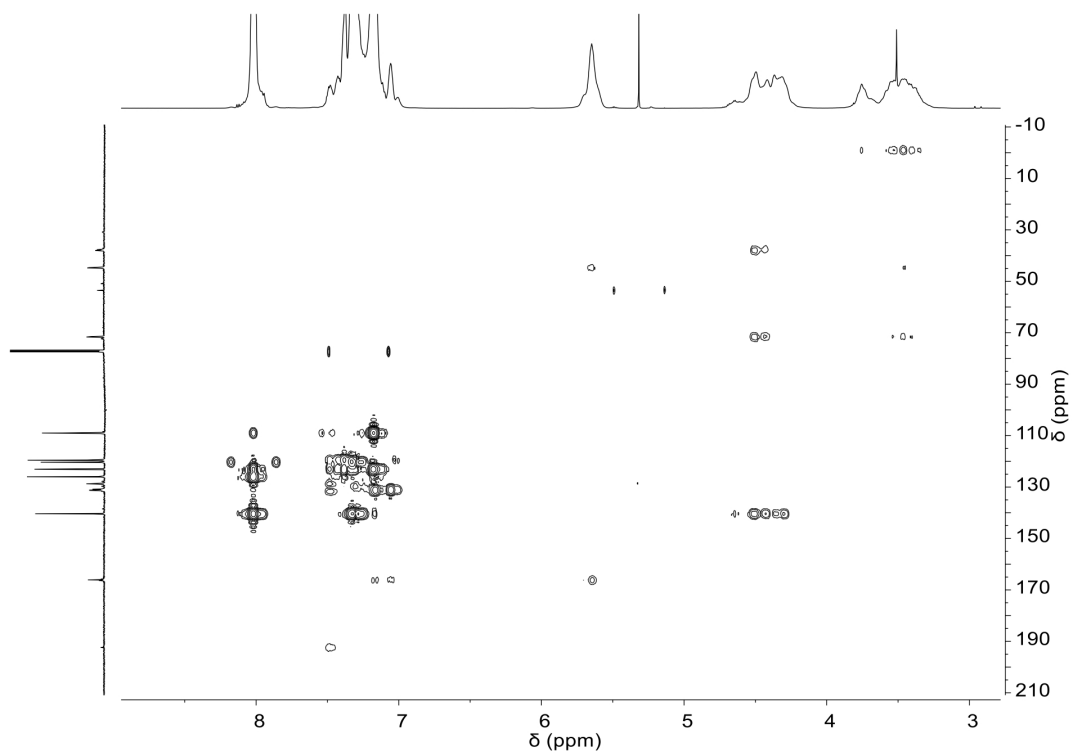


Figure S 69:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #12.

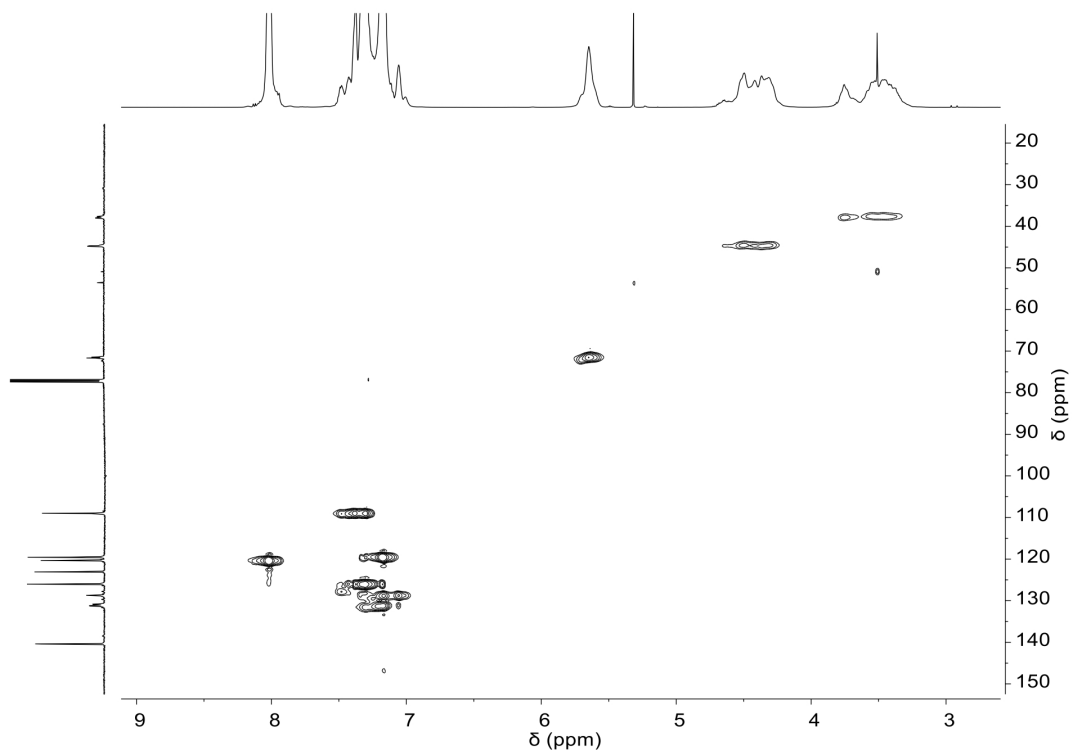


Figure S 70:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #12.

$M_n = 26 \text{ kg/mol}$   
 $M_w = 35 \text{ kg/mol}$   
 $\bar{D} = 1.3$   
 table 1 run #12

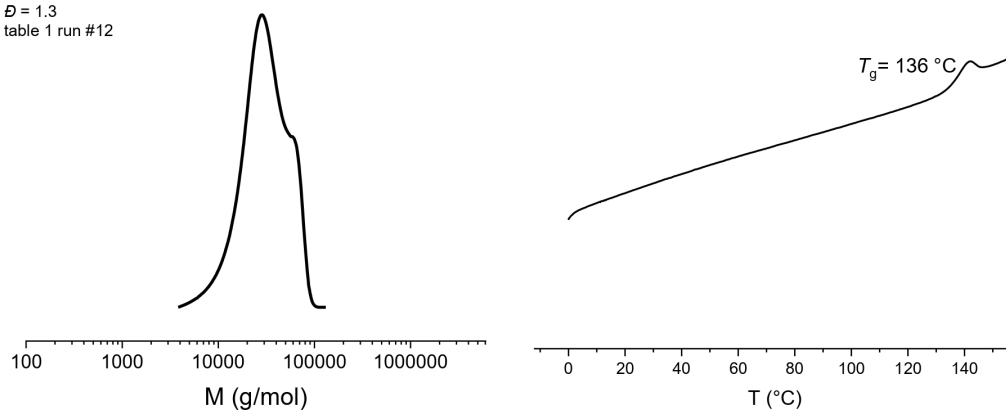


Figure S 71: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #12.



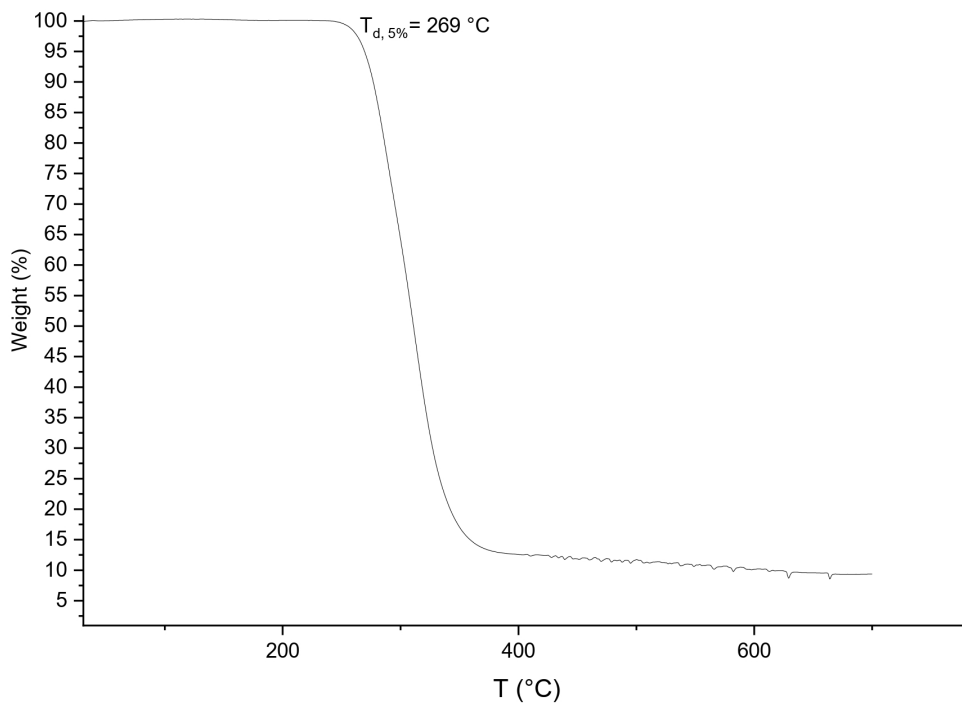


Figure S 72: TGA data of the precipitated polymer corresponding to table 1 run #12.

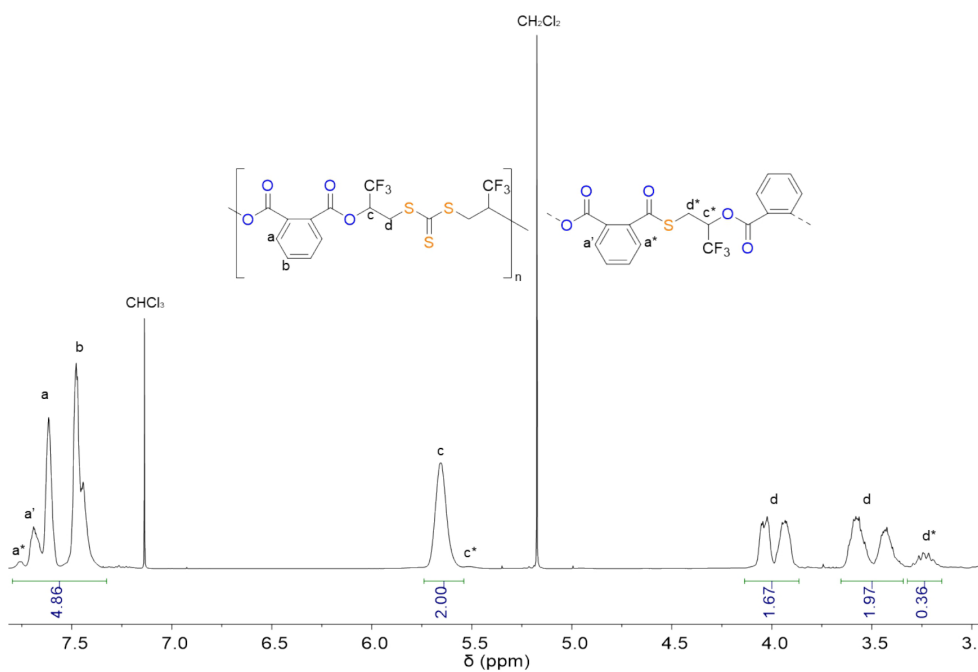


Figure S 73: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #13.

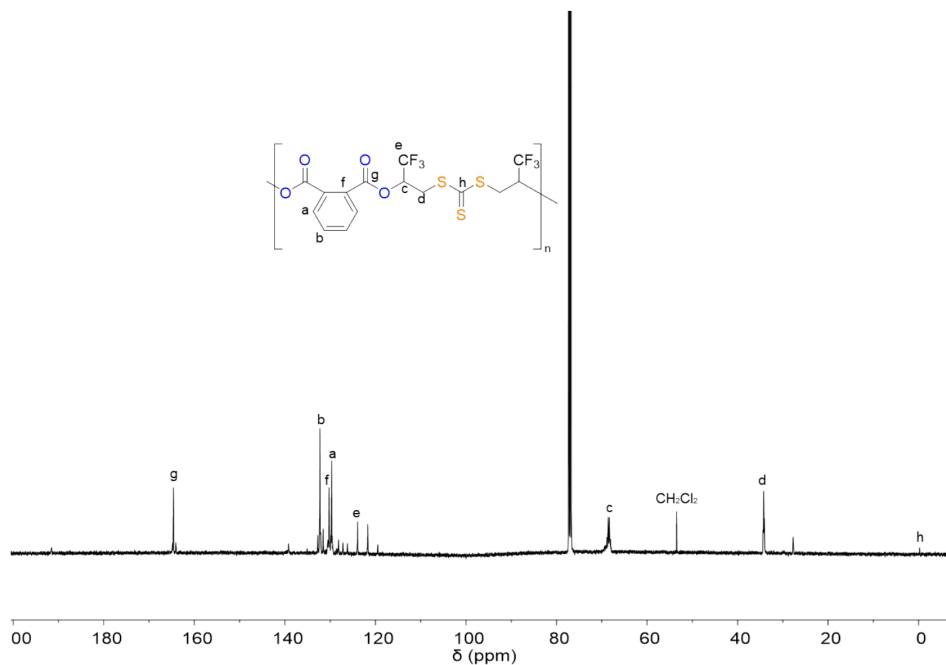


Figure S 74:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #13.

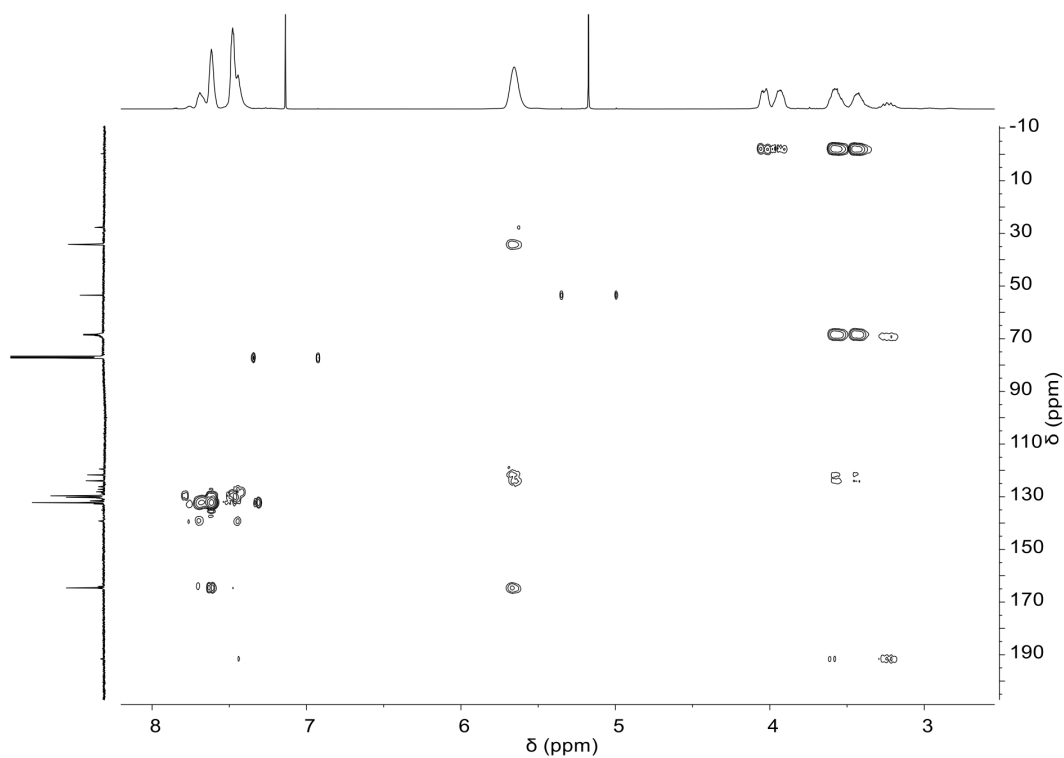


Figure S 75:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #13.

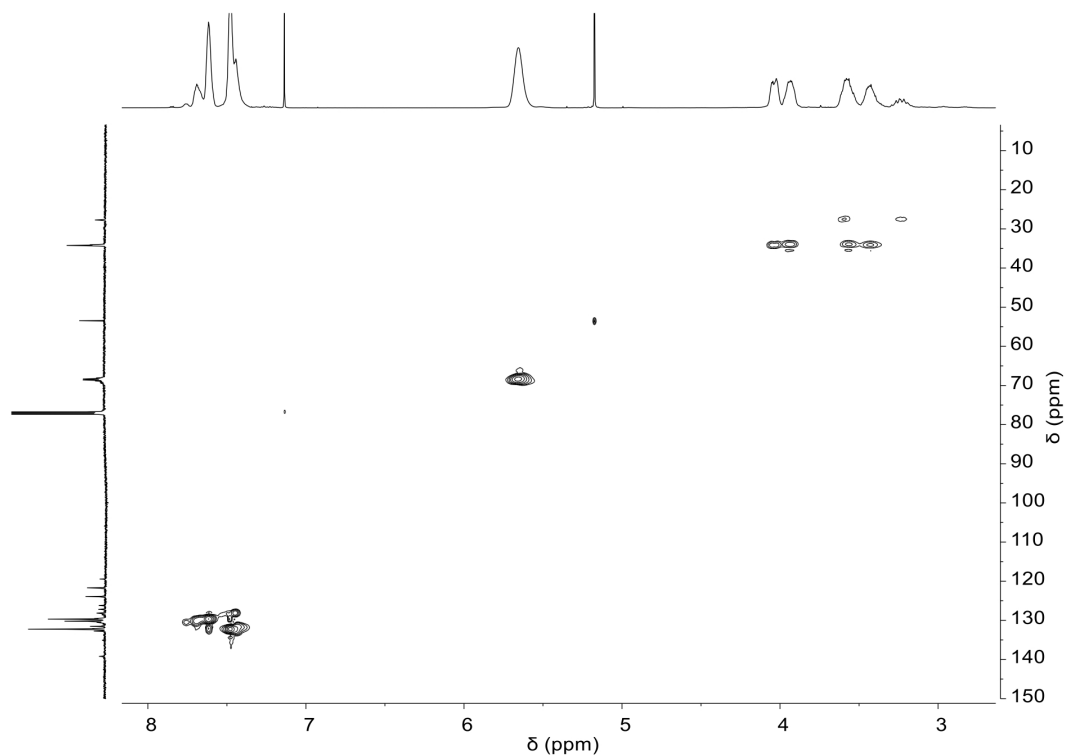


Figure S 76:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #13.

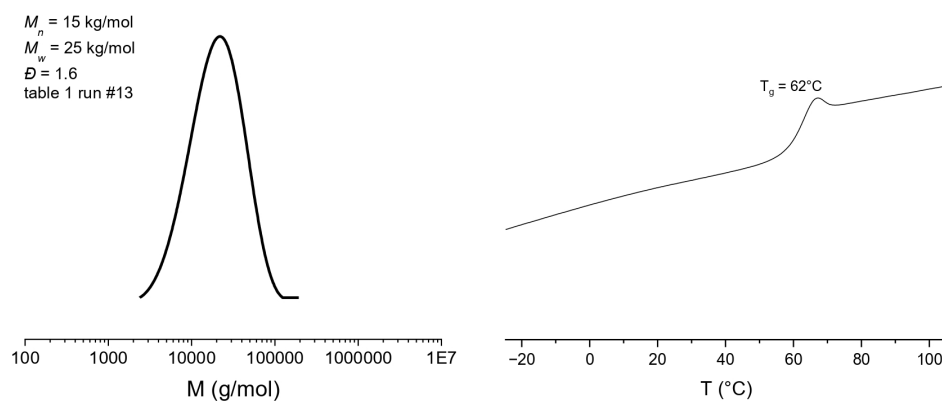


Figure S 77: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #13.

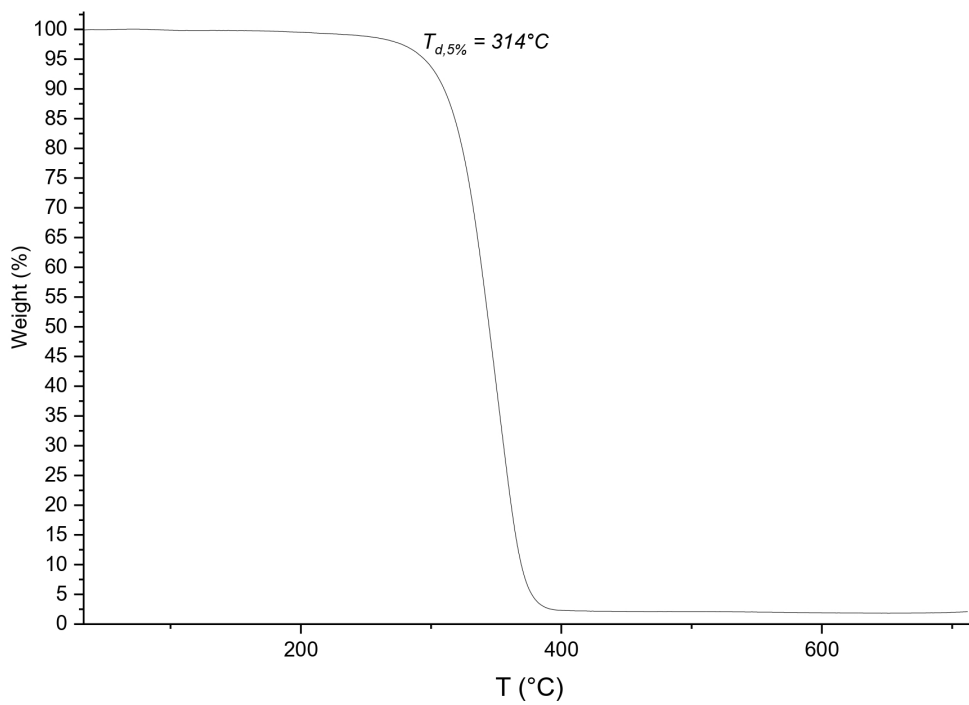


Figure S 78: TGA data of the precipitated polymer corresponding to table 1 run #13.

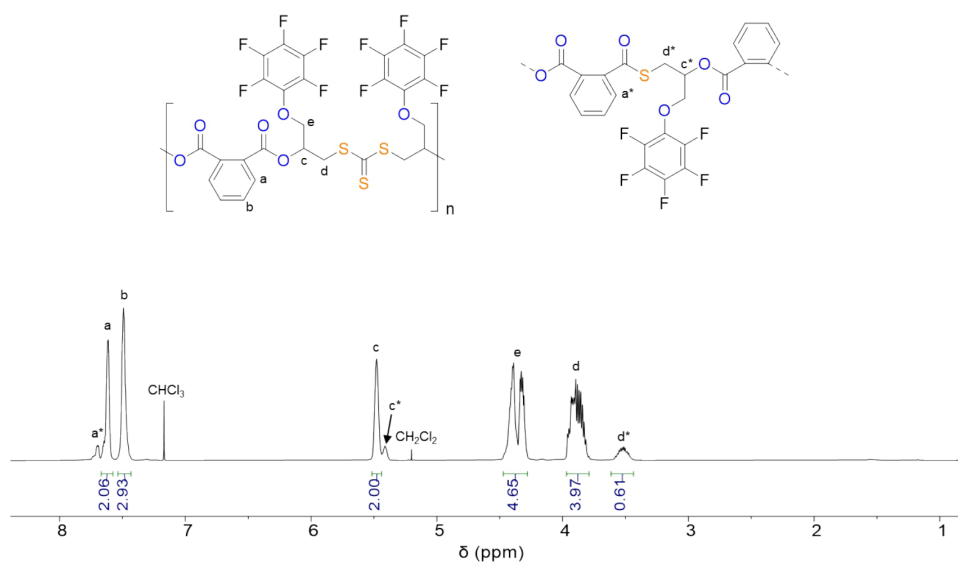


Figure S 79: <sup>1</sup>H-NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #14.

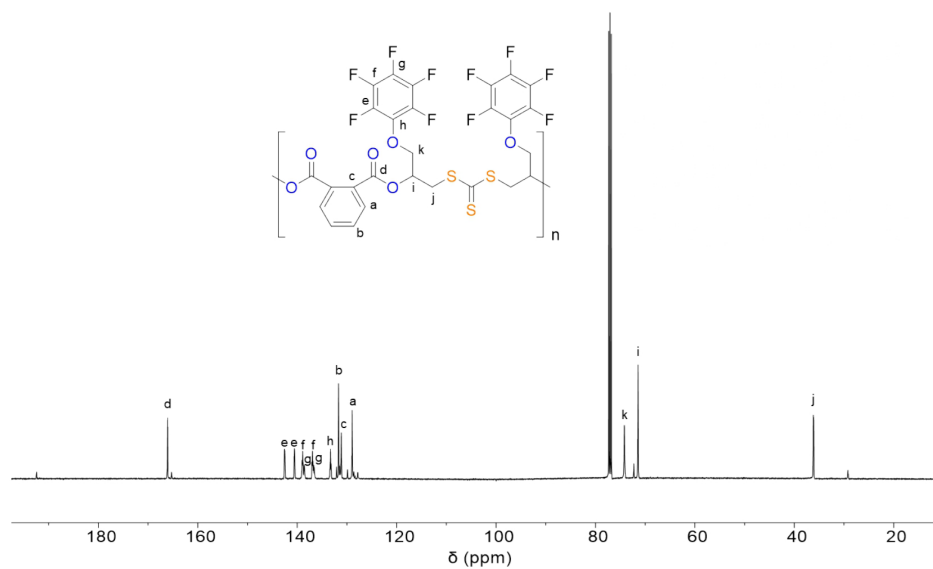


Figure S 80:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #14.

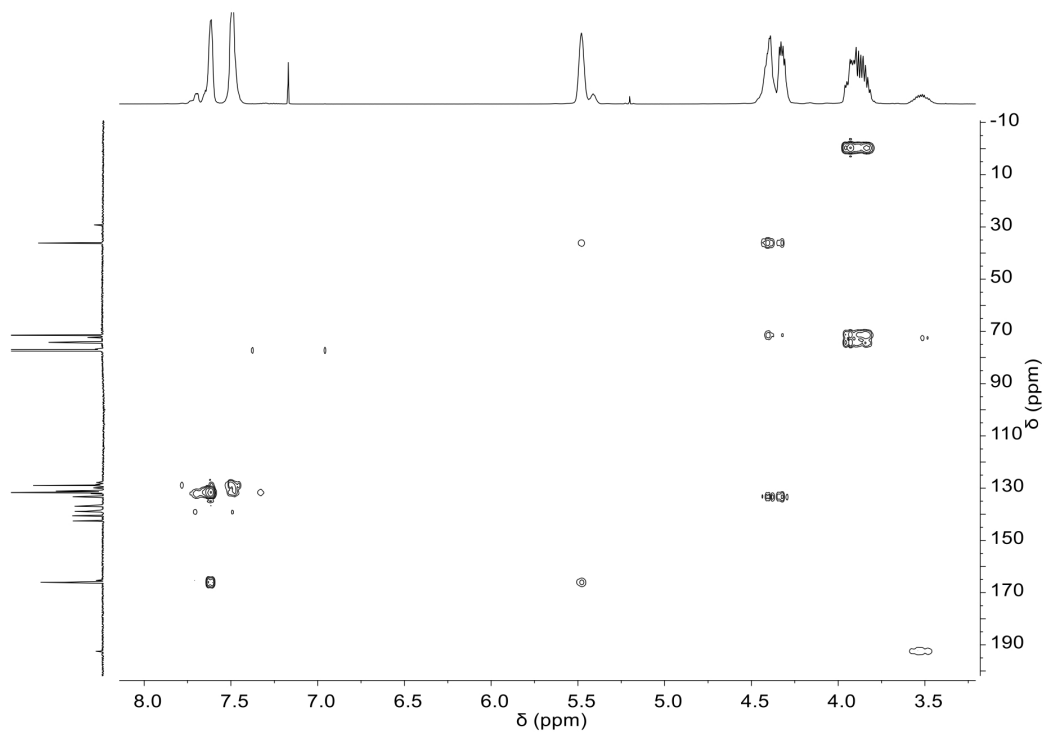


Figure S 81:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ , 25°C) of the precipitated polymer corresponding to table 1 run #14.

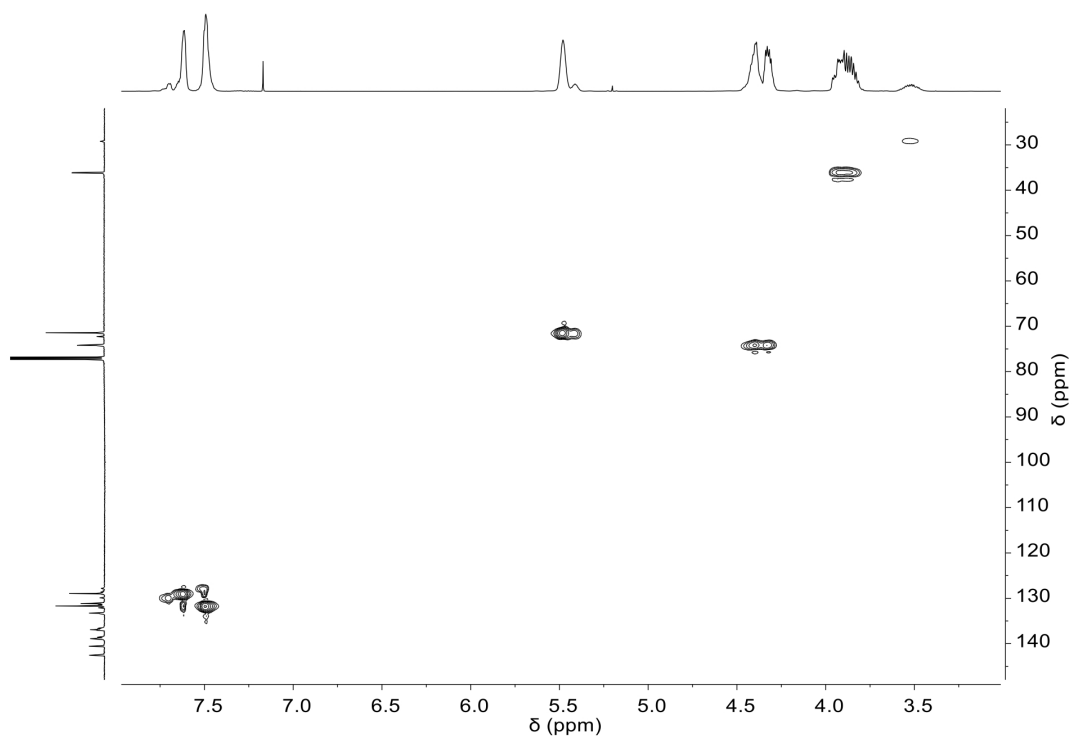


Figure S 82:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #14.

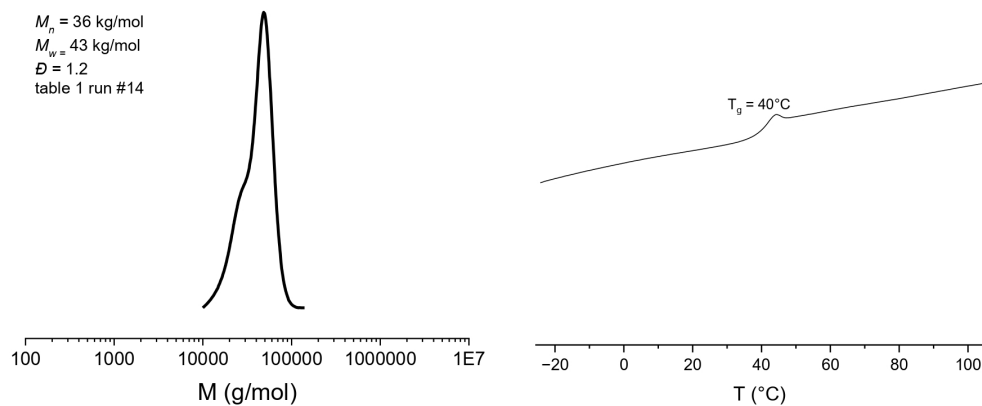


Figure S 83: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #14.

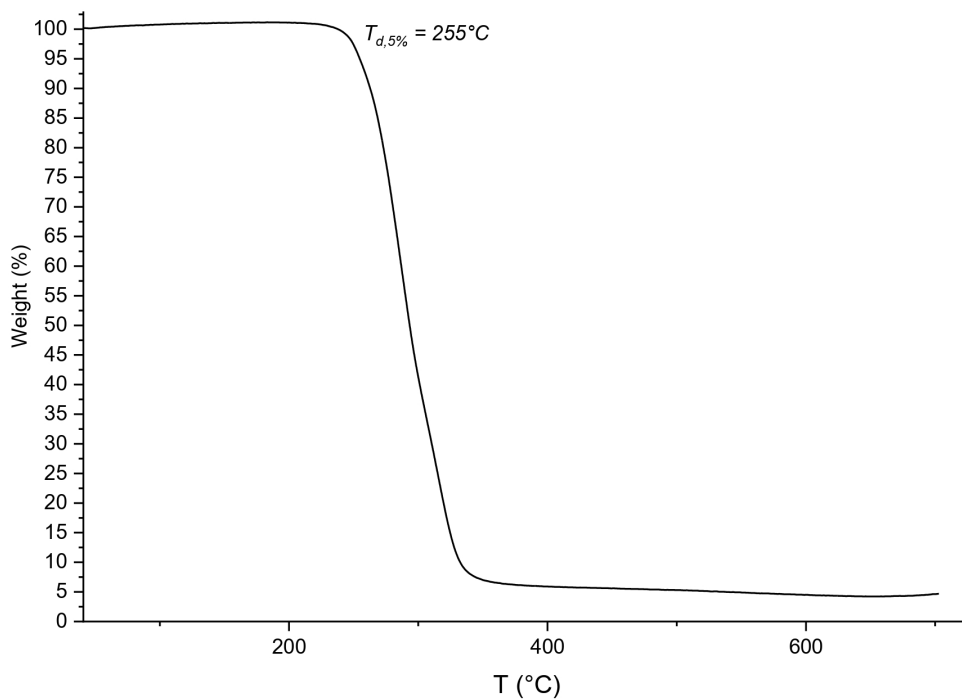


Figure S 84: TGA data of the precipitated polymer corresponding to table 1 run #14.

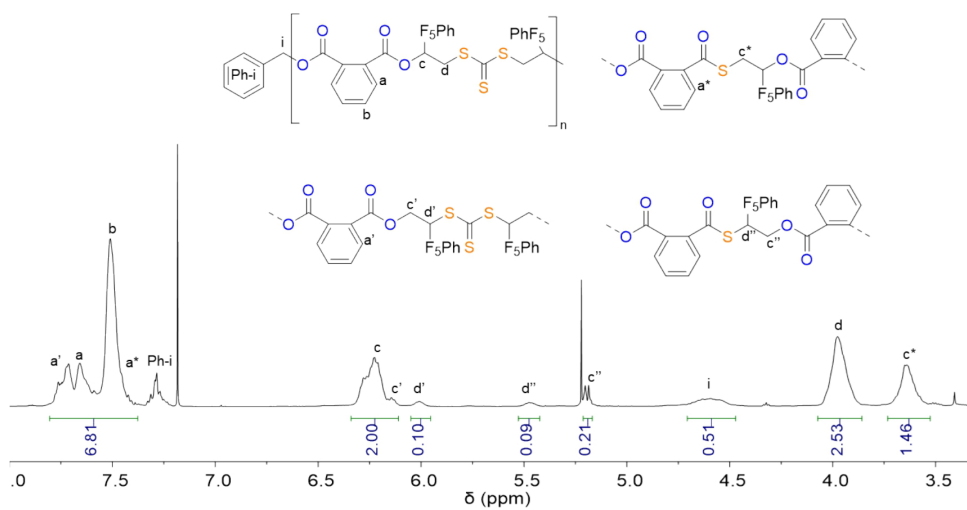


Figure S 85:  $^1\text{H-NMR}$  spectrum (500 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ) of the precipitated polymer corresponding to table 1 run #15.

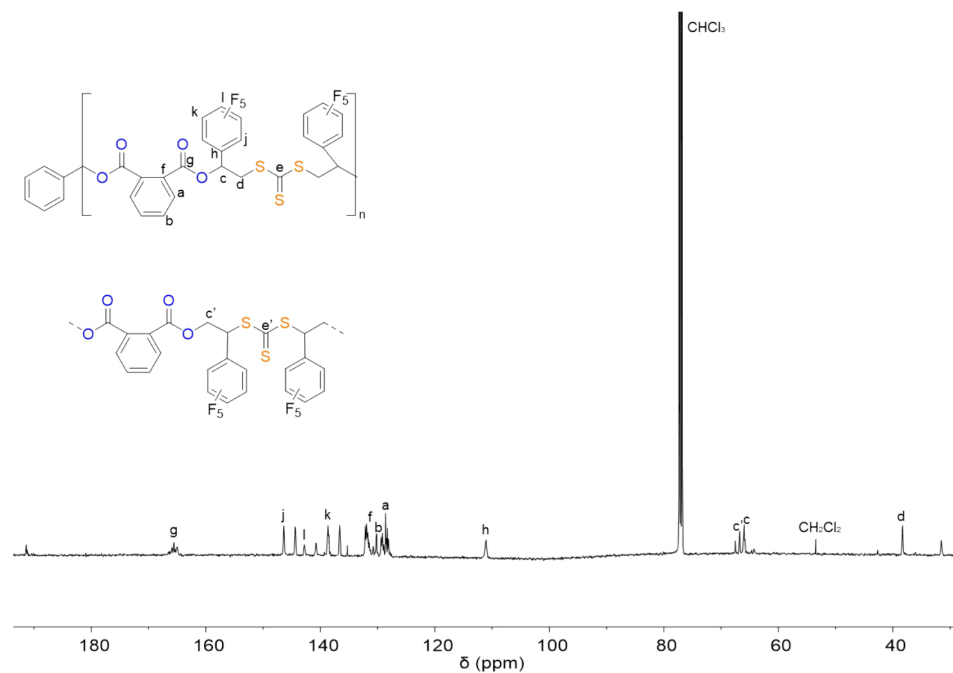


Figure S 86: <sup>13</sup>C-NMR spectrum (151 MHz, CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #15.

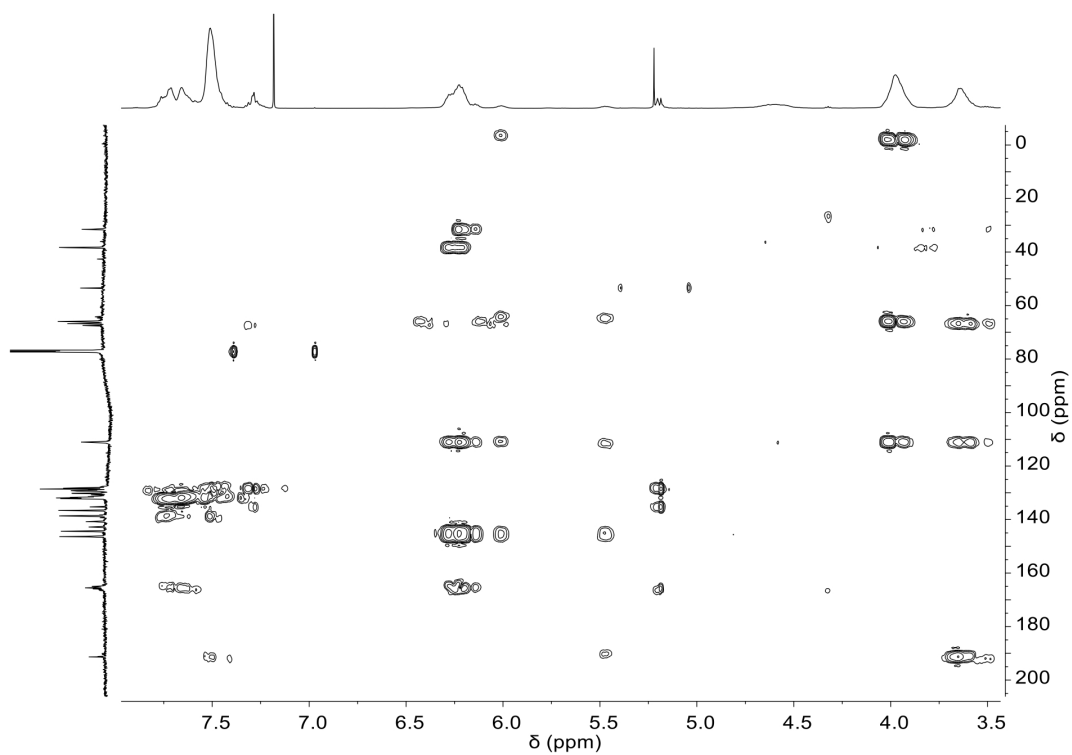


Figure S 87: <sup>1</sup>H-<sup>13</sup>C HMBC NMR spectrum (CDCl<sub>3</sub>, 25°C) of the precipitated polymer corresponding to table 1 run #15.



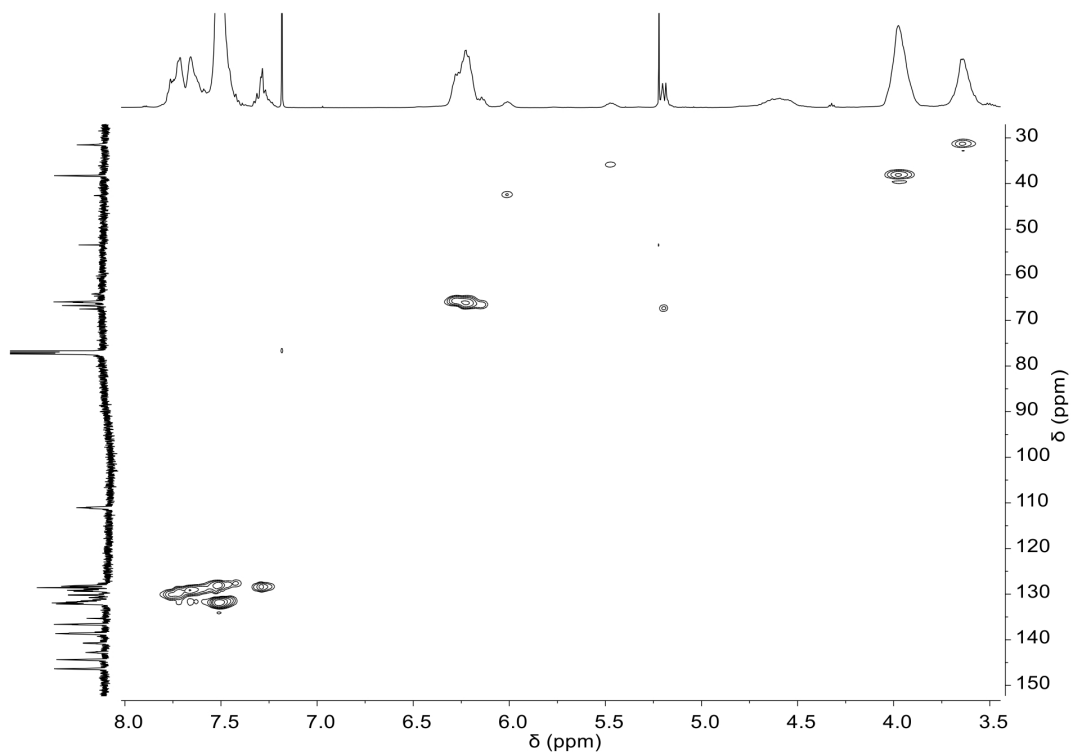


Figure S 88:  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of the precipitated polymer corresponding to table 1 run #15.

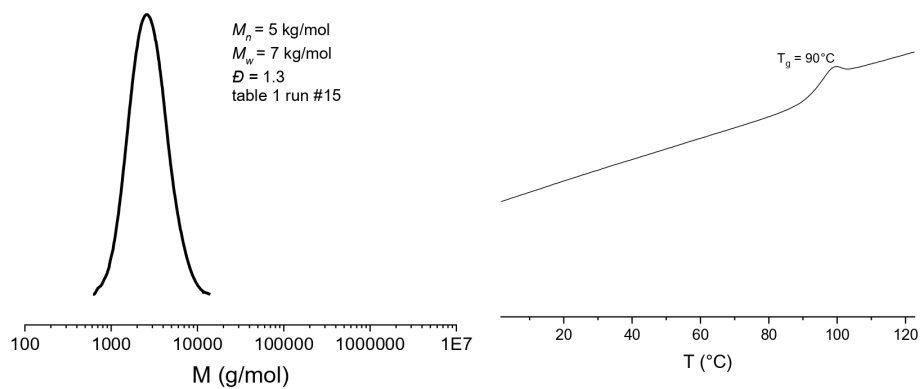


Figure S 89: (left) GPC curve and (right) DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #15.

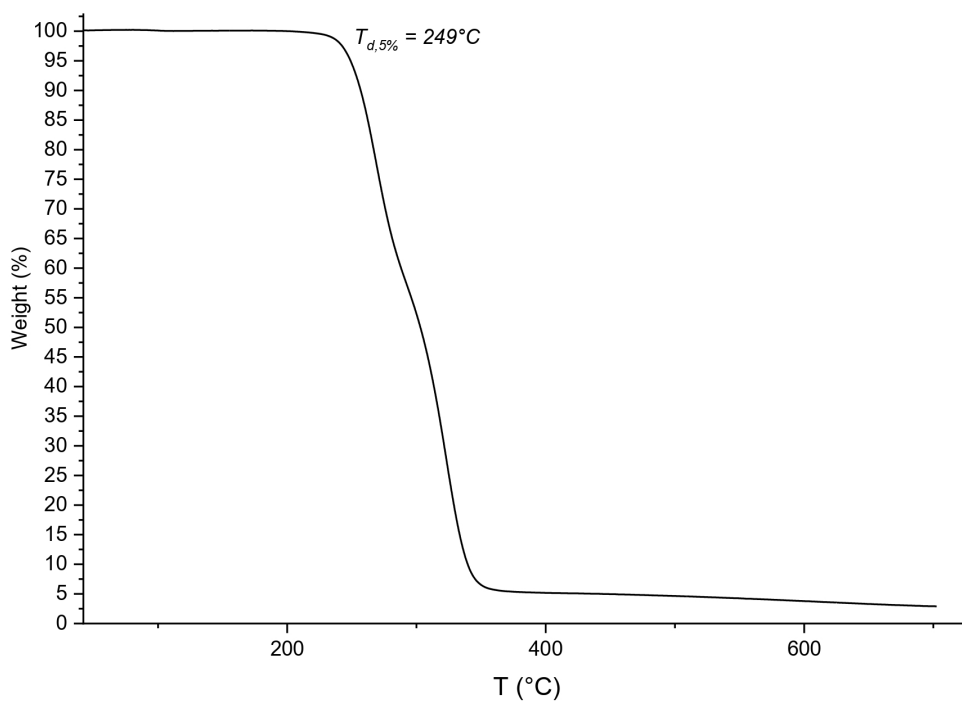


Figure S 90: TGA data of the precipitated polymer corresponding to table 1 run #15.

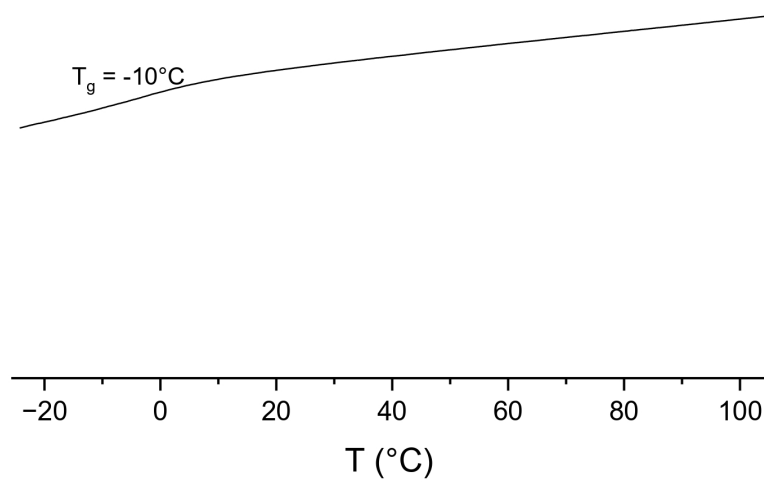


Figure S 91: DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #16.

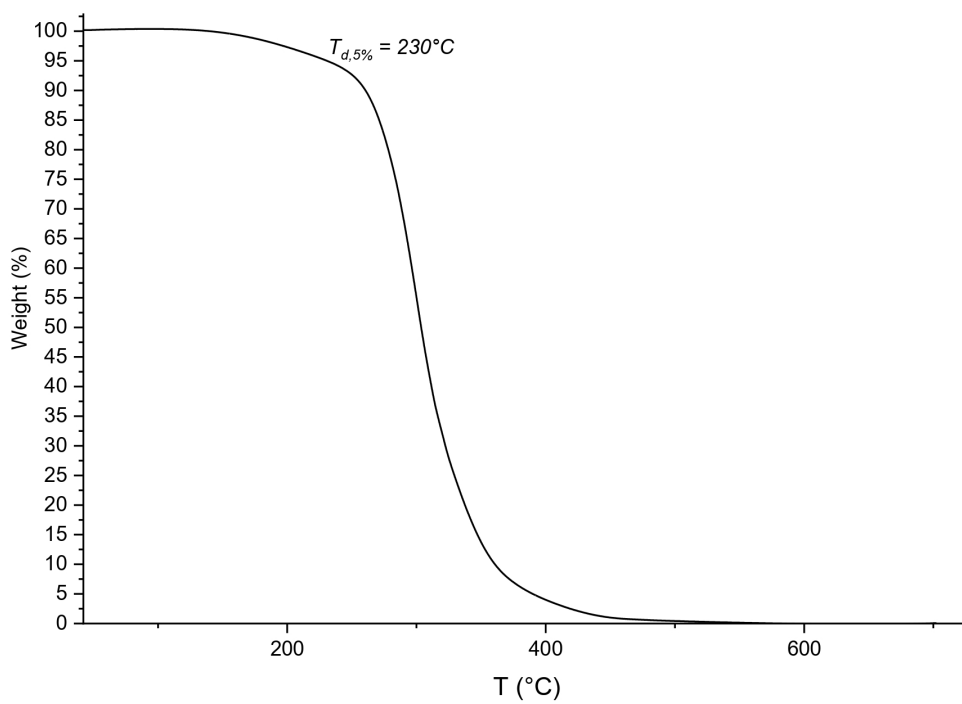


Figure S 92: TGA data of the precipitated polymer corresponding to table 1 run #16.

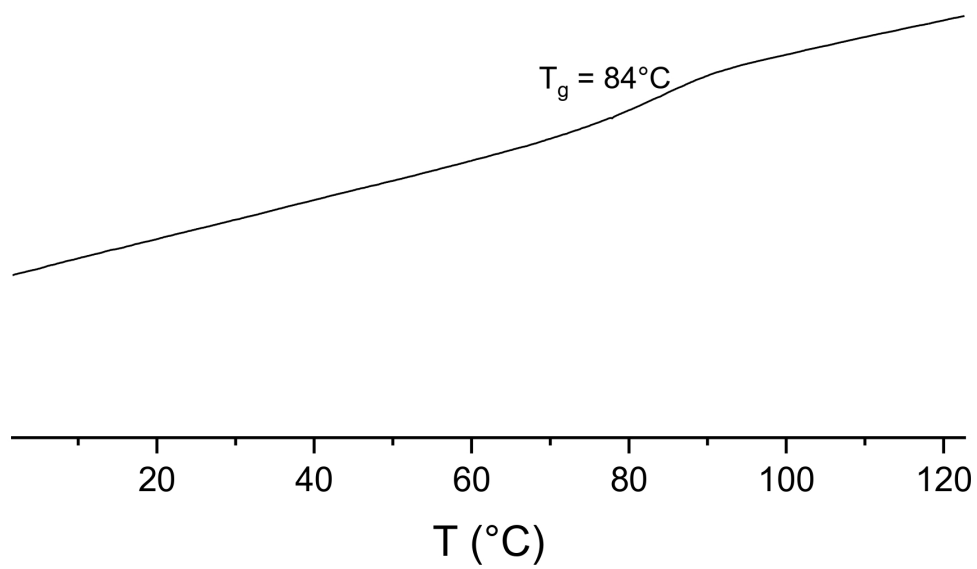


Figure S 93: DSC 2<sup>nd</sup> heating curve (endo up) of the precipitated polymer corresponding to table 1 run #17.

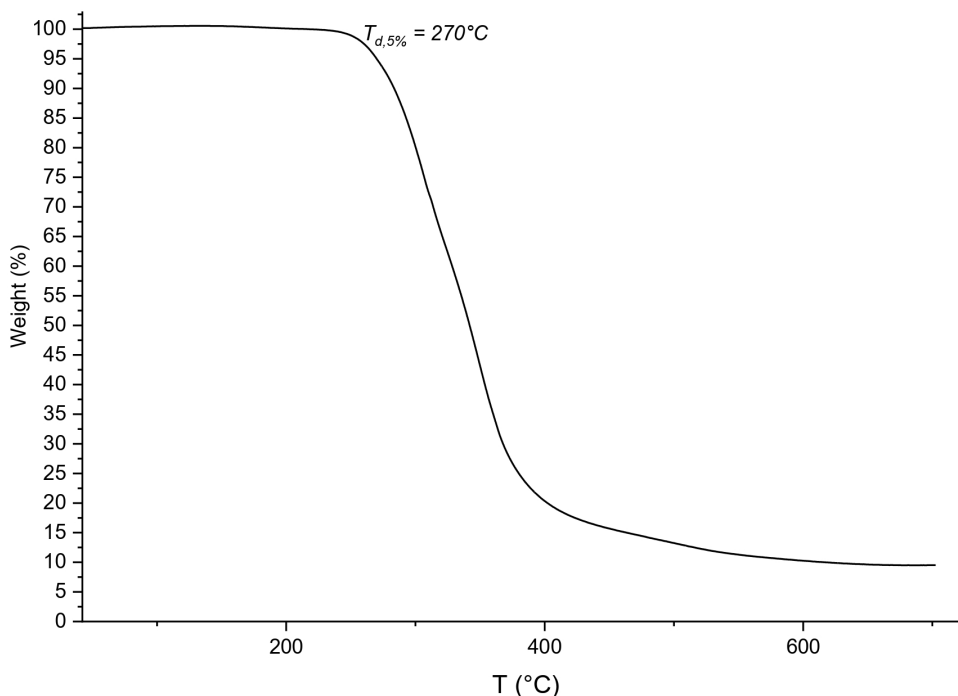


Figure S 94: TGA data of the precipitated polymer corresponding to table 1 run #17.

#### Section S4: Nanoparticles synthesis and functionalization:

##### Synthesis of citrate-reduced gold nanoparticles (Au NPs).

A hot aqueous solution of sodium citrate (5 mL, 39 mM, 3.9 equivalents) was rapidly added to a vigorously stirred boiling solution of gold (III) chloride trihydrate ( $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ , 100 mL, 0.50 mM, 1.0 equivalent). The reaction mixture was refluxed for 30 minutes, after which it was allowed to cool to room temperature. The gold nanoparticles (Au NPs) had an average diameter of approximately 17 nm (by DLS) and a concentration of 0.48 mM (in terms of gold-atom concentration determined via optical extinction spectroscopy.<sup>[5]</sup>)

Based on the nanoparticle concentration and size, a target grafting density of 1.0 nm<sup>-2</sup> was selected for polymer functionalization. 1 mL of the Au NP solution was first concentrated by centrifugation at 15,600 × g for 45 minutes. After removing the supernatant, the nanoparticles were re-dispersed in a minimal volume of the remaining water. The concentrated Au NPs were then added to polymer solutions (1 mL, ~0.02 mg/mL for PVGE and ~0.13 mg/mL for polystyrene (PSt)) prepared in a 1: 1 (v/v) mixture of DMF and THF, giving ruby-red colored dispersions. The resulting mixture was left undisturbed at room temperature for 2 hours to allow for the surface grafting of polymer molecules.

The resulting AuNP dispersions were purified from excess polymer ligands by three centrifugation–redispersion cycles at 14,000 g, 90 min; redispersion in 1 mL of the DMF/THF mixture (1:1 volume ratio).

The solution was subsequently diluted fivefold with solvent and analysed using extinction spectroscopy and dynamic light scattering (DLS).

##### Imine condensation of PVGE with rhodamine 110 chloride

20 mg of the aldehyde-functionalized polymer (VGE, Figure 1) was dissolved in 1 mL of DMF. To this solution, 1 mL of rhodamine 110 chloride (0.143 mg/mL in THF-DMF) was added. The resulting mixture was allowed to react, and the resulting polymeric material was purified via threefold precipitation in methanol, followed by drying overnight at room temperature.

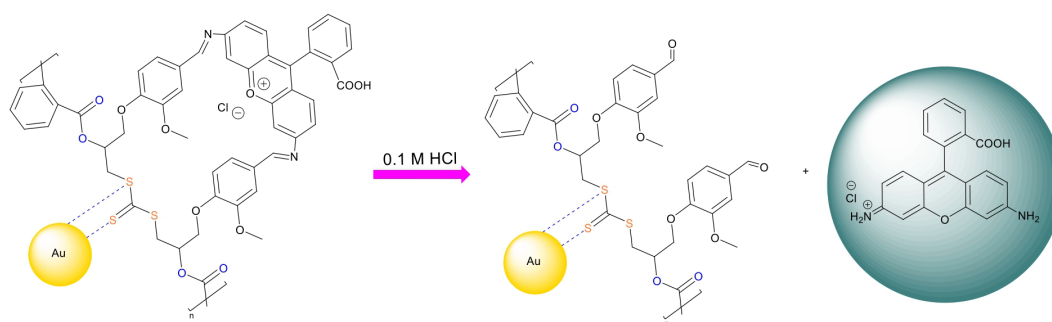
### Acid-Induced Dye Release

To investigate dye release, 50  $\mu\text{L}$  of 0.1 M HCl was added to the solution of polymer-functionalized AuNPs. The mixture was centrifuged at  $15,600 \times g$  for 90 minutes. The supernatant was collected and subjected to a second centrifugation under the same conditions to ensure complete removal of residual nanoparticles. The final supernatant was then analyzed using extinction spectroscopy to assess dye release.

As a control experiment, AuNPs functionalized with polystyrene that was pre-treated with dye in a similar way as described above for VGE terpolymer, served for comparison to prove that the dye release is via dynamic covalent chemistry (imine bond formation/cleavage) in PVGE.

### Analysis of fluorescence Quenching

For quenching experiments, the AuNP solutions functionalized with VGE terpolymer (imine condensed with the fluorescent dye) were measured at an excitation wavelength of 496nm. The solutions before and after the addition of acid were analyzed.



Scheme S 1: Schematic illustration of the dye release process, showing the polymer with the dye, grafted to the gold nanoparticles, and subsequent dye release upon acid treatment.

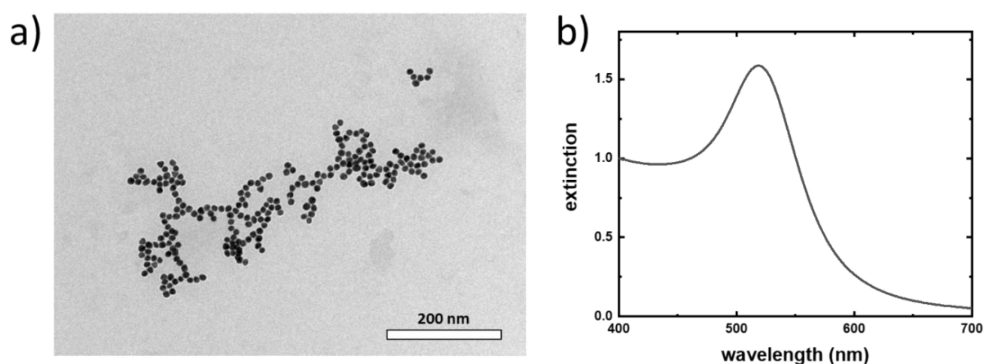


Figure S 95: a). TEM image of Au nanoparticles deposited from an aqueous dispersion onto a carbon-coated copper grid by drop-casting. b) visible extinction spectrum of Au nanospheres dispersed in water, showing the characteristic localized surface plasmon resonance (LSPR) peak.

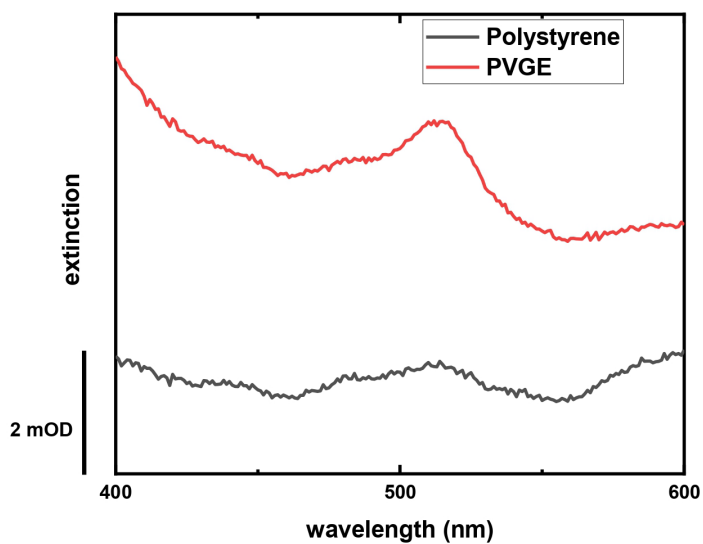


Figure S 96: Visible extinction spectra of the supernatant collected after acid treatment, confirming the release of Rhodamine 110 dye from the PVGE -functionalized gold nanoparticles.

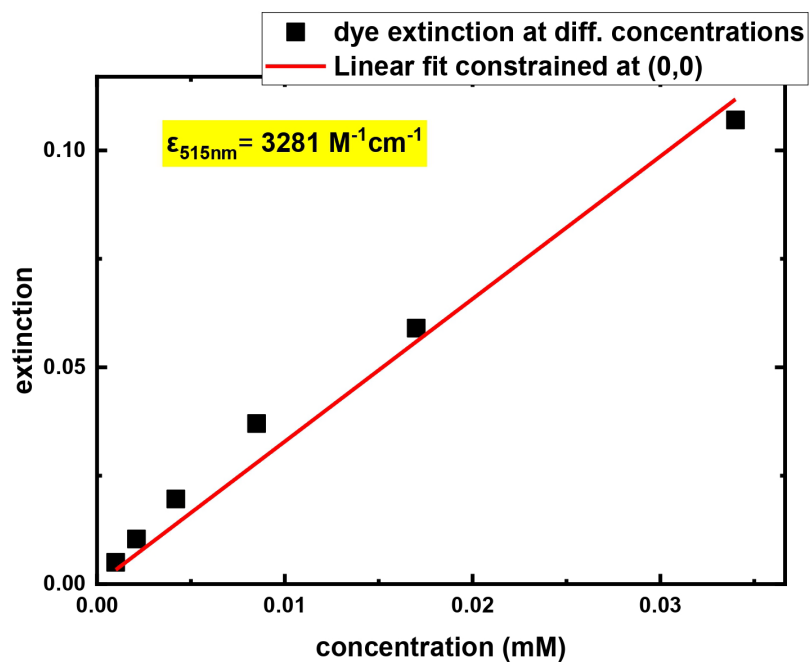


Figure S 97: Calibration curve of the dye extinction at 515 nm varying concentrations in solvent THF-DMF mixture.



## Section S5: References

- [1] M. J. Kates and J. H. Schauble, "Synthesis of small-medium ring thioanhydrides," *J. Heterocycl. Chem* 1995, 32 (4), 971–978.
- [2] A. Roig, A. Petrauskaitė, X. Ramis, S. De la Flor, and À. Serra, "Synthesis and characterization of new bio-based poly(acylhydrazone) vanillin vitrimer," *Polym. Chem.*, 2022, 13, 1510–1519.
- [3] Y. Zhang, V. K. R. Tangadanchu, Y. Cheng, R.-G. Yang, J.-M. Lin, and C.-H. Zhou, "Potential antimicrobial isopropanol-conjugated carbazole azoles as dual targeting inhibitors of *Enterococcus faecalis*," *ACS Med. Chem. Lett.*, 2018, 9 (3), 244–249.
- [4] M. P. Cava and M. V. Lakshmikantham, "Aspects of thioanhydride chemistry," *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1989, 43 (1–2), 95–109.  
<https://doi.org/10.1080/10426508908040280>
- [5] L. Scarabelli, A. Sánchez-Iglesias, J. Pérez-Juste, and L. M. Liz-Marzán, "A 'Tips and Tricks' practical guide to the synthesis of gold nanorods," *J. Phys. Chem Lett.*, 2015, 6 (21), 4270–4279.



## Acknowledgments

First and foremost, I would like to thank my doctoral supervisor, Jun.-Prof. Dr. Alex Plajer, for welcoming me into his group and entrusting me with this project. I am deeply grateful for his mentorship, his openness to new topics and suggestions, and his continuous professional and personal support.

I would also like to thank the *Fonds der Chemischen Industrie* for its financial support during my PhD studies.

A huge thank you goes to Peter Deglmann for performing all the fundamental DFT calculations that helped me understand the mechanisms behind my reactions and resolve mysteries that would have otherwise remained unsolved.

I would like to thank Dr. Christian Neuber and Dr. Reiner Giesa for their supervision and instruction in the use of the equipment at the chair. My sincere thanks also go to the technical staff, Jutta Failner and Sandra Opel, for their invaluable support in the laboratory and with the instruments. I am also grateful to Alexander Kern for his help with IT issues and to Petra Weiss for her tireless support with administrative, organizational, and many other tasks. Furthermore, I would like to thank all the cooperation partners with whom I had the pleasure of working during my doctoral studies.

I am also grateful to all the employees and members of the Chair of Macromolecular Chemistry I, whose professional exchange and friendship made my time there so enjoyable. I would also like to thank the interns I had the privilege of supervising: Sara, David, Juan, Paula, and Nina.

My heartfelt thanks go to my fellow students in Berlin and Bayreuth. Starting with my early colleagues Bhargav and Christoph, with whom I began my research career, shared games of Briscola, and built a friendship I hope will last beyond the laboratory. I also want to thank Merlin, whose successes and goals continue to be a source of inspiration and admiration. I am equally thankful to Debsena, Malte, and Niracha, who joined our group in Bayreuth and immediately enriched our environment with their presence.

From my previous time in Berlin, I also want to thank Lara, who has always provided me with emotional support—and the perfect excuse to take a break and chat about everyday life and other fundamental topics.

I am deeply grateful to Maria, who has supported me since my bachelor's studies in Pavia. No matter how stressed I am, you always listen patiently and help me relax and regain perspective.

My sincere thanks also go to Sebastian and Robert, the fellow members of the GPC support team, who always did their best to keep the instrument running—despite my occasional suggestions to “solve” the issue more dramatically. Patience truly is a virtue of chemists.

A special thanks goes to Anne for her technical support with NMR samples and for always trying to make us feel included in the group after our move to Bayreuth.

Of course, I owe an enormous debt of gratitude to my family, who have supported me throughout my education and my PhD journey. Without your encouragement, I would never have dared to undertake such a challenge and knowing that you are always there for me gives me immense strength.

Last but by no means least, I would like to thank Charlotte for being the most wonderful partner I could have ever wished for. You have been my greatest source of support, and I am constantly amazed by how every problem, no matter how big, feels easier to face with you by my side. When we first met, I could never have imagined how much we would come to share, yet we made it through distance, stress, and every challenge. If I managed to complete this PhD, it is mostly thanks to you. I have no fear of what comes next, if you are walking beside me.



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