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New Routes Toward Patchy Micelles with Crystalline Cores

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Table of Contents

Summary	I
Zusammenfassung.....	V
List of Publications.....	IX
1 Introduction.....	1
1.1 Crystallization-Driven Self-Assembly (CDSA)	1
1.2 Block Copolymer Micelles <i>via</i> Polylactide Stereocomplexation	8
1.3 Surface-Compartmentalized Block Copolymer Micelles.....	13
1.4 Objective of the Thesis.....	22
1.5 References	24
2 Synopsis.....	37
2.1 Thesis Overview	37
2.2 Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly	39
2.3 Patchy Stereocomplex Micelles as Efficient Compatibilizers in Polymer Blends	43
2.4 From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co- Crystallization-Driven Self-Assembly	47
2.5 Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles	53
2.6 Individual Contributions to Joint Publications	57
3 Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly	59
4 Patchy Stereocomplex Micelles as Efficient Compatibilizers for Polymer Blends.....	87
5 From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co- Crystallization-Driven Self-Assembly	133
6 Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles	191
7 Outlook.....	227
Glossary.....	229
Appendix	233
Acknowledgement	239
(Eidesstattliche) Versicherungen und Erklärungen.....	241

Table of Contents

Summary

Crystallization-driven self-assembly (CDSA) is a powerful tool for the preparation of cylindrical (one-dimensional) patchy core-crystalline micelles (CCMs), whereas other morphologies remain difficult to access by this approach. Reports on spherical patchy micelles are scarce, and two-dimensional structures (platelets) have not yet been demonstrated. In addition, patchy CCMs have so far been limited to block copolymers containing polyethylene (PE) or poly(ferrocenyl dimethylsilane) as crystallizable core-forming blocks, having drawbacks in terms of thermal stability or demanding synthesis, respectively. This highlights the need for alternative approaches to patchy CCMs, which is addressed in this thesis. Based on polylactide-containing block copolymers, new routes toward patchy micelles of diverse morphologies were developed and their interfacial activity and related potential in emulsion stabilization and blend compatibilization were tested.

First, stereocomplex-driven self-assembly (SCDSA) of diblock copolymers bearing enantiomeric poly(*L*-lactide)/poly(*D*-lactide) (PLLA/PDLA) blocks and highly incompatible corona-forming blocks (polystyrene (PS) and poly(*tert*-butyl methacrylate) (PtBMA)) was introduced as facile method to prepare uniform spherical micelles with a semicrystalline stereocomplex (SC) core and a shamrock-like microphase-separated corona. The patchy micelles showed a significantly higher interfacial activity compared to analogously prepared SC micelles with a homogenous PS corona, which is attributed to the synergistic combination of an amphiphilic corona with the Pickering effect of (nano)particles. Furthermore, they were successfully employed in the stabilization of emulsions.

Building on this concept, the synthesis of patchy SC micelles was upscaled, allowing their use as efficient compatibilizers for strongly immiscible PS/PtBMA (30/70 (w/w)) blends. While the neat blend showed macrophase separation into two millimeter-sized phases, compatibilization with patchy SC micelles led to finely dispersed, micrometer-sized PS droplets embedded in a PtBMA matrix. An optimal compatibilizer content of 7 wt% was identified for achieving a homogeneous blend with maximum reduction in PS droplet size ($D = 2.5 \pm 0.9 \mu\text{m}$) employing Raman imaging and scanning electron microscopy. Compared to SC micelles with a homogeneous PS corona, the patchy micelles demonstrated superior compatibilization efficiency regarding blend homogeneity and droplet size reduction. Moreover, Janus micelles with a PS/PtBMA corona showed a comparable reduction in PS droplet size, but only compatibilization with the patchy SC micelles resulted in a monomodal size distribution. The superior performance of patchy micelles is attributed to their adaptive corona structure that

enables selective swelling and collapse of the respective miscible and immiscible patches at the blend interface. SCDSA was further employed to selectively incorporate a fluorescently (rhodamine B) labelled PDLA homopolymer into the SC core without altering the corona morphology. Utilizing confocal fluorescence microscopy, it could be shown that the patchy micelles are predominantly assembled at the PS/*Pt*BMA blend interface.

Since SCDSA solely produced spherical micelles, co-crystallization-driven self-assembly (CCDSA) of PS-*b*-PLLA-*b*-*Pt*BMA (SLT) triblock terpolymers with the corresponding PLLA homopolymer was explored as alternative to realize new morphologies. This, for the first time, allowed the formation of twisted platelet-like micelles featuring a non-concentric, nanometer-sized, stripe-like patterned corona. These patchy platelets further assemble into defined three-dimensional (3D) structures. When a PLLA homopolymer with a much shorter chain length than the PLLA middle block of SLT was used in CCDSA, thereby altering the crystallization rate, stacked 3D pyramidal structures emerged. The formation of twisted, multilayered assemblies is attributed to screw dislocation defects or anisotropic stresses at the platelet fold surface. Notably, the presence of the homopolymer is essential to induce crystallization. The neat SLT assembled to Janus micelles with an amorphous PLLA core, attributed to the strongly hindered crystallization of the PLLA middle block. The interfacial activity of the patchy platelets was found to be significantly higher compared to spherical patchy micelles, and they proved effective in stabilizing emulsions.

Finally, CDSA and SCDSA were combined to selectively address the PLLA patches within worm-like CCMs (wCCMs) formed by a double-crystalline PS-*b*-PE-*b*-PLLA triblock terpolymer. When CDSA is conducted in THF, a good solvent for both PS and PLLA corona blocks, only the PE middle block crystallized and wCCMs with an amorphous, patchy PS/PLLA corona were formed. However, when the solvent quality for PLLA was sufficiently reduced (xylene/cyclohexane mixtures), crystallization within the PLLA patches was induced without altering the overall micelle morphology. The stereoregular PLLA patches were then selectively loaded *via* stereocomplexation with enantiomeric PDLA homopolymers, yielding micelles with PLLA/PDLA SC domains in the corona showing a significantly increased size. This strategy can also be utilized for the incorporation of functional moieties, as demonstrated by using a fluorescently labelled PDLA homopolymer. This allowed to prove stereocomplexation directly in dispersion *via* fluorescence correlation spectroscopy owing to the slower diffusion of the selectively loaded, fluorescence-tagged wCCMs.

In conclusion, this thesis demonstrates the enormous potential of stereoregular polylactide-based block copolymers for the preparation of patchy micelles utilizing stereocomplex- and co-crystallization-driven self-assembly. This gives access to patchy CCMs of varying shape and tailored corona functionalities that are highly interesting for potential applications, as proven by their excellent performance in emulsion stabilization and blend compatibilization.

Zusammenfassung

Die kristallisationsgetriebene Selbstassemblierung (engl. *crystallization-driven self-assembly*, CDSA) ist eine effiziente Methode zur Herstellung patch-artiger Zylindermizellen mit kristallinem Kern (engl. *core-crystalline micelles*, CCMs). Andere Morphologien sind mit diesem Verfahren jedoch nur schwer zugänglich. Berichte über patch-artige Kugelmizellen sind selten, und zweidimensionale Strukturen (Plättchen) konnten bislang nicht realisiert werden. Zudem beschränkte sich die Herstellung von CCMs bisher auf Blockcopolymere mit kristallisierbaren Polyethylen- (PE) oder Polyferrocenyldimethylsilan-Blöcken, die entweder durch eine begrenzte thermische Stabilität oder eine anspruchsvolle Synthese limitiert sind. Dies verdeutlicht die Notwendigkeit alternativer Ansätze für patch-artige CCMs, wie sie in dieser Arbeit entwickelt wurden. Auf Grundlage polylactidhaltiger Blockcopolymere wurden neue Strategien zur Herstellung patch-artiger Mizellen unterschiedlicher Morphologien erarbeitet. Darüber hinaus wurden ihre Grenzflächenaktivität sowie ihr Potenzial als Emulsionsstabilisatoren und Phasenvermittler in Polymermischungen (Blends) untersucht.

Die stereokomplexgetriebene Selbstassemblierung (engl. *stereocomplex-driven self-assembly*, SCDSA) von Diblockcopolymeren mit enantiomeren Poly(*L*-lactid)/Poly(*D*-lactid)-Blöcken (PLLA/PDLA) und stark unverträglichen Koronablöcken wie Polystyrol (PS) oder Poly(*tert*-butylmethacrylat) (PtBMA) erwies sich dabei als effiziente Methode zur Herstellung einheitlicher Kugelmizellen. Diese besitzen einen teilkristallinen Stereokomplex (engl. *stereocomplex*, SC) im Kern und eine kleeblattartige, mikrophasenseparierte Korona. Die patch-artigen SC-Mizellen zeigten im Vergleich zu analogen SC-Mizellen mit homogener PS-Korona eine deutlich erhöhte Grenzflächenaktivität. Dies wird auf die Synergie zwischen der amphiphilen Koronastruktur und dem Pickering-Effekt von Nanopartikeln zurückgeführt. Entsprechend erwiesen sie sich als effiziente Emulsionsstabilisatoren.

Aufbauend auf diesen Ergebnissen wurde die Herstellung der patch-artigen SC-Mizellen zunächst aufskaliert, um sie als wirksame Phasenvermittler für stark unverträgliche PS/PtBMA-(30/70 Gew.-%)-Blends einsetzen zu können. Während der reine Blend eine Makrophasenseparation in millimetergroße Bereiche aufwies, führte die Zugabe der patch-artigen SC-Mizellen zu fein verteilten, mikrometergroßen PS-Tröpfchen in einer PtBMA-Matrix. Raman-Imaging und Rasterelektronenmikroskopie zeigten, dass ein Phasenvermittlergehalt von 7 Gew.-% zu einer homogenen Verteilung und einer minimalen PS-Tröpfchengröße ($D = 2,5 \pm 0,9 \mu\text{m}$) führte. Im Vergleich zu SC-Mizellen mit homogener PS-Korona wiesen die patch-artigen SC-Mizellen eine höhere Kompatibilisierungseffizienz auf. Interessanterweise führten

Janus-Mizellen zu einer ähnlich starken Verkleinerung der PS-Tröpfchen, jedoch wurde eine homogene Größenverteilung ausschließlich mit den patch-artigen SC-Mizellen erreicht. Dies wird auf das adaptive Verhalten der patch-artigen Korona zurückgeführt, welches ein selektives Quellen bzw. Kollabieren der entsprechenden mischbaren bzw. unmischbaren Kompartimente an der Grenzfläche ermöglicht. Zudem wurde SCDSA genutzt, um ein fluoreszenzmarkiertes (Rhodamin B) PDLA-Homopolymer in den SC-Kern einzubringen, ohne dabei die Koronastruktur zu verändern. Dadurch konnte mittels konfokaler Fluoreszenzmikroskopie die Anreicherung der patch-artigen Mizellen an den PS/PtBMA-Grenzflächen eindeutig nachgewiesen werden.

Da über SCDSA ausschließlich kugelförmige Mizellen zugänglich waren, wurde die co-kristallisationsgetriebene Selbstassemblierung (engl. *co-crystallization-driven self-assembly*, CCDSA) von PS-*b*-PLLA-*b*-PtBMA (SLT)-Triblockterpolymeren mit dem entsprechenden PLLA-Homopolymer als alternativer Ansatz zur Realisierung neuer Morphologien untersucht. Damit konnten erstmals verdrillte, plättchenförmige Mizellen mit einer nicht konzentrischen, nanometergroßen, streifenartigen Korona erzeugt werden, die sich weiter zu dreidimensionalen (3D)-Strukturen assemblieren. Liegt der Polymerisationsgrad des PLLA-Homopolymers deutlich unter dem des PLLA-Mittelblocks im SLT-Triblockterpolymer, führt die veränderte Kristallisationsrate zur Bildung pyramidalen 3D-Strukturen aus gestapelten Plättchen. Die Bildung der verdrillten Plättchen und ihrer 3D-Überstrukturen lässt sich auf Schraubversetzungen oder anisotrope Spannungen an der Faltoberfläche der teilkristallinen Plättchen zurückführen. Für die Nukleierung ist die Anwesenheit des PLLA-Homopolymers essenziell, da sich ohne dessen Zugabe aufgrund der gehemmten PLLA-Kristallisation lediglich Janus-Mizellen mit amorphem Kern bilden. Im Vergleich zu patch-artigen Kugelmizellen zeigten die plättchenförmigen Strukturen eine erhöhte Grenzflächenaktivität und erwiesen sich ebenfalls als wirksame Emulsionsstabilisatoren.

Abschließend wurden CDSA und SCDSA miteinander kombiniert, um gezielt die PLLA-Koronakompartimente wurm-artiger CCMs (engl. *worm-like core-crystalline micelles*, wCCMs) zu adressieren. Diese wurden zunächst mittels CDSA von PS-*b*-PE-*b*-PLLA Triblockterpolymeren hergestellt. In einem für beide Koronablöcke guten Lösungsmittel (Tetrahydrofuran) kristallisiert ausschließlich der PE-Mittelblock, sodass wCCMs mit einer amorphen, patch-artigen PS/PLLA-Korona entstehen. Durch gezielte Verschlechterung der Lösungsmittelqualität für PLLA (Xylol/Cyclohexan-Mischungen) gelang es die PLLA-Kristallisation innerhalb der Korona zu induzieren, ohne dabei die Mizellmorphologie zu verändern. Dies ermöglichte anschließend die Beladung der PLLA-Kompartimente mittels

Stereokomplexierung mit einem enantiomeren *PDLA*-Homopolymer, wodurch deutlich vergrößerte SC-Domänen in der Korona entstanden. Dieser Ansatz wurde ebenfalls zur Einführung eines fluoreszenzmarkierten *PDLA*-Homopolymers genutzt. Mittels Fluoreszenzkorrelationsspektroskopie konnte die erfolgreiche Bildung des Stereokomplexes über die stark verringerte Diffusionsgeschwindigkeit der fluoreszenzmarkierten wCCMs direkt in der Dispersion nachgewiesen werden.

Zusammenfassend zeigt diese Arbeit das große Potenzial der stereokomplex- und co-kristallisationsgetriebenen Selbstassemblierung von *PLLA*-/*PDLA*-haltigen Blockcopolymeren für die Herstellung patch-artiger Mizellen. Dadurch werden neue Zugänge zu patch-artigen CCMs mit unterschiedlichen Morphologien und maßgeschneiderten Eigenschaften eröffnet. Die vorgestellten Systeme bieten vielversprechende Anwendungsmöglichkeiten, wie insbesondere ihr Einsatz als effiziente Emulsionsstabilisatoren und Phasenvermittler in Polymerblends gezeigt hat.

List of Publications

This dissertation is submitted in the form of a cumulative thesis and comprises four scientific articles. All of which have been published in peer-reviewed journals. The following scientific articles are the subject of this thesis:

- 1 R. Schaller, C. Hils, M. Karg, H. Schmalz
Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly
Published in *Macromol. Rapid Commun.* **2023**, 44 (3), 2200682.
- 2 R. Schaller, M. Schmidt, K. Schweimer, H. Schmalz
Patchy Stereocomplex Micelles as Efficient Compatibilizers for Polymer Blends
Published in *Polym. Chem.* **2024**, 15 (30), 3100-3112.
- 3 R. Schaller, E. Fuchs, L. M. Günther, H. Schmalz
Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles
Published in *J. Polym. Sci.* **2025**, 63 (10), 2319-2332.
- 4 R. Schaller, M. Foith, L. M. Günther, M. Hund, K. Busse, M. Karg, H. Schmalz
From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co-Crystallization-Driven Self-Assembly
Published in *Macromolecules* **2026**, 59 (5), 3092–3103.

During the work on this thesis, I was involved in a collaboration and co-authored the following peer-reviewed publication, which will not be part of this thesis:

- 5 M. Safari, C. Ocando, Y. Liao, M. Drechsler, N. Volk, R. Schaller, M. Held, V. Abetz, H. Schmalz, A. J. Müller
Morphology and Confinement Effects on Crystallization Kinetics in Polyethylene Containing Block Copolymers
Published in *Polymer* **2024**, 298, 126863.

1 Introduction

1.1 Crystallization-Driven Self-Assembly (CDSA)

The self-assembly of macromolecules into ordered structures at the nanometer scale is a fundamental phenomenon observed in both biological and synthetic systems. In nature, proteins fold into highly specific architectures through well-defined assembly pathways, which impart distinct biological functions.^{1,2} Inspired by these natural examples, synthetic block copolymers can also undergo self-organization in solution, giving rise to an extensive variety of morphologies. Depending on molecular design and assembly conditions, these materials can form structures ranging from simple spherical micellar aggregates to elongated, planar, or hollow nanostructures, as well as more complex compartmentalized and hierarchically organized assemblies.^{3,4} The self-assembly behavior of block copolymers is governed by a variety of weak, non-covalent interactions, including hydrogen bonding, π - π interactions, liquid-crystalline effects, solvophilic-solvophobic contrast, and dipole-dipole forces.^{5,6} Fine tuning of these interactions enables fine control over the resulting assemblies, allowing systematic adjustment of their dimensions, morphology, and functional characteristics. In general, the morphology of amphiphilic diblock copolymers emerges from a set of thermodynamic conditions, primely influenced by the interaction between the two blocks in solution (polymer-polymer interaction parameter, χ_{AB}) and the affinity of the respective block to the solvent (polymer-solvent interaction parameters, χ_{AS} and χ_{BS}).⁷ This behavior can be predicted by the dimensionless packing parameter p (Equation 1), where v is the volume of the hydrophobic segment, a_0 the head group area and l_c the hydrophobic tail length.^{8,9} Different ranges of p values predict specific aggregate morphologies, such as spherical ($p \leq 1/3$), cylindrical ($1/3 < p < 1/2$), lamellar ($p = 1$), and vesicular structures ($1/2 \leq p \leq 1$). However, the prediction of the morphology becomes increasingly difficult for block copolymers comprising three or more blocks.

$$p = \frac{v}{a_0 l_c} \quad (1)$$

The development of living and controlled polymerisation techniques, such as living anionic polymerization, reversible addition-fragmentation chain transfer, nitroxide-mediated, and atom transfer radical polymerisation, enabled the synthesis of block copolymers with precise control over molecular weight, composition and architecture.¹⁰⁻¹² This was the foundation for systematic investigations into solution self-assembly. Early work in this area predominantly focused on amorphous coil-coil block copolymer systems, whereas studies involving

crystalline-coil architectures were comparatively rare and largely limited to examples incorporating poly(ethylene oxide) (PEO) as the crystallizable segment.^{13,14} The controlled formation of one-dimensional (1D) cylindrical (or worm-like) micelles or two-dimensional (2D) platelet-like assemblies with well-defined dimensions long remained a significant challenge. This situation changed following the pioneering work of the *Manners* and *Winnik* groups, who investigated the solution self-assembly of block copolymers containing a crystallizable poly(ferrocenyl dimethylsilane) (PFS) block in combination with amorphous corona-forming segments.^{15–17} In these systems, crystallization of the core-forming block predominantly governs the micelle formation. The self-assembly process, where block copolymers bearing one or more crystallizable blocks are utilized, is called crystallization-driven self-assembly (CDSA) and has gained increasing attention over the last decades.^{18–20} Next to PFS based block copolymers, several other block copolymers with crystallizable core-forming blocks were used in CDSA, including poly(ferrocenyl dimethylgermane),^{21,22} polyethylene (PE),^{23–26} PEO,^{27,28} polycarbonates,^{29–32} poly(ϵ -caprolactone) (PCL),^{33–36} polyoxazolines,^{37–39} liquid crystalline polymers,^{40–43} poly(vinylidene fluoride),⁴⁴ poly(L-lactide) (PLLA),^{45–53} and different conjugated polymers, such as poly(3-hexyl thiophene),^{54–58} polyfluorene⁵⁹ or oligo(*p*-phenylene vinylene).^{60–63}

Two widely employed strategies for generating 1D and 2D micelles are temperature- and solvent-induced CDSA.^{18,64} In the first approach, a solvent is employed, where the polymer chains remain molecularly dissolved at elevated temperatures above the melting point of the crystallizable segment ($T > T_m$). As the solvent becomes selective for the corona-forming block upon cooling. When the crystallization temperature (T_c) is reached, the core-forming block becomes insoluble, initiating crystallization and micelle formation. The second method begins by dissolving the block copolymer in a non-selective solvent. Subsequently, this solution is introduced into a solvent that is selective for the corona block. This change in solvent environment triggers the collapse of the crystallizable block, thereby inducing CDSA. Typically, this procedure yields micelles with fibrous or platelet-like morphologies. Although these morphologies can be tuned by adjusting the corona-to-core ratio, the resulting micelles often display polydisperse size distributions.

1.1.1 Living CDSA

The concept of living CDSA represents a significant conceptual breakthrough, as it permits fine tuning of micellar size, narrow size distributions, and tailored corona functionalities.^{64,65} This approach can be compared to principles of living polymerization, as growth proceeds without termination under appropriate conditions.^{66,67} There are two main routes to living CDSA, both

relying on the use of small micellar fragments, commonly referred to as seed micelles, as a shared fundamental principle. In the self-seeding approach, polydisperse fibers are first prepared by conventional CDSA. Subsequent thermal treatment induces partial dissolution of these fibers, releasing molecularly dissolved block copolymer chains (unimers). The remaining micellar fragments then act as seeds for epitaxial growth upon cooling. In this process, the annealing temperature is a key parameter for controlling the length of the resulting micelles (**Figure 1.1**, top).^{65,67} Alternatively, in the seeded growth approach, the micelle seeds are prepared by intense sonication of the polydisperse fiber micelles. Subsequently, the addition of further unimers results in the formation of monodisperse fibers, whereby the cylinder lengths show a linear dependence on the employed unimer/seed ratio (**Figure 1.1**, bottom).

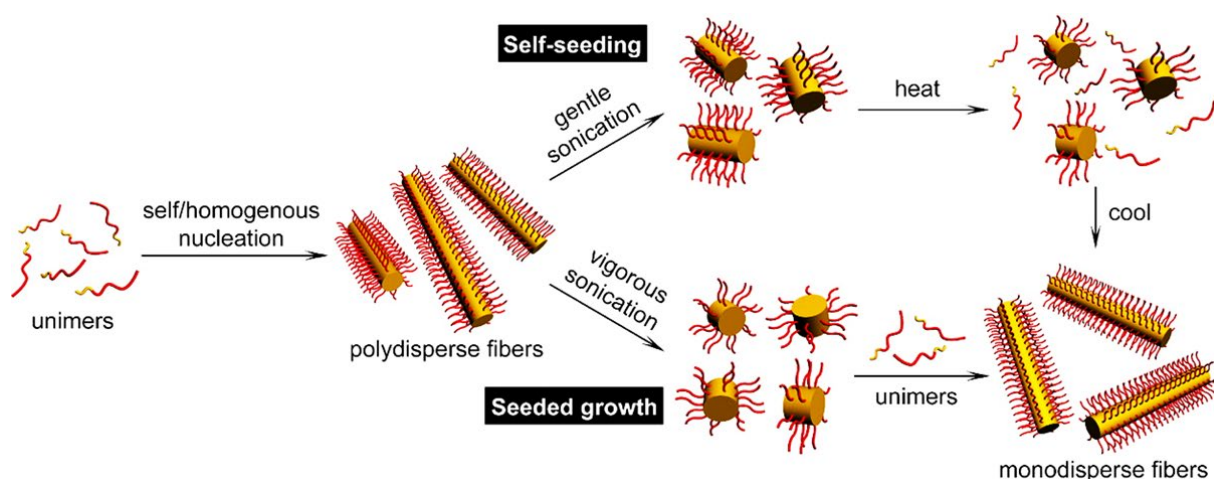


Figure 1.1 Schematic representation of two living CDSA routes: Self-seeding (top) and seeded growth (bottom). Initially, polydisperse cylindrical micelles are generated using conventional CDSA. During the self-seeding process, thermal treatment induces partial dissolution of the micelles, releasing unimers. The residual micellar fragments then act as seeds for epitaxial growth upon cooling. In the seeded growth approach, intense sonication is employed to fragment polydisperse micelles into short seed particles. Subsequent addition of unimers leads to controlled elongation *via* epitaxial growth from the seed termini. Reproduced from Ref.⁶⁷ (© 2015) with permission of the *American Chemical Society*.

Living CDSA also opened the way to a variety of well-defined micellar assemblies that were not accessible before, for example, non-centrosymmetric block comicelles,⁶⁸ non-covalent supermicelles of various shapes (fish-spine-, cross-, train-track-like, or single -stranded),^{69–71} colloidosomes,⁷² and π -conjugated 1D and 3D nanostructures.^{73–75}

1.1.2 2D and 3D Micelle Morphologies *via* CDSA

Moreover, living CDSA at ambient or near ambient temperature became the preferred method for preparing 2D platelet micelles with defined shape and size, as crystallization usually favours structures of low curvature.^{76,77} There are two efficient ways for generating core-crystalline

platelet micelles. Firstly, by increasing the core-corona block length ratio, and secondly, by co-crystallization-driven self-assembly (CCDSA) of a crystalline-coil block copolymer together with the respective crystallizable homopolymer, shown first for PCL and PFS based block copolymers.^{77–81} The latter approach was utilized by *Manners* and co-workers to prepare 2D micelles showing a centrosymmetric arrangement of the corona domains.⁸¹ This architecture was achieved by the sequential addition of different blends of crystalline-coil block copolymers, namely PFS-*block*-polydimethylsiloxane (PFS-*b*-PDMS) and PFS-*b*-poly(2-vinylpyridine) (PFS-*b*-P2VP), with the corresponding crystallizable PFS homopolymer. Subsequent selective cross-linking of one corona domain, followed by the dissolution of the other led to hollow rectangular rings with controllable dimensions, as well as perforated platelet-like structures (Figure 1.2).

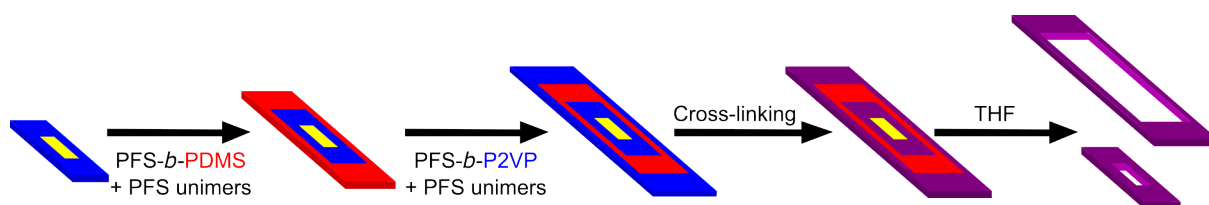


Figure 1.2 Schematic illustration of concentric rectangular platelet micelles prepared through the sequential, alternate addition of PFS₃₆-*b*-P2VP₅₀₂/PFS₂₀ and PFS₂₈-*b*-PDMS₅₆₀/PFS₂₀ blend unimers (indices correspond to number-average degree of polymerization). Cross-linking and selective dissolution resulted in hollow rings and perforated platelets. Adapted from Ref.⁸¹ (© 2016) with the permission of the *American Association of the Advancement of Science*.

The concept of sequential addition of different block copolymer/homopolymer blends was further extended, enabling the formation of 2D micelles with distinct corona compartments and interesting functionalities. *Manners* and co-workers demonstrated that competitive crystallization kinetics of the PFS core-forming species, during seeded CDSA of PFS-*b*-P2VP/PFS blends, enable the formation of low-dispersity 2D platelet micelles with spatially controlled distributions of the P2VP corona, giving rise to well-defined coronal surface patterns.⁸² Similarly, *O'Reilly, Dove*, and co-workers employed a variety of blends comprising crystallizable polylactone homopolymers and block copolymers to obtain 2D platelet micelles with compositionally differentiated core regions.^{83,84} Selective hydrolytic degradation of these structures yielded platelet micelles with hollow cores. In related work, blends of polyester-based block copolymers and homopolymers with varying stability were used to prepare platelets capable of fragmenting without external stimuli.⁸⁵ Fragmentation occurred naturally during aging, providing a simple, one-step method for producing hollow particles. Furthermore, the combination of living CDSA, sequential addition, and fluorescent coding enabled the creation

of 2D microbarcodes with precisely defined fluorescence patterns, which can be applied to optical storage applications.⁸⁶

Although symmetry breaking is common in nature and offers unique pathways to hierarchical structures in artificial materials, it has rarely been explored in 2D systems. This challenge was addressed by surface immobilization of cylindrical seed micelles, which permitted epitaxial growth of PFS-*b*-P2VP/PFS homopolymer blend unimers exclusively on one lateral side, resulting in unilateral platelets.⁸⁷ In a subsequent study, *Manners* and co-workers demonstrated that sequential living CDSA of block copolymers with poly(di-*n*-hexylfluorene) cores and corona-forming blocks such as PEG, P2VP, or quaternized polyfluorene, combined with spatially confined nanoparticle attachment and localized nanofiber fragmentation, produces non-centrosymmetric multiblock co-nanofibers. These structures show potential for application as chemically driven nanomotors.⁸⁸

Despite the ability to produce well-defined nanostructures, CDSA is limited by long processing times and low throughput, largely due to the need for time-consuming seed preparation and the restriction to small batch scales. These factors hinder the scalability of CDSA and limit the practical application of the resulting nanostructures. To address this challenge, an integrated flow cascade combining seed formation by flash-freezing and living CDSA was developed, to produce platelets directly from polymer solution within a time span of minutes.⁸⁹ The method has already been applied to the fabrication of platelets based on PCL and PLLA block copolymers.^{53,89}

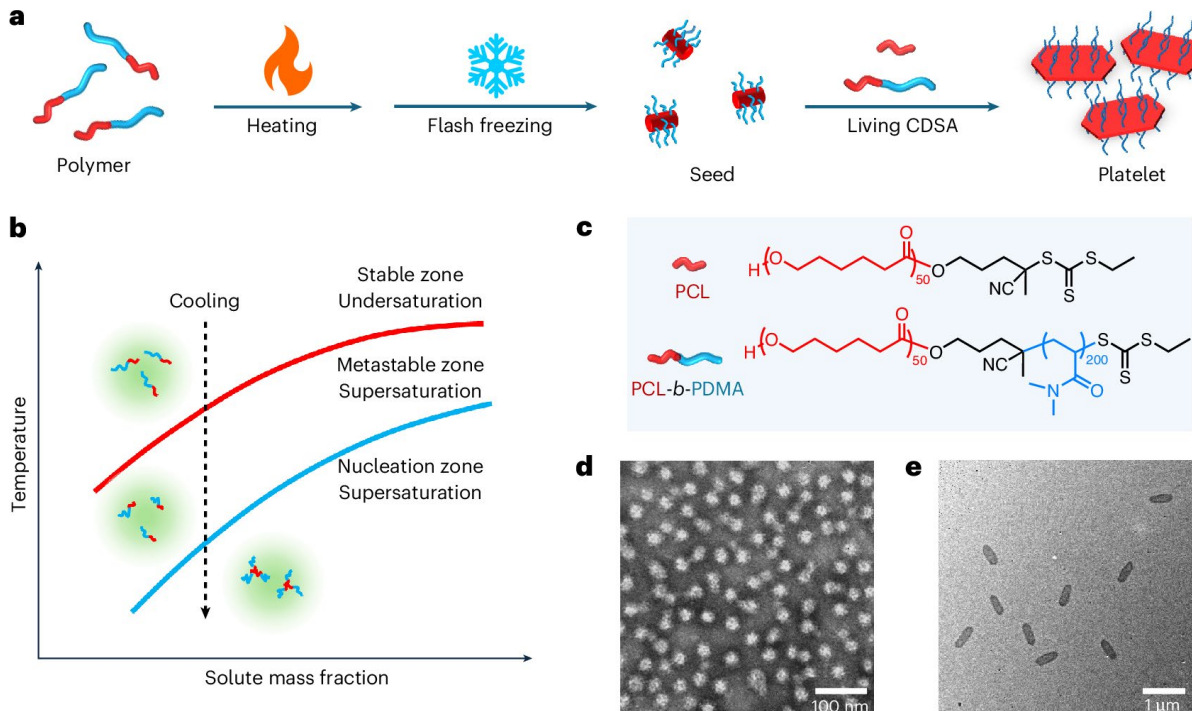


Figure 1.3 (a) Schematic illustration of the flow cascade process for the production of platelet-like block copolymer micelles utilizing flash-frozen seeds. (b) A phase diagram illustrating diblock copolymer crystallization using the flash-freezing strategy. (c) Chemical structures of PCL-based homo- and diblock copolymers. TEM micrographs of (d) flash-frozen seeds prepared at 0.1 mg ml^{-1} with 2 min heating at 75°C and rapid cooling (e) the resulting platelets prepared by living CDSA. Staining with 1 wt% uranyl acetate aqueous solution. Reprinted from Ref.⁸⁹ under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0), published by *Springer Nature* (© 2012, the Author(s)).

CDSA and CCDSA have been extensively employed to prepare 1D and 2D core-crystalline micelles, however, the creation of three-dimensional (3D) structures remains comparatively rare.⁹⁰ These 3D architectures, such as stacked, branched, spherulitic, or flower-like shapes, typically arise from defects in the crystalline lamellar precursors. Examples include screw dislocations during crystal growth, the formation of secondary nucleation sites, or lamellar stacking during the self-assembly process.^{52,91–96}

1.1.3 CDSA of Poly(*L*-lactide)-Containing Block Copolymers

While early studies primarily focused on PFS-containing block copolymers, CDSA has since been widely extended to polyester-based systems. Among these, block copolymers incorporating crystallizable poly(*L*-lactide) (PLLA) segments have emerged as particularly versatile materials owing to their biocompatibility and biodegradability. In addition, the presence of specific intermolecular interactions, such as hydrogen bonding, leads to distinct self-assembly behavior in PLLA-based block copolymers. For this reason, these systems will be discussed in greater detail below.

This field was pioneered by the groups of *O'Reilly* and *Dove*, who first described CDSA of PLLA-*b*-poly(acrylic acid) (PLLA-*b*-PAA) in water and THF/water mixtures, yielding well-defined cylindrical micelles.^{50,51} Higher unimer concentrations, achieved by increasing THF content, allow faster growth into longer cylinders. In a related strategy, CDSA was coupled with the *in situ* hydrolysis of PLLA-*b*-poly(tetrahydropyran acrylate) (PLLA-*b*-PTHPA) in THF/H₂O at 65 °C, yielding PLLA-*b*-PAA cylindrical micelles.⁹⁷ In this system, the length of the cylinders was governed by the degree of polymerization of the crystalline PLLA core, whereas the cylinder width was controlled by the length of the PAA corona block. The scope of CDSA of PLLA-containing polymers was extended to block copolymers with different corona-forming blocks, such as poly(4-acryloyl morpholine), PEO, and poly(*N,N*-dimethylacrylamide) (PDMA).⁴⁹ A key finding for improving the living character of CDSA of PLLA-containing block copolymers was the addition of a hydrogen-bond disruptor as a cosolvent to prevent self-nucleation and unimer aggregation.⁹⁸ Uniform fiber-like PLLA-*b*-poly(*N*-isopropyl acrylamide) (PLLA-*b*-PNiPAAm) and PLLA-*b*-P2VP micelles were prepared by seeded growth methods in the presence of trifluoroethanol (TFE) (**Figure 1.4**). CDSA of PLLA-*b*-poly(α -D-glucose carbonate) diblock copolymers resulted in fully degradable micelles of varying shapes.⁹⁹

A further study examined how the hydrophilicity influences the shape selectivity in CDSA of PLLA-based diblock co- and triblock terpolymers bearing corona-forming PDMA blocks.⁴⁸ Polymers with a higher hydrophilicity (i.e. higher PDMA content) preferential formed 2D platelets, while CDSA of less hydrophilic polymers resulted in either “transition-state” or pure 1D cylindrical micelles. In addition, it was shown that a longer core block length at a fixed core/corona ratio drives the self-assembly toward cylindrical structures, because of reduced solubility. This behavior contrasts with the conventional CDSA trends observed in PFS-based systems (cf. section 1.1.2), where longer solvophilic blocks relative to the core-forming block favour increased interfacial curvature and thus the formation of cylindrical or spherical micelles. Size control of 2D nanoplatelets was achieved *via* CDSA of PLLA-*b*-poly(2-dimethylaminoethyl methacrylate) (PLLA-*b*-PDMAEMA) diblock copolymers, and the resulting platelets were successfully applied as water-in-water emulsifiers.⁴⁶ Additionally, antibacterial 2D diamond-shaped nanoplatelets were prepared by CDSA of block copolymers featuring PNiPAAm and poly(ethyl acrylamide) blocks.⁴⁵ Ring-opening polymerization-induced crystallization-driven self-assembly (ROPI-CDSA) displays another interesting approach as it gives access to different 1D, 2D, and 3D nanostructures.⁵²

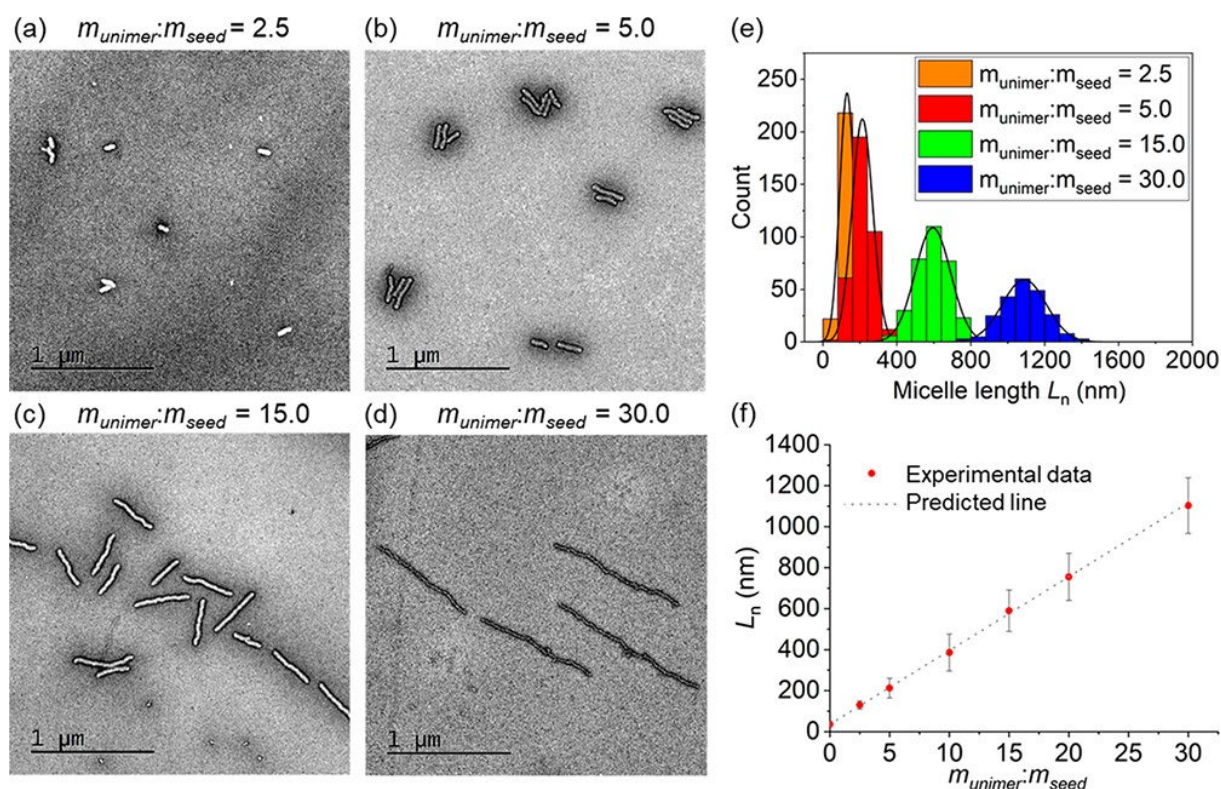
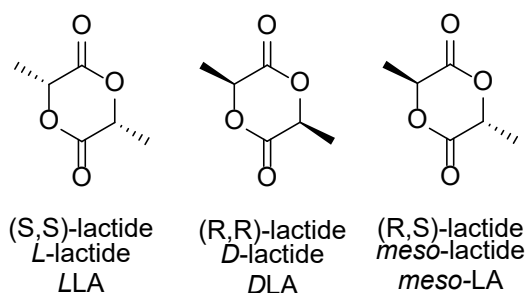


Figure 1.4 TEM micrographs of uniform PLLA₄₇-*b*-PNiPAAm₂₆₇ micelles obtained by seeded growth from seed micelles after 5 days of aging ($L_n = 36$ nm, $L_w/L_n = 1.10$, $\sigma/L_n = 0.26$). Assembly was carried out in TFE/EtOH mixtures with volume ratios of (a) 3:97, (b) 3:97, (c) 8:92, and (d) 15:85 following the addition of unimers dissolved in DMSO, using unimer-to-seed mass ratios of (a) 2.5, (b) 5.0, (c) 15.0, and (d) 30.0, respectively. (e) Summary of contour-length histograms corresponding to the micelle length distributions. (f) Number-average micelle length plotted as a function of the unimer-to-seed mass ratio (error bars represent the standard deviation). TEM samples were stained with a 2 wt % solution of uranyl acetate in ethanol. Reproduced from Ref.⁹⁸ (© 2019) with permission of the *American Chemistry Society*.

1.2 Block Copolymer Micelles via Polylactide Stereocomplexation

Another strong and efficient driving force for the construction of defined micelles is the formation of semi-crystalline stereocomplexes between block copolymers with enantiomeric polylactide (PLA) blocks.^{100–103} This can be referred as stereocomplex-driven self-assembly (SCDSA). Lactide, the dimer of lactic acid, occurs in three stereoisomeric forms: *L*-lactide, *D*-lactide, and *meso*-lactide (**Scheme 1.1**).¹⁰⁴ Among these, only isotactic polymers produced *via* ring-opening polymerization of either *L*- or *D*-lactide display crystallinity. Remarkably, when PLLA and poly(*D*-lactide) (PDLA) are combined in equimolar amounts, they can co-crystallize from the melt or solution to form a stereocomplex (SC), which has been mentioned first by Ikada *et al.* in 1987.¹⁰⁵



Scheme 1.1 Structures of *L*-, *D*- and *meso*-lactide.

SC crystals consist of a parallel packing of PLLA and PDLA 3_1 helices (**Figure 1.5**).¹⁰² This alternating arrangement of left- or right-handed helices allows the formation of hydrogen bonds between the proton of the methine group and the oxygen of the carbonyl group, resulting in a denser chain packing within the crystal. The SC crystals exhibit different physical and chemical properties in comparison to the neat homopolymer crystals. They have an enhanced thermal stability with a melting point ($T_m(\text{SC}) \approx 220 - 230^\circ\text{C}$), which is about 50°C higher compared to that of PLLA and PDLA homopolymers ($T_m \approx 170 - 180^\circ\text{C}$).¹⁰² Furthermore, they are insoluble even in the solvents or solvent mixtures they have been prepared.¹⁰⁶

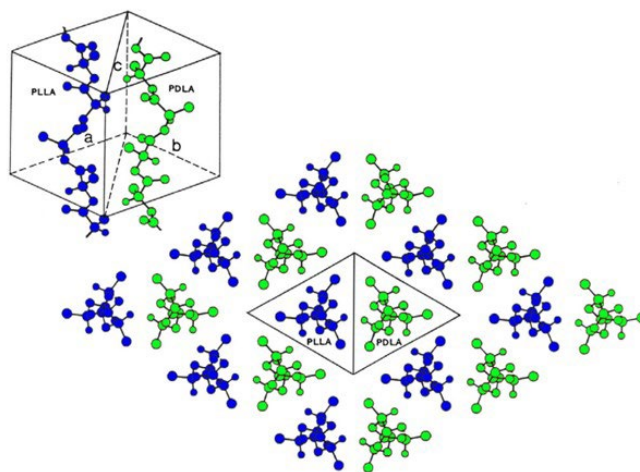


Figure 1.5 Illustration of the crystal structure of PLA SC. Parallel packing of PLLA (blue) and PDLA (green) 3_1 helices. Reproduced from Ref.¹⁰⁰ (© 2016) with permission from Elsevier.

This in turn has been harnessed to produce a variety of SC blends featuring different properties and, thus, leading to new applications.¹⁰⁰ Moreover, the formation of SCs is not limited to the blending of PLLA and PDLA, but can be applied for PLA based block copolymers. In this case, stereocomplexation was utilized for the formation of non-covalent polystyrene-SC-poly(lactide)-polyisoprene (PS-*sc*-PLA-PI) or PS-*sc*-PLA-P2VP triblock terpolymers, which were prepared

by the solution precipitation method employing the enantiomeric diblock copolymers PS-*b*-PDLA, PI-*b*-PLLA and P2VP-*b*-PLLA, respectively.^{107,108}

Furthermore, this concept has been extended to produce stable SC micelles from mixtures of PLLA and PDLA containing block copolymers in water as well as organic solvents.¹⁰¹ Actually, the first report on SC micelles employed a racemic mixture of PCL-*b*-PLLA / PCL-*b*-PDLA diblock copolymers and SC formation was studied directly in THF as a non-selective solvent.¹⁰⁹ Here, SC formation takes multiple days, until the SC micelles are formed due to the insolubility of the PLLA/PDLA SC core.^{110,111} In addition, SC micelles in THF have been reported employing polystyrene (PS) as soluble corona block (PS-*b*-PLLA/PS-*b*-PDLA).¹¹² Thereby, a kinetic study indicated that a higher polymer concentration and higher PLA fraction promotes aggregation. Additionally, a faster growth rate is observed when a diblock copolymer is blended with the respective enantiomeric homopolymer counterpart. In view of the shape of the SC micelles prepared in water as well as organic solvents, most commonly spherical micelles or particles were observed, except of only a few reports on the formation of cylindrical^{110,113–115} or disc-like¹¹⁴ SC micelles, and vesicles¹¹⁶. Water-dispersible SC micelles can be formed through two main approaches, depending on the fraction of the hydrophobic PLLA and PDLA blocks. The first method involves dissolving 1/1 mixtures of the block copolymers with enantiomeric PLA blocks directly in water. The second approach begins by dissolving the mixture in a common organic solvent, followed by gradual addition of water and subsequent dialysis against pure water. In general, SC micelles exhibit a lower critical micelle concentration and smaller size compared to micelles formed from the individual enantiomeric homopolymers. This difference arises from the denser chain packing within the SC core of the micelles.

Most studies on SC micelles have focused on linear block copolymers (AB-, ABA-, and ABC-type), star-shaped block copolymers, and graft copolymers incorporating poly(ethylene glycol) (PEG) or poly(oligo(ethylene glycol) methacrylate) (POEGMA) blocks. These systems primarily yield water-soluble SC micelles, which have been developed mainly to produce biodegradable micelles, particles, and gels for biomedical applications. Interestingly, the self-assembly of a pair of block copolymers with a mismatching size of the enantiomeric PLA blocks, i.e. different *D/L*-lactide ratio, led to several distinct nanostructures like nanospheres, 2D triangles and vesicles (**Figure 1.6a-c**).¹¹⁷ A similar system employing a triblock terpolymer composed of a water-soluble PEG block and PLA blocks with enantiomeric repeating units arranged in a defined sequence demonstrated that, in dilute solutions, intramolecular stereocomplexation is favoured.¹¹⁸ This preference leads to nanostructures that differ

significantly from those formed through intermolecular stereocomplexation between two triblock terpolymers. Building on this concept, subsequent work extended the approach to the formation of three-dimensional triangular prisms.¹¹⁹ CDSA of PDLA-*b*-PLLA-*b*-PEG triblock terpolymers with asymmetric sequential polylactide blocks enables programmed chain folding *via* intramolecular stereocomplexation between size-matched enantiomeric oligolactide units. This arrangement allows the excess PDLA domain to coexist with stabilizing PEG blocks on the top and bottom surfaces of the triangular core. These surface-exposed homochiral PDLA domains act as nucleation sites for epitaxial growth, driving the transformation of triangular cores into triangular prisms (Figure 1.6d,e).

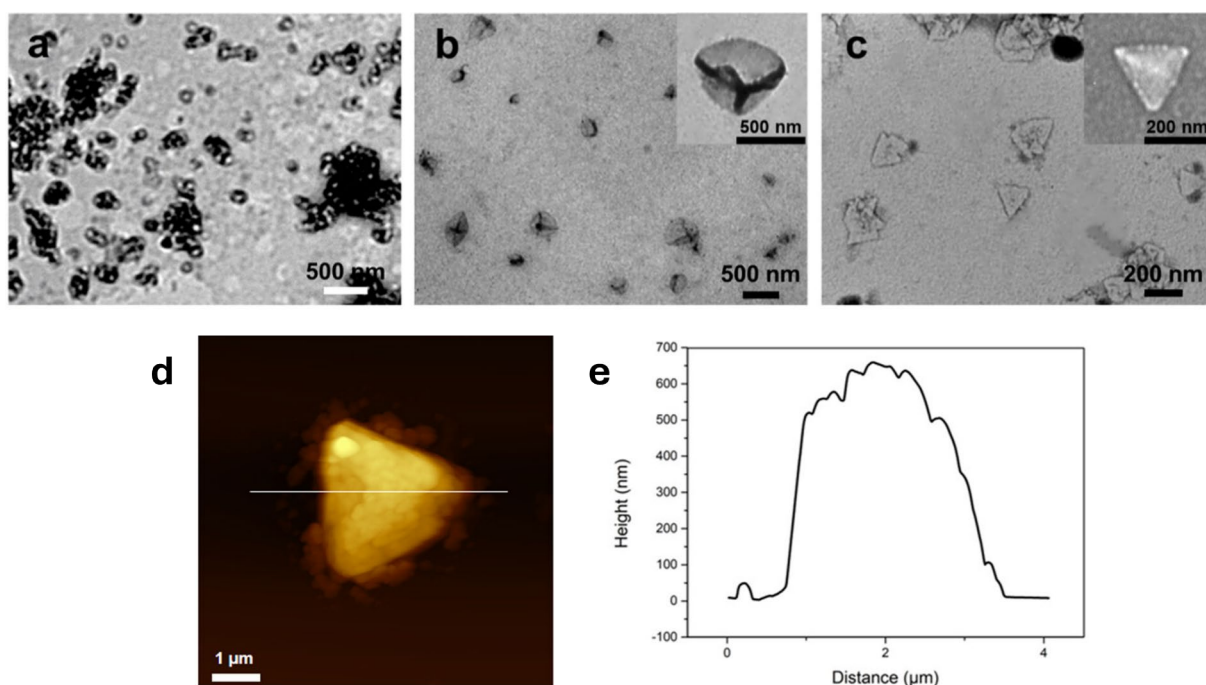


Figure 1.6 TEM micrographs of self-assembled structures with different shapes from mismatched SCs. (a) Nanoparticles prepared by co-assembly of DLA₄₀-*b*-PEG₄₅/LLA₃₂-*b*-PEG₄₅ (1/1 mol/mol, *D/L* = 1.250). (b) Vesicles formed by co-assembly of DLA₆₄-*b*-PEG₄₅/LLA₃₂-*b*-PEG₄₅ (1/1 mol/mol, *D/L* = 2.000). (c) Triangular 2D structures prepared by co-assembly of DLA₇₂-*b*-PEG₄₅/LLA₆₄-*b*-PEG₄₅ (1/1 mol/mol, *D/L* = 1.125). (d) AFM height image and (e) respective height profile of 3D triangular prisms prepared by CDSA of DLA₃₂-LLA₁₆-*b*-PEG₄₅. (a-c) Reproduced from Ref.¹¹⁷ (© 2021) and (d,e) from Ref.¹¹⁹ (© 2025) with permission of the *American Chemistry Society*.

Other hydrophilic blocks, such as poly(acrylic acid),^{120,121} poly(*N,N*-dimethylaminoethyl methacrylate),¹²² poly(isoglycerol methacrylate),¹¹⁶ PNiPAAm,¹²³ and poly(*N*-hydroxyethyl acrylamide) (PHEAAm),¹²⁴ have also been employed. Moreover, stereoregular PLLA-*b*-PAA and PDLA-*b*-PAA diblock copolymers have been investigated for the formation of cylindrical micelles with controllable dimensions in tetrahydrofuran (THF)/H₂O mixtures *via* CDSA.⁹⁷

Interestingly, when these stereoregular diblock copolymers were combined under identical self-assembly conditions, a morphology transition occurred, yielding spherical micelles with a PLA SC core.¹²⁰ A similar reorganization into spherical SC micelles was observed when homochiral cylindrical micelles were mixed under CDSA conditions (**Figure 1.7**). To gain deeper insight into the unimer-exchange mechanism, the system was modified to ABA triblock copolymers consisting of an enantiomeric PLA middle block (PLLA or PDLA) surrounded by PHEAAm end blocks.¹²⁴ This study revealed that the solubility of the block copolymers, specifically, longer corona-forming blocks and shorter core-forming blocks, results in a faster transition. Furthermore, the initial dissolution of unimers from the homochiral assemblies was identified as the likely rate-determining step of the transition.

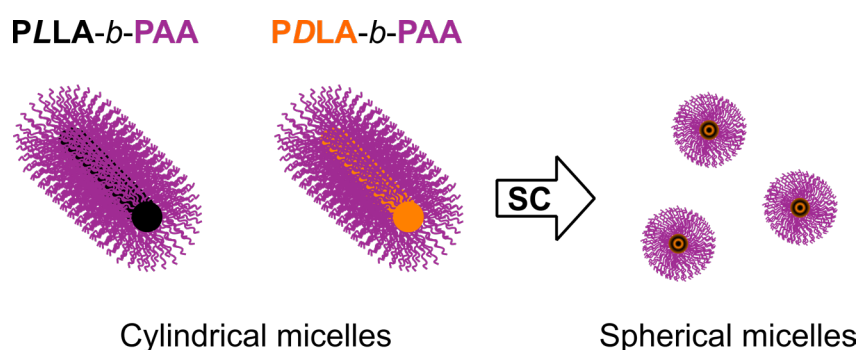


Figure 1.7 Schematic representation of the SC-induced morphological transition from cylindrical to spherical micelles in mixtures of enantiomeric PLLA₆₂-*b*-PAA₃₃₂ and PDLA₅₆-*b*-PAA₃₁₅ diblock copolymers in THF/H₂O (80/20, v/v) mixtures at 65 °C. Adapted from Ref.¹²⁰ under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0), published by *Springer Nature* (© 2012, the Author(s)).

SC micelles with a mixed corona composed of two chemically distinct and potentially immiscible blocks have been rarely reported to date.^{125–127} The group of Hedrick *et al.* described the formation of patchy SC micelles in water from a racemic mixture of PNiPAAm-*b*-PLLA and PEG-*b*-PDLA, directly dissolved in water (**Figure 1.8a**).¹²⁵ These micelles exhibited reversible, temperature-induced aggregation due to the PNiPAAm corona blocks, which display a cloud point at approximately 20 °C. Transmission electron microscopy (TEM) was employed to confirm the patchy corona structure, however, visualization proved challenging because of the small feature size (**Figure 1.8b**). In the other studies SC micelles with a corona consisting of mixed PEG and zwitterionic units,¹²⁷ or PEG and quaternized PDMAEMA were prepared,¹²⁶ whereas no information about the corona structure was provided.

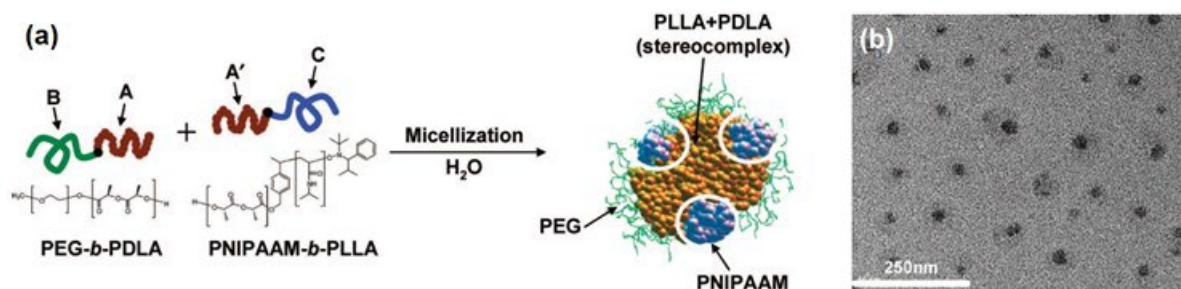


Figure 1.8 (a) Schematic illustration of mixed micelles prepared from PEG-*b*-PDLA + PNIPAAm-*b*-PLLA diblock copolymers in water. (b) TEM micrograph of the respective SC micelles. TEM samples were stained with phosphotungstic acid to visualize the corona structure. Reproduced from Ref.¹²⁵ (© 2009) with permission of the *American Chemistry Society*.

1.3 Surface-Compartmentalized Block Copolymer Micelles

In recent years anisotropic particles attracted increasing attention due to their novel morphologies paving the way for a multitude of potential applications.^{3,128–130} Anisotropic polymeric micelles can be classified into three categories, namely multicompartment core micelles (MCM), surface-compartmentalized micelles or a combination of both (Figure 1.9a).⁶⁵

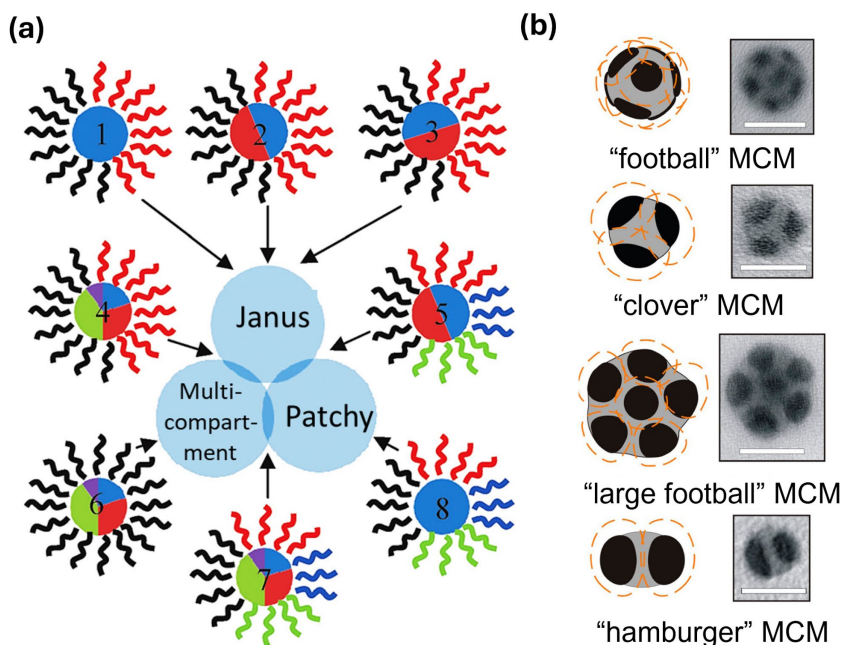


Figure 1.9 (a) Representation of different anisotropic polymeric micelles: Janus micelles (1-3), patchy micelles (5,7,8) and multicompartment micelles (4,6). (b) Sketches and TEM micrographs (scale bar 50 nm) of different MCMs prepared from PS-*b*-PB-*b*-PMMA triblock terpolymers: Football, clover, large football and hamburger MCMs (top to bottom). TEM samples were stained with OsO₄ (PS grey, PB black, PMMA not visible). (a) Reproduced from Ref.¹²⁸ (© 2011) with permission of the *Royal Society of Chemistry*. (b) Reproduced from Ref.¹³¹ (© 2011) with permission of the *American Chemistry Society*.

MCMs refer to micellar nanostructures composed of a solvophilic corona and a solvophobic core that is internally microphase-separated. Within the core, the individual domains must exhibit sufficiently distinct chemical compositions or physical properties in order to act as separate functional compartments.^{132,133} MCMs are commonly formed *via* hierarchical self-assembly strategies using appropriately designed molecular building blocks, which allows access to a broad spectrum of micellar morphologies.^{134–148} In addition to internal compartmentalization, surface-compartmentalized micellar assemblies can be classified into different categories. Janus-type micelles are characterized by coronas divided into two opposing regions with contrasting chemical composition and/or polarity, whereas patchy-like (patchy) micelles display multiple microphase-separated corona domains with varying surface chemistry.¹²⁸ Cylindrical block comicelles represent a specific subtype of patchy micelles, as they possess a segmented arrangement of surface compartments distributed along the longitudinal axis of the cylinder.⁶⁵ **Figure 1.10** illustrates this differentiation for one-dimensional (1D), cylindrical or worm-like micelles.

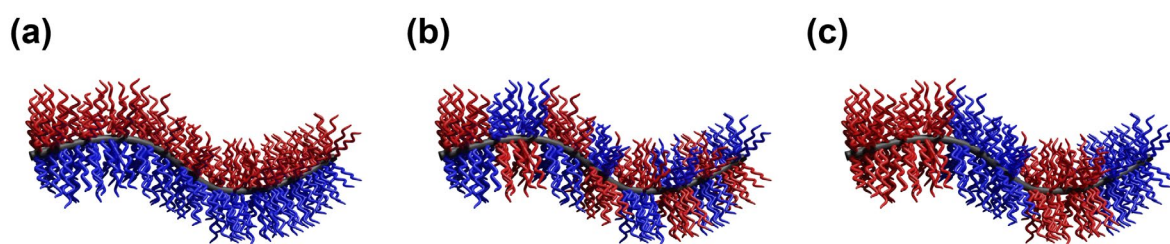


Figure 1.10 Illustration of a cylindrical (or worm-like) (a) Janus micelle, (b) patchy micelle and (c) block comicelle. Reproduced from Ref.⁶⁵ under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0), published by MDPI (© 2021, the Author(s)).

1.3.1 Janus Micelles

Janus micelles and particles, named after the two-faced Roman god Janus, have attracted significant interest, with research predominantly focusing on spherical architectures. This bias largely reflects the greater synthetic challenges associated with anisotropic Janus structures, such as cylindrical or disc-like morphologies.^{135,149–155} One approach to polymeric Janus micelles of varying shape is based on polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (PS-*b*-PB-*b*-PMMA) triblock terpolymer bulk morphologies, where the PB middle block can form spheres, cylinders, or lamellae sandwiched in between PS and PMMA lamellae.¹⁵⁶ Subsequent crosslinking of the PB domains in bulk followed by dissolution yields Janus spheres, cylinders and discs, respectively (**Figure 1.11a**). Building on this concept, amphiphilic spherical Janus micelles were prepared by alkaline hydrolysis of the PMMA ester

groups.¹⁵⁷ Stepwise dialysis against water resulted in a collapse of the PS chains and the formation of supermicelles consisting of several Janus micelles.

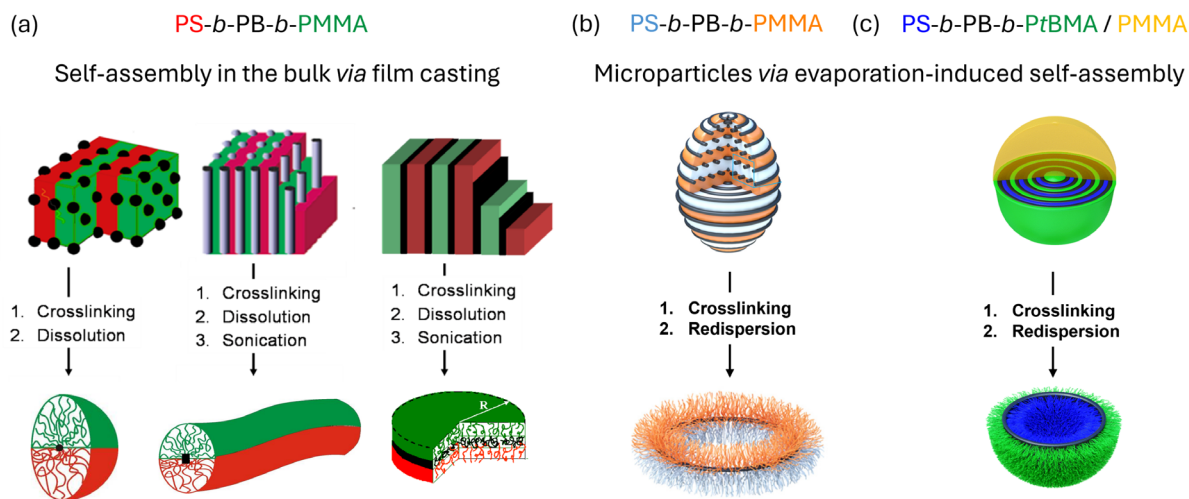


Figure 1.11 (a) Bulk morphologies formed by PS-*b*-PB-*b*-PMMA triblock terpolymers *via* film casting from solution (top) and the resulting architectures of Janus micelles (bottom). (b,c) Formation of Janus rings and Janus nanobowls originating from multicompartiment microparticles formed *via* evaporation-induced self-assembly of PS-*b*-PB-*b*-PMMA triblock terpolymer or blends of PS-*b*-PB-*b*-PtBMA triblock terpolymer and PMMA homopolymer. (a,c) Reproduced from Ref.¹⁵⁶ (© 2008) and Ref.¹⁵⁸ (© 2023) with permission of *Royal Society of Chemistry*. (b) Reproduced from Ref.¹⁵⁸ (© 2019) with permission of the *American Chemistry Society*.

However, the requirement for tailored polymer block sequences, highly specific conditions, or multistep processes considerably limits both the diversity and the quantity of materials that can be produced. To address these limitations, *Müller* and co-workers developed a facile solution-based approach that enables the formation of homogeneous Janus particles at significantly higher concentrations, reaching up to 100 g L⁻¹, through guided hierarchical self-assembly of ABC triblock terpolymers.¹³¹

An alternative strategy for creating Janus-type micellar assemblies involves the self-assembly of ABC triblock terpolymers under confinement. *Gröschel* and co-workers demonstrated that a PS-*b*-PB-*b*-PMMA triblock terpolymer can self-assemble within the confinement of nanoemulsion droplets resulting in prolate ellipsoidal microparticles exhibiting an axially stacked lamellar-ring (*lr*) morphology.¹⁵⁹ Cross-linking of the PB rings enabled disassembly of these microparticles into Janus nanorings bearing two strictly separated polymer brushes of PS and PMMA on opposite surfaces. Using the same concept, Janus discs with controllable shapes and sizes were prepared by combining Shirasu porous glass membrane (SPG) emulsification with evaporation-induced confinement assembly.¹⁶⁰ Furthermore, blending a PS-*b*-PB-*b*-PtBMA (PtBMA = poly(*tert*-butyl methacrylate) triblock terpolymer with high-molecular

weight PMMA homopolymers yielded Janus nanoplates, -bowls, and -cups with tuneable dimensions.¹⁵⁸

Most concepts rely on the self-assembly of amorphous block copolymers combined with core cross-linking. In contrast, Janus micelles with a crystallizable core-forming block remain far less explored. *Schmalz* and co-workers reported the formation of amphiphilic, worm-like Janus micelles *via* CDSA of a double-crystalline PS-*b*-PE-*b*-PEO triblock terpolymer.¹⁶¹ In this system, the pronounced incompatibility between the two corona blocks (PS and PEO) appears to be crucial for generating a Janus-type microphase-separated corona.

1.3.2 Patchy Micelles

Several approaches have been developed to generate patchy micelles from amorphous block copolymers. One strategy involves the self-assembly of ABC triblock terpolymers in solvents that are selective for the two incompatible outer blocks A and C.^{162–168} A second route relies on the co-assembly of AB and CD diblock copolymers, where specific interactions between the B and C segments, such as hydrogen bonding, ionic interactions, or solvophobic effects, drive the formation of patchy micelles featuring an insoluble mixed B/C core.^{169–172} In a third approach, AB and BC diblock copolymers are co-assembled, with the shared B block constituting the insoluble micellar core.^{173–176} Apart from the fact that mostly spherical patchy micelles have been reported, there is one rare example for the production of worm-like patchy micelles. Poly(*n*-butyl acrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (P*n*BA-*b*-PCEMA-*b*-P*t*BA) triblock terpolymers are able to form cylindrical micelles with a patchy corona upon self-assembly in a non-solvent for the PCEMA middle block.^{162,163} This intermediate structure further on transforms into double and triple helices *via* hierarchical self-assembly (**Figure 1.12**).

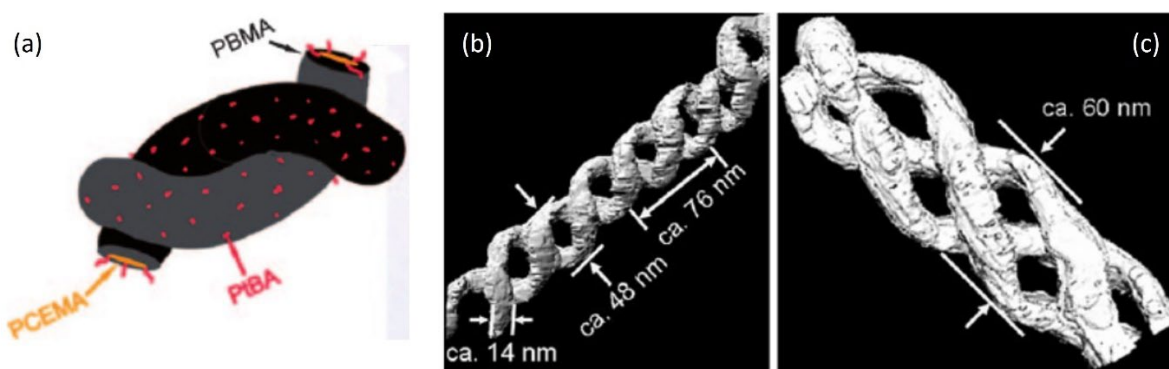


Figure 1.12 Self-assembly of P*n*BA-*b*-PCEMA-*b*-P*t*BA triblock terpolymer. (a) Schematic illustration of the chain packing in a double-helix section. TEM tomography micrograph of (b) double and (c) triple helices spray-coated from CH₂Cl₂/CH₃OH. Reproduced from Ref.¹⁶³ (© 2009)) with permission from John Wiley and Sons.

Moreover, CDSA is another efficient method for the preparation of 1D (cylindrical or worm-like) patchy micelles.⁶⁵ Hereby two main concepts can be employed: Firstly, CDSA of linear triblock terpolymers with crystallizable middle blocks,^{23,24,177} and secondly, CDSA of a mixture of diblock copolymers bearing a common crystallizable block.^{178–181} However, in the latter approach the corona patches of the resulting micelles are typically arranged in a block-like rather than alternating fashion. Up to now, patchy micelles with crystalline cores have exclusively been prepared from block copolymers with crystallizable PE or PFS blocks. In case of PE a solvent has to be used that is able to dissolve PE at elevated temperatures and, thus, CDSA can be induced by cooling. Thereby, a dependency of the micelle morphology on the solvent quality for the PE middle block can be observed, as shown for PS-*b*-PE-*b*-PMMA (SEM) triblock terpolymers in **Figure 1.13a**.²³ In a good solvent (e. g. THF or toluene) the triblock terpolymer is molecularly dissolved as unimers at elevated temperatures. Upon cooling stable nuclei are formed, which are able to initiate the 1D epitaxial growth of the remaining unimers to generate worm-like crystalline-core micelles (wCCMs). In bad solvents like dioxane the PE block is insoluble even at high temperatures and spherical micelles with an amorphous (molten) PE core are formed. These crystallize independently upon cooling to generate spherical crystalline-core micelles (sCCMs). Because of the incompatibility of the PS and PMMA corona-forming blocks, both wCCMs and sCCMs show a patchy microphase-separated corona structure (**Figure 1.13b, c**).

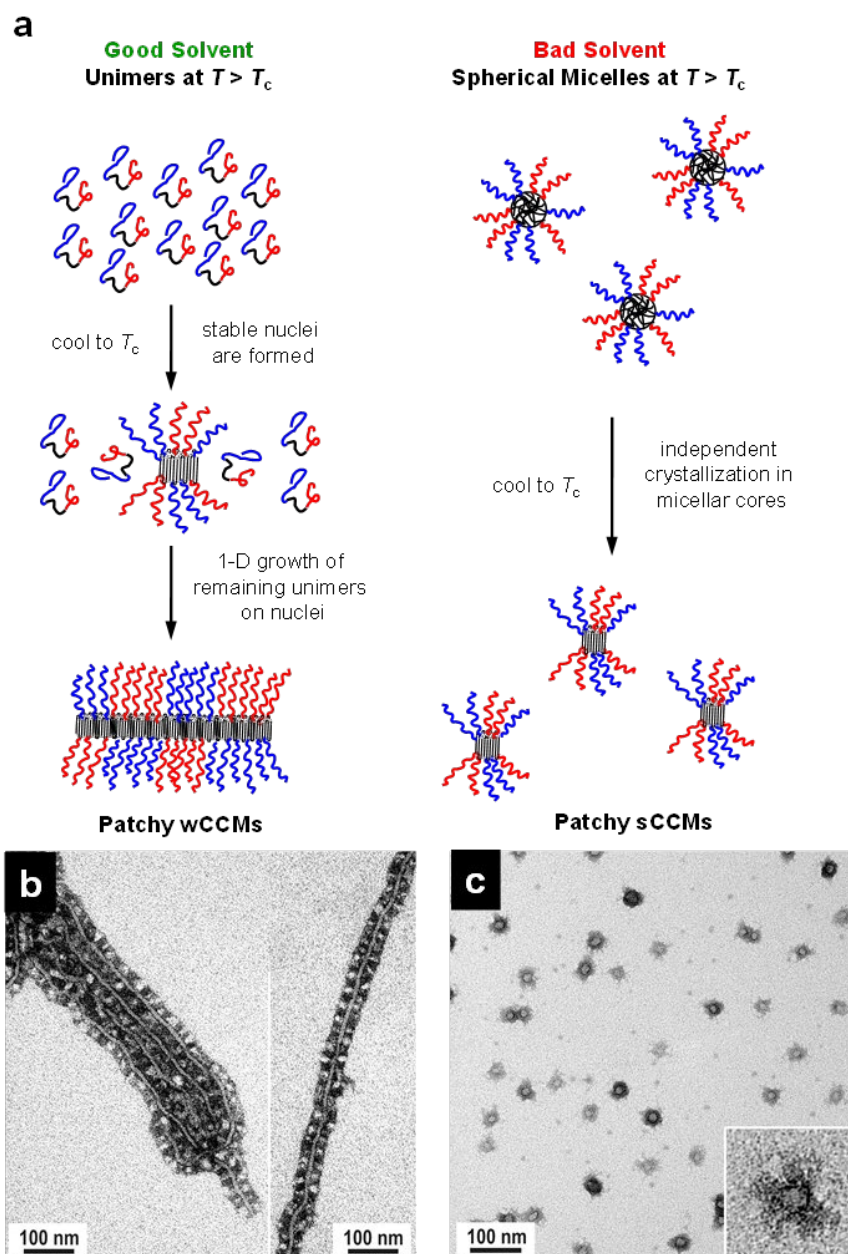


Figure 1.13 (a) Schematic representation of the proposed mechanism for the formation of patchy wCCMs and sCCMs from SEM triblock terpolymers (PS blocks are represented in blue, PE in black, and PMMA in red). TEM micrograph of (b) patchy $S_{340}E_{700}M_{360}$ wCCMs prepared by CDSA in THF and subsequent annealing at 45 °C for 3 h, and (c) patchy $S_{340}E_{700}M_{360}$ sCCMs formed in dimethylacetamide (subscripts denote the respective average degrees of polymerization). PS was selectively stained with RuO_4 vapour and appears dark. Reproduced from Ref.⁶⁵ under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0), published by MDPI (© 2021, the Author(s)).

For the formation of patchy wCCMs with PFS-based block copolymers some successful examples are μ -SIF (polystyrene-*arm*-polyisoprene-*arm*-poly(ferrocenyl dimethylsilane)) miktoarm star terpolymer (**Figure 1.14a**),¹⁸² as well as triblock terpolymers of PS-*b*-PFS-*b*-PMMA (**Figure 1.14b**), PS-*b*-PFS-*b*-PMVS (PMVS = polymethylvinylsiloxane and PI-*b*-PFS-*b*-PMMA (PI = polyisoprene)).^{177,183} Due to corona chain crowding and a limitation in solvents,

CDSA of PFS-based triblock terpolymers tend to be more difficult than for the diblock copolymers previously mentioned in section 1.1.2. By co-crystallization of PS-*b*-PFS-*b*-PMMA triblock terpolymers with varying corona chain lengths (PS and PMMA) block comicelles with a patchy corona could be obtained (**Figure 1.14c, d**). Interestingly, the different corona thicknesses were still visible in TEM analyses.

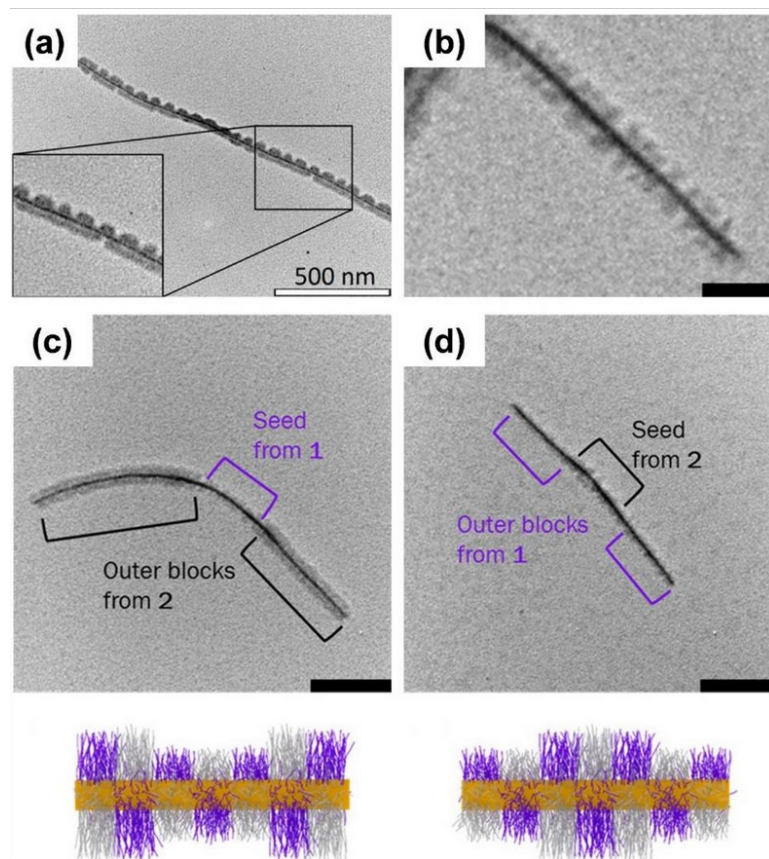


Figure 1.14 (a) Patchy micelles formed by CDSA of a μ -SIF miktoarm star terpolymer in ethyl acetate. (b) Patchy cylindrical micelles and (c, d) patchy ABA-type triblock comicelles with a crystalline PFS core and a patchy PS/PMMA corona prepared in acetone (scale bars = 100 nm). (c, d) Triblock terpolymers with PS and PMMA blocks of systematically varied lengths were used to control the width of the patchy corona in the middle and outer domains of the triblock comicelles (in the sketches PS is depicted in light grey and PMMA in purple). (a) Reproduced from Ref.¹⁸² (© 2014) and (b-d) reproduced from Ref.¹⁸³ (© 2018) with permission of the *American Chemistry Society*.

1.3.3 Application of Surface-Compartmentalized Micelles

The distinctive corona architecture of surface-compartmentalized polymer micelles offers access to a broad spectrum of potential applications. Janus micelles have been employed in diverse fields, including the use as highly effective particulate surfactants,^{184–186} as nanosensors and for biological imaging,^{187,188} in interfacial catalysis,^{189,190} in drug delivery^{191,192} and cancer therapy (**Figure 1.15**).^{193,194} Furthermore, due to their exceptional interfacial activity, Janus micelles have been extensively investigated as compatibilizers in polymer blends, even under conditions relevant to technological applications.^{195–199}

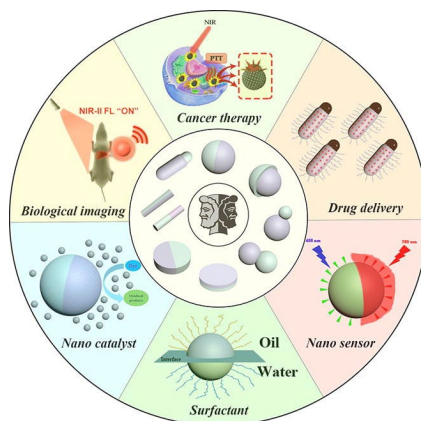


Figure 1.15 Overview of the applications of Janus particles across different fields. Reprinted from Ref.²⁰⁰ (© 2022) with permission from *Elsevier*.

In comparison to Janus micelles, patchy micelles have been studied with a strong focus on hierarchical self-assembly and considerably less with respect to applications.^{201–207} Notably, worm-like patchy micelles show a comparable interfacial activity with respect to that of cylindrical Janus micelles (**Figure 1.16a**).²⁰⁸ This is attributed to the ability of the patchy corona to adjust to the interface through selective swelling or collapse of the respective soluble and insoluble surface patches. This makes patchy micelles highly interesting as compatibilizers for polymer blends. However, up to now there is only one report on the use of patchy carbon nanotubes for the compatibilization of PS/PMMA blends (**Figure 1.16b**).²⁰⁹

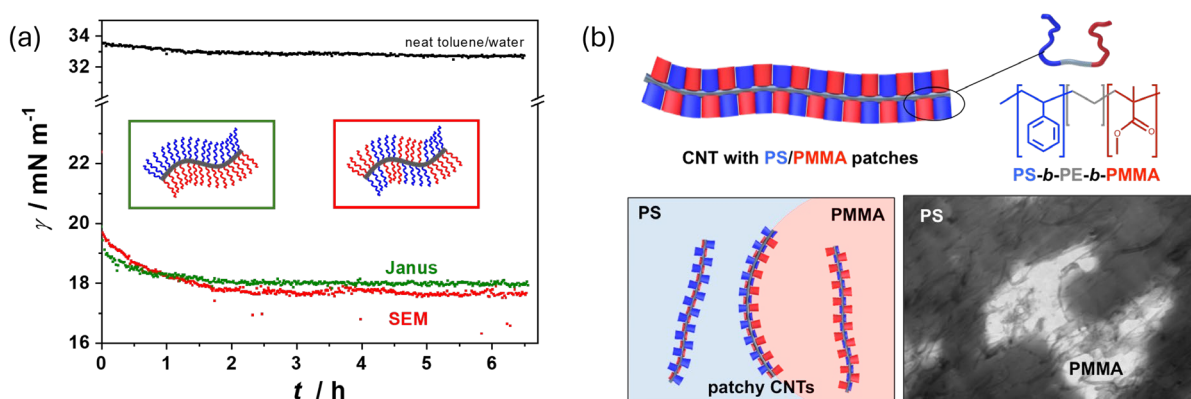


Figure 1.16 (a) Interfacial tension isotherms for PS-*b*-PB-*b*-PMMA Janus cylinders compared to patchy wCCMs of PS-*b*-PE-*b*-PMMA at the toluene/water interface. (b) Schematic illustration of carbon nanotubes coated with patchy wCCMs and their application as compatibilizer for PS/PMMA blends. (a) Reproduced from Ref.²⁰⁸ (© 2013) with permission of the *Royal Society of Chemistry*. (a) Reproduced from Ref.²⁰⁹ (© 2016) with permission of the *American Chemistry Society*.

Patchy wCCMs with functional patches featuring tertiary amino groups were further immobilized on PS fibers by coaxial electrospinning, resulting in catalytic active patchy hybrid

nonwovens, after loading with gold nanoparticles.²¹⁰ Notably, both patch size and chemistry were found to play a critical role in determining catalytic activity.²¹¹

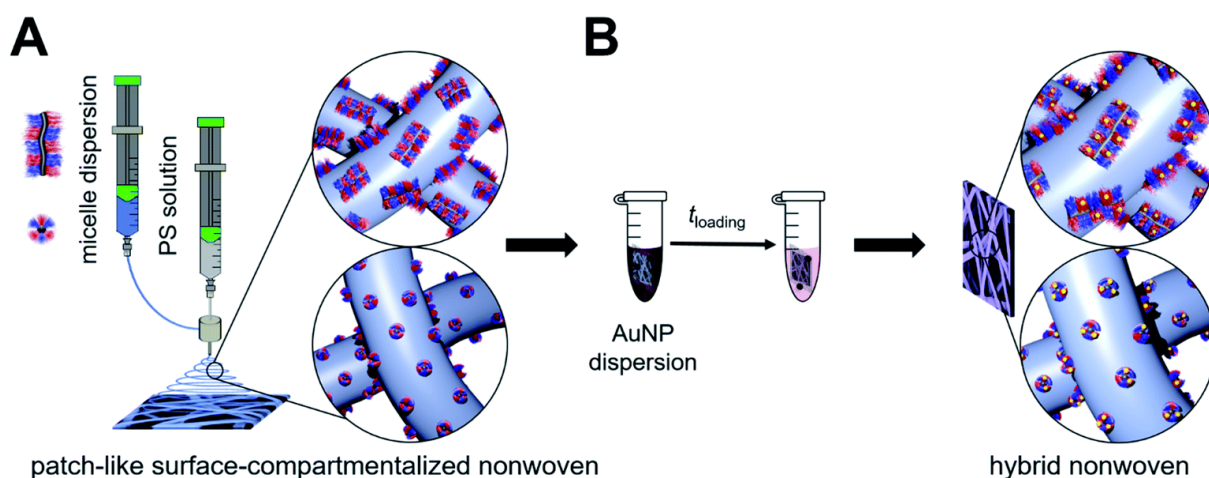


Figure 1.17 Preparation of catalytically active hybrid nonwovens: (A) functional, patch-like surface-compartmentalized nonwovens are produced by coaxial electrospinning of PS as the core (grey) and patchy wCCMs or sCCMs as the shell (blue), followed by loading with preformed citrate-stabilized Au NPs by a simple ligand exchange (dipping process (B)). Reproduced from Ref.²¹¹ under the terms of the Creative Commons Attribution NonCommercial 3.0 Licence (CC BY-NC 3.0), published by *Royal Society of Chemistry*.

Moreover, these patchy nonwovens could also be utilized in constructing well-defined, complex hierarchical superstructures with fir-tree or barbed wire-like shapes when combined with supramolecular self-assembly.^{212,213} In this context, the distinctive corona architecture of patchy wCCMs is utilized to initiate and regulate the molecular self-assembly of a rationally designed benzene-1,3,5-tricarboxamide (BTA). Patch-mediated assembly of the BTA from the surface of the patchy fibers is governed by the chemical compatibility between functional groups present within the corona patches and the peripheral substituents of the BTA. This chemical matching determines both the local solubility of the BTA and its ability to access and interact with the surface patches.

1.4 Objective of the Thesis

Crystallization-driven self-assembly (CDSA) has proven to be an effective strategy for the production of patchy cylindrical or worm-like (1D) micelles, however, has only been applied to block copolymers with crystallizable PE and PFS blocks so far. CDSA of PFS based block copolymers is limited to the use of non-solvents for the PFS block, and, furthermore, their synthesis can be quite demanding. On the other hand, surface-compartmentalized micelles with PE cores suffer from a comparably low melting point of the PE core even in the dry state ($T_m \approx 90\text{ }^{\circ}\text{C}$), hindering their use at elevated temperatures. Moreover, reports on patchy spherical micelles are scarce and platelet-like (2D) structures with a stripe-like arrangement of the patches have not been demonstrated to date. Hence, there is a substantial need for new concepts toward patchy micelles, owing to their unique properties, including superior interfacial activity, the ability to serve as templates for hierarchical self-assembly, and potential as platforms for heterogeneous catalysis.

This thesis aims to develop new routes for the preparation of patch-like surface-compartmentalized core-crystalline micelles with diverse morphologies and corona functionalities, focusing on PLA based block copolymers (**Figure 1.18**).

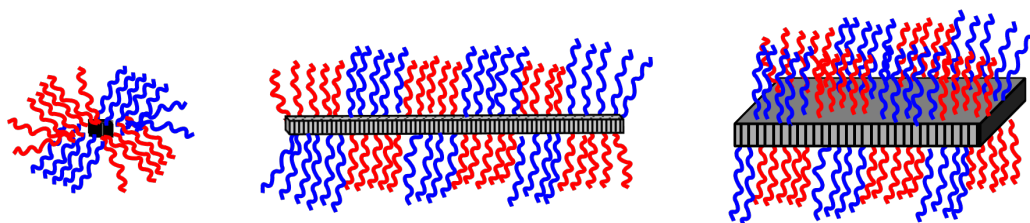


Figure 1.18 Patchy micelles with spherical, cylindrical and platelet-like morphologies.

Stereocomplex-driven self-assembly (SCDSA) of block copolymers with enantiomeric PLA blocks has proven as versatile tool for the preparation of micelles with a PLA stereocomplex core, showing an increased melting point ($T_m \approx 200\text{ }^{\circ}\text{C}$) and stability against solvents compared to the respective diblock copolymer constituents. One central question of this thesis is whether SCDSA of enantiomeric PLLA and PDLA based diblock copolymers with highly incompatible corona-forming blocks, e.g. PS and *Pt*BMA, can be harnessed for the production of stereocomplex micelles with a surface-compartmentalized corona and varying shape. Moreover, the obtained patchy micelles should be screened for their efficiency in the compatibilization of highly immiscible polymer blends and for the stabilization of emulsions. While Janus micelles have been widely explored for these applications, there are hardly any

reports on the use of patchy micelles. Here, a systematic investigation of the influence of the corona chemistry as well as the compatibilizer/stabilizer content is needed to compare the performance with that of Janus micelles.

Co-crystallization driven self-assembly (CCDSA) of crystalline-coil diblock copolymers with the respective crystallizable homopolymer is a powerful tool for the construction of well-defined 2D platelet micelles, including surface-compartmentalized 2D micelles with a concentric arrangement of surface compartments. However, “truly” patchy platelets with a non-concentric arrangement of the corona patches have not yet been realized. This challenge is addressed by employing triblock terpolymers with a crystallizable PLLA middle block and two incompatible PS and *Pt*BMA corona-forming blocks together with the corresponding PLLA homopolymer in CCDSA experiments. Next to this, the self-assembly behavior of the neat triblock terpolymers will be investigated for its potential to produce surface-compartmentalized micelles with spherical or cylindrical morphologies.

Another central objective of this thesis is to explore whether CDSA and SCDSA can be combined to selectively address the surface patches of core-crystalline micelles. To this end, patchy micelles with a crystalline PE core and stereoregular PLLA patches within the corona will be prepared by CDSA and subsequently loaded with PDLA homopolymer through stereocomplexation. This raises the broader question of whether SCDSA can serve as an elegant strategy for the incorporation of functional guest molecules into the micellar corona, thereby expanding the scope of surface-compartmentalized micelles toward advanced applications.

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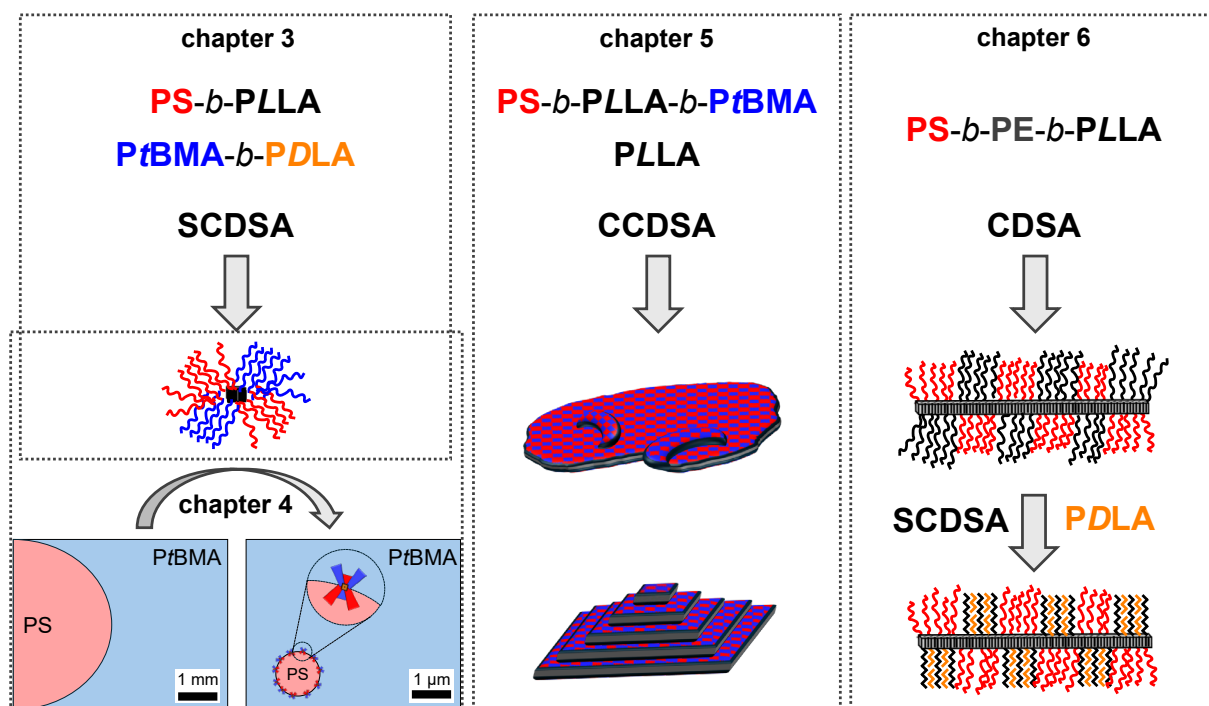
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2 Synopsis

2.1 Thesis Overview

This thesis consists of four scientific articles, three of which have been published, and one is under revision. The aim of this work was to develop new concepts for the preparation of patch-like surface-compartmentalized core-crystalline micelles (CCMs) with diverse morphologies and tailored corona functionalities. The central theme connecting all contributions is harnessing the distinct crystallization characteristics of block copolymers containing stereoregular, crystallizable polylactide segments to direct self-assembly and control micelle shape. A general overview of the thesis is provided in **Scheme 2.1**.



Scheme 2.1 Overview of the key findings of this thesis. Chapter 3 introduces SCDSA of PS-*b*-PLLA and PtBMA-*b*-PDLA diblock copolymers as facile strategy for the preparation of spherical micelles with a semicrystalline PLLA/PDLA SC core and a patchy PS/PtBMA corona. In chapter 4 these patchy SC micelles are applied as efficient compatibilizers for strongly immiscible polymer blends. Chapter 5 explores CCDSA of PS-*b*-PLLA-*b*-PtBMA triblock terpolymers with PLLA homopolymer, resulting in the formation of twisted patchy platelets and their 3D assemblies. Chapter 6 combines CDSA and SCDSA of PS-*b*-PE-*b*-PLLA triblock terpolymers for the selective loading of patchy wCCMs.

Although crystallization-driven self-assembly (CDSA) is an effective method for the production of one-dimensional CCMs with a surface-compartmentalized corona, access to other structures remains limited. In addition, its application has so far been restricted to block copolymers containing crystallizable polyethylene (PE) or poly(ferrocenyl dimethylsilane) blocks.

Chapter 3 introduces stereocomplex-driven self-assembly (SCDSA) as a facile route to micelles with a semicrystalline stereocomplex (SC) core and a patch-like microphase separated corona. This approach employs diblock copolymers with enantiomeric poly(*L*-lactide)/poly(*D*-lactide) (PLLA/PDLA) blocks and highly incompatible corona-forming blocks, namely polystyrene (PS) and poly(*tert*-butyl methacrylate) (PtBMA). The resulting spherical micelles were tested for their interfacial activity and potential use as emulsion stabilizers. Notably, variations in self-assembly conditions and diblock copolymer compositions did not yield any morphologies other than spherical micelles.

Building on this concept, **chapter 4** deals with the application of the patchy SC micelles as compatibilizers for strongly immiscible PS/PtBMA blends. This work investigates the influence of the corona chemistry and compatibilizer content on blend homogeneity and compatibilization efficiency, i.e. size reduction of the dispersed minority phase. Furthermore, fluorescent labelling of the patchy SC micelles is introduced as an elegant method to localize the micelles within the blend employing confocal fluorescence microscopy. Finally, the compatibilization efficiency of patchy micelles is compared to that of Janus micelles.

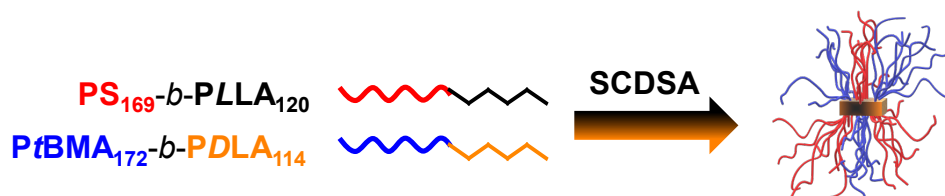
Since SCDSA solely resulted in spherical structures, **Chapter 5** presents co-crystallization-driven self-assembly (CCDSA) of PS-*b*-PLLA-*b*-PtBMA (SLT) triblock terpolymers with the corresponding PLLA homopolymer as alternative approach to access different morphologies. For the first time, the formation of twisted, patchy platelet-like micelles is demonstrated. This work further investigates the self-assembly conditions of CCDSA, leading to defined three-dimensional assemblies of multilayered stacked platelets. The interfacial activity of the patchy platelets is also evaluated and compared to that of the spherical patchy SC micelles.

Chapter 6 explores the combination of CDSA and SCDSA to selectively address the stereoregular patches of worm-like CCMs (wCCMs). This work examines the CDSA of double crystalline PS-*b*-PE-*b*-PLLA triblock terpolymers to yield wCCMs with a PE core and a patchy PS/PLLA corona. Subsequently, the PLLA patches were selectively loaded with PDLA homopolymer *via* stereocomplexation. The potential of SCDSA to incorporate functional guest molecules into the micellar corona is also demonstrated.

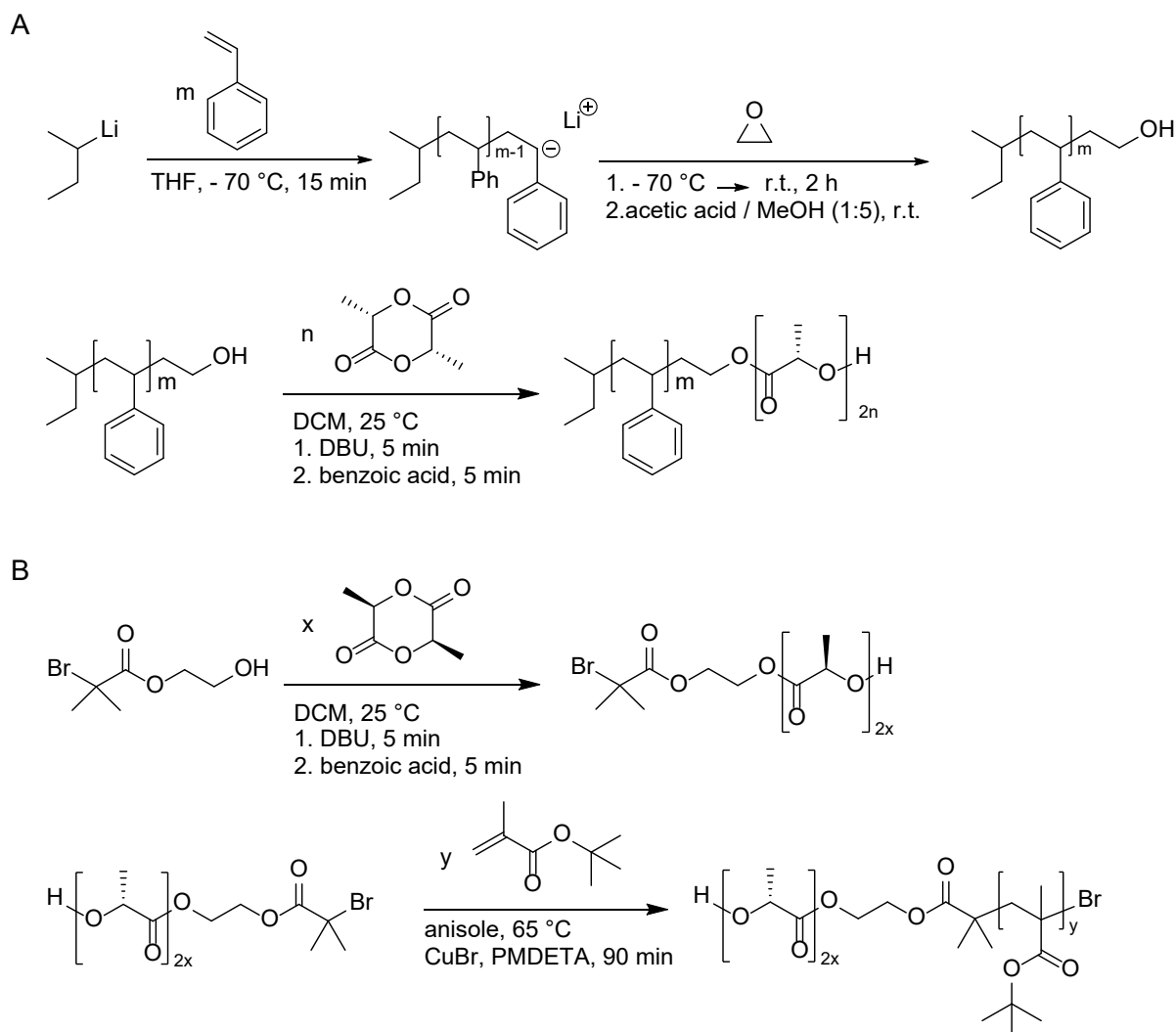
A brief summary of the key findings is given in the following sections.

2.2 Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly

This work demonstrates that SCDSA of diblock copolymers bearing enantiomeric PLLA and PDLA blocks as well as strongly incompatible, amorphous corona-forming blocks is a versatile approach toward spherical patchy micelles with excellent interfacial activity (**Scheme 2.2**).



Scheme 2.2 Concept for the preparation of patchy SC micelles *via* SCDSA.



Scheme 2.3 Synthesis of (A) PS₁₆₉-*b*-PLLA₁₂₀ and (B) PDLA₁₁₄-*b*-PtBMA₁₇₂ diblock copolymers.

The used PS₁₆₉-*b*-PLLA₁₂₀ diblock copolymer (subscripts denote number-averaged degrees of polymerization) was synthesized by combining living-anionic polymerisation of styrene, followed by end-capping with ethylene oxide, and organo-base catalyzed ring-opening polymerization (ROP) of *L*-lactide using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst (**Scheme 2.3A**). For the synthesis of the enantiomeric counterpart, PDLA₁₁₄-*b*-PtBMA₁₇₂, a combination of ROP and atom transfer radical polymerization (ATRP) was utilized (**Scheme 2.3B**).

For the preparation of the micelle dispersions, a mixture of the diblock copolymers in dichloromethane (DCM), employing a 1/1 (w/w) ratio with respect to the enantiomeric PLA blocks, was added drop-wise to cyclohexane (CH) being a selective solvent for the corona-forming blocks ($c = 0.9 \text{ g L}^{-1}$, CH/DCM = 10/1 (v/v)). This resulted in the formation of micelles with an insoluble PLLA/PDLA SC core and a soluble PS/PtBMA corona (denoted as PS-*sc*-PLA-PtBMA). Dynamic light scattering (DLS) revealed a narrow size distribution with a hydrodynamic diameter of $D_{h,app} = 104 \pm 30 \text{ nm}$ (**Figure 2.1A**). From the transmission electron microscopy (TEM) micrograph shown in **Figure 2.1B** a patch-like microphase-separated corona of the micelles can be clearly deduced. Due to selective staining with RuO₄ vapor PS domains appear dark and the semicrystalline PLA SC core as well as the PtBMA domains in the corona bright. The micelles feature different numbers of PS patches, mostly 3–5, and hence the micelle structure might be described best as a shamrock-like morphology. The patchy corona structure becomes even clearer by comparison with PS-*sc*-PLA-PS micelles prepared by SCDSA of PS₁₆₉-*b*-PLLA₁₂₀ and PS₁₆₉-*b*-PDLA₁₉₀ under identical conditions. The micelles show a narrow size distribution with a comparable $D_{h,app}$ of $82 \pm 25 \text{ nm}$ (**Figure 2.1A**) and from TEM the difference in corona structure is evident, appearing now homogeneously dark. (**Figure 2.1C**).

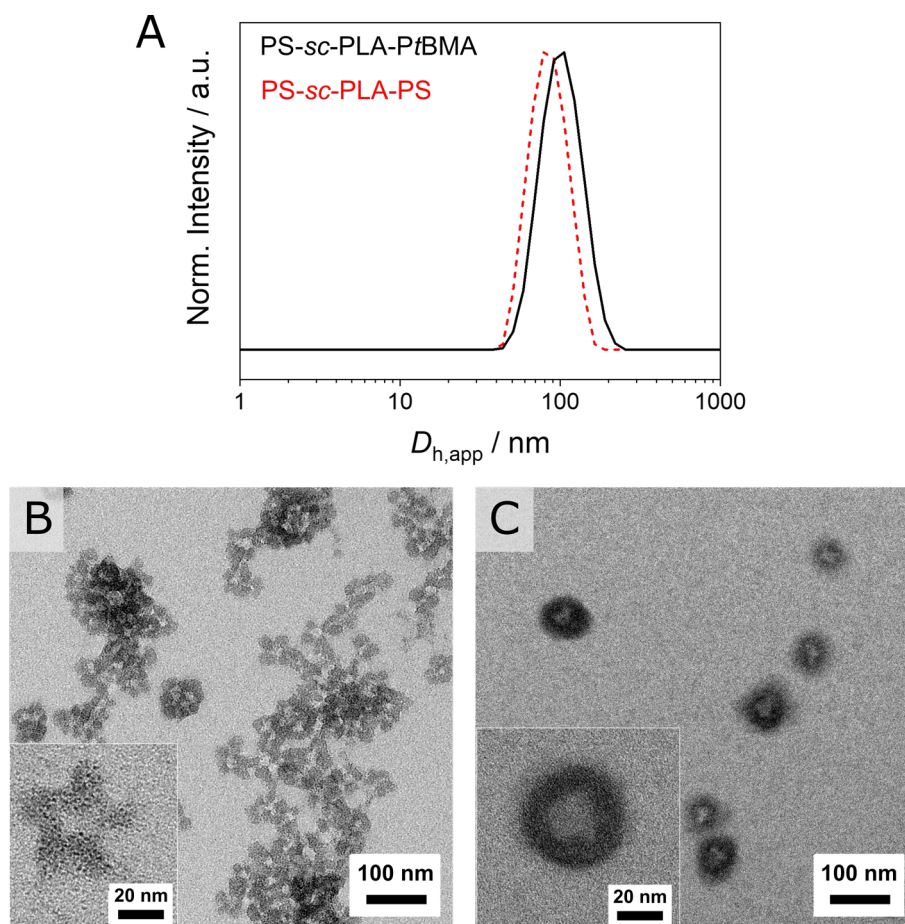


Figure 2.1 (A) Concept for the preparation of patchy SC micelles *via* SCDSA. (B) Hydrodynamic diameter distributions from DLS for SC micelles prepared from PS₁₆₉-*b*-PLLA₁₂₀/PDLA₁₁₄-*b*-PtBMA₁₇₂ and PS₁₆₉-*b*-PLLA₁₂₀/PS₁₆₉-*b*-PDLA₁₉₀ mixtures, respectively ($c = 0.9 \text{ g L}^{-1}$, CH/DCM = 10/1 (v/v)). TEM micrographs of the corresponding SC micelles with (C) a patchy PS/PtBMA corona and (D) a homogeneous PS corona. PS was selectively stained with RuO₄ and appears dark.

Raman spectroscopy was employed to confirm that self-assembly is driven by SC formation as a characteristic shift of the carbonyl stretching vibration from $\tilde{\nu} \approx 1771 - 1773 \text{ cm}^{-1}$ for the individual diblock copolymers to lower wavenumbers ($\tilde{\nu} \approx 1752 - 1755 \text{ cm}^{-1}$) was observed. This finding is supported by differential scanning calorimetry (DSC), which shows significantly higher melting temperatures for the freeze-dried SC micelles. DSC further revealed a degree of crystallinity of $\alpha = 34\%$ for the PS-*sc*-PLA-PtBMA micelles indicating that the majority of the PLLA/PDLA core remains amorphous allowing the PS and PtBMA corona chains to self-assemble into distinct nanometer-sized patches. The size and corona structure of the PS-*sc*-PLA-PtBMA SC micelles was found to depend on the dilution upon micelle preparation. When smaller amounts of the diblock copolymer mixture in DCM were added to CH the size of the obtained micelles substantially decreased as revealed by DLS (**Figure 2.2A**). The same effect was observed for PS-*sc*-PLA-PS micelles. Interestingly, the micelles prepared at higher dilution show a distinct difference regarding the corona morphology. Now, a mixture of both patchy

and a Janus-like micelles is formed (**Figure 2.2B**). If the Janus spheres are aligned in a proper way on the carbon-coated grid, they can be distinguished as micelles with a bright appearing PLLA core, which is surrounded by a dark PS and a bright PtBMA hemisphere. The PtBMA hemisphere is hardly discernible due to low electron contrast on the carbon film and partial electron beam degradation. The Janus-like corona segregation is attributed to the smaller micelle size, which favours the separation into two distinct PS and PtBMA faces due to denser chain packing.

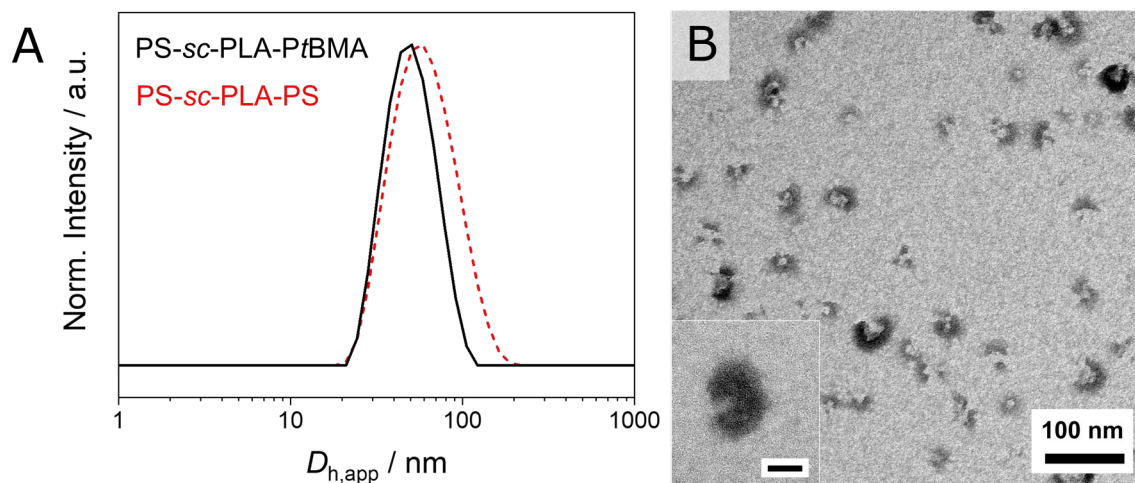


Figure 2.2 (A) Hydrodynamic diameter distributions from DLS for SC micelles prepared from PS₁₆₉-*b*-PLLA₁₂₀/PDLA₁₁₄-*b*-PtBMA₁₇₂ and PS₁₆₉-*b*-PLLA₁₂₀/PS₁₆₉-*b*-PDLA₁₉₀ mixtures, respectively ($c = 0.1 \text{ g L}^{-1}$, CH/DCM = 100/1 (v/v)). (B) TEM micrograph of the corresponding SC micelles with a Janus and patchy PS/PtBMA corona (scale bar inset = 20 nm). PS was selectively stained with RuO₄ and appears dark.

To test the potential of PS-*sc*-PLA-PtBMA micelles for the use as particulate surfactants the interfacial tension at the CH/water interface was studied employing the pendant drop method. The patchy SC micelles exhibit a higher interfacial activity compared to the SC micelles with a homogenous corona, resulting in a decrease of the quasi-equilibrium interfacial tension to $\gamma = 25.9 \pm 0.1 \text{ mN m}^{-1}$ ($\gamma = 31.6 \pm 0.1 \text{ mN m}^{-1}$ for PS-*sc*-PLA-PS and $\gamma = 40.3 \pm 0.1 \text{ mN m}^{-1}$ for pristine CH/water interface) (**Figure 2.3A**). The high interfacial activity is attributed to the amphiphilic corona in combination with the Pickering effect of nanoparticles. Finally, the patchy SC micelles were successfully employed as stabilizers for CH/water and CH/methanol emulsions, being stable for several months (**Figure 2.3B**).

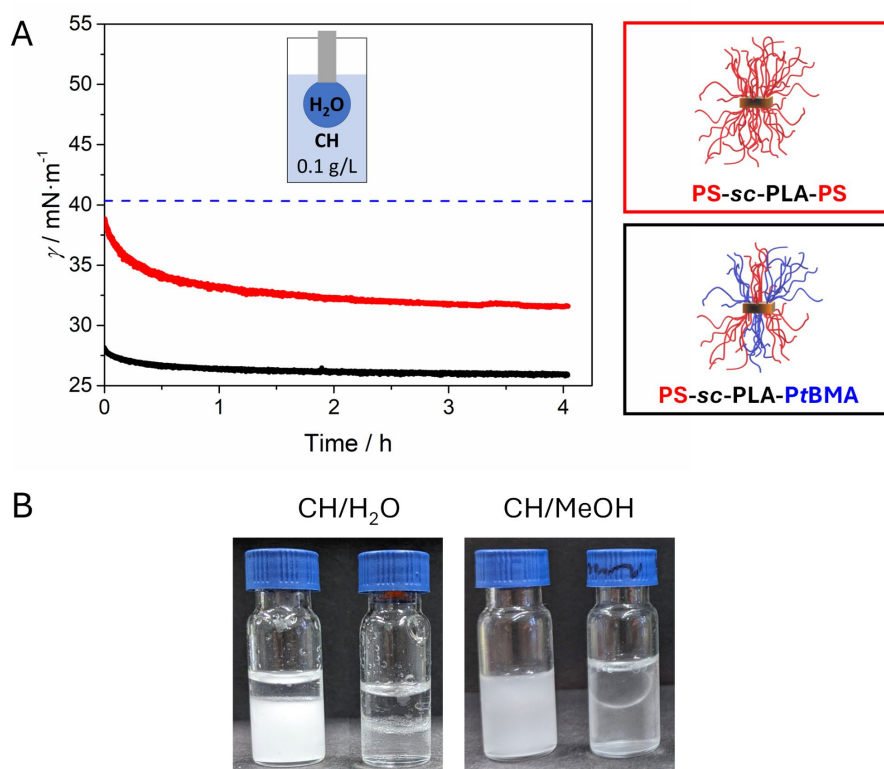


Figure 2.3 (A) Interfacial tension isotherms of spherical PS-*sc*-PLA-*Pt*BMA micelles with a patchy corona (black, $D_{h,app} = 104 \pm 30$ nm) compared to spherical PS-*sc*-PLA-PS micelles with a homogeneous corona (red, $D_{h,app} = 82 \pm 25$ nm) at the CH/water interface. The dashed blue line is the interfacial tension at the pristine CH/water interface measured as reference. (B) CH/water and CH/methanol mixtures emulsified with patchy PS-*sc*-PLA-*Pt*BMA micelles ($c = 0.9$ g L⁻¹ in CH). The photographs on the right of each mixture correspond to the respective pure solvent mixtures that separated immediately after shaking.

2.3 Patchy Stereocomplex Micelles as Efficient Compatibilizers in Polymer Blends

In this study, the patchy PS-*sc*-PLA-*Pt*BMA micelles introduced previously were applied as compatibilizers for strongly immiscible PS/*Pt*BMA blends. After upscaling their preparation, the effects of corona chemistry and compatibilizer content on blend homogeneity and compatibilization efficiency were examined. Fluorescently labelled SC micelles were further used to locate the micelles at the blend interface.

In previous work, the maximum achievable concentration was only 1 g L⁻¹ in CH, which was impractical for solvent casting. The scale-up was accomplished by increasing the initial concentration of the diblock copolymer mixture (PS₁₆₉-*b*-PLLA₁₀₆ + *Pt*BMA₁₃₂-*b*-PDLA₁₀₀) in DCM from 10 g L⁻¹ to 50 g L⁻¹ and concomitantly increasing the volume of the mixture added to CH for SCDSA, while keeping all other preparation parameters constant. Complete removal of residual DCM proved crucial for efficient SC formation and enhanced corona segregation.

Finally, a stable dispersion with a concentration of 5 g L^{-1} was obtained, yielding 100 mg SC micelles per batch. DLS and TEM confirmed that the scale-up did not compromise the formation of well-defined, spherical patchy SC micelles.

Following the successful scale-up, the compatibilization efficiency of the patchy SC micelles was evaluated in immiscible PS/PtBMA blends. This system was chosen as a model due to the pronounced incompatibility of the polymers and the chemical match with the micellar corona blocks. The neat PS/PtBMA (30/70 (w/w)) blend, prepared by solvent casting at 45°C from CH, exhibited clear macrophase separation into millimeter-sized PS and PtBMA domains, underlining their high incompatibility. In contrast, when patchy PS-*sc*-PLA-PtBMA micelles were used as compatibilizer (7 wt%), no macrophase separation was observed. Spatial component distributions extracted from Raman imaging showed PS droplets homogeneously dispersed in a continuous PtBMA matrix, consistent with the asymmetric blend composition (**Figure 2.4A**). To evaluate the role of the corona chemistry a PS/PtBMA (30/70 (w/w)) blend compatibilized with 7 wt% of PS-*sc*-PLA-PS micelles with a homogenous PS corona, prepared by SCDSA of PS₁₆₉-*b*-PLLA₁₀₆ and PS₁₅₆-*b*-PDLA₁₀₆, was also examined. In this case, although PS droplets were likewise dispersed in the PtBMA matrix, their distribution appeared markedly inhomogeneous (**Figure 2.4B**). Statistical evaluation of the PS droplet sizes further confirmed this difference. For the blend compatibilized with the patchy PS-*sc*-PLA-PtBMA micelles the size of the PS droplets was significantly smaller and their size distribution narrower ($D_{\text{PS}} = 3.9 \pm 1.3 \text{ }\mu\text{m}$) as compared to the blend containing SC micelles with a homogeneous PS corona ($D_{\text{PS}} = 46.8 \pm 66.4 \text{ }\mu\text{m}$). The improved compatibilization is attributed to a combination of the Pickering effect of nanoparticles and the adaptive nature of the patchy PS/PtBMA corona, which can expand or collapse depending on its miscibility with the surrounding blend component, thereby stabilizing the interface. In contrast, for the SC micelles with a homogeneous PS corona, only the Pickering effect contributes to the stabilization, making them considerably less effective.

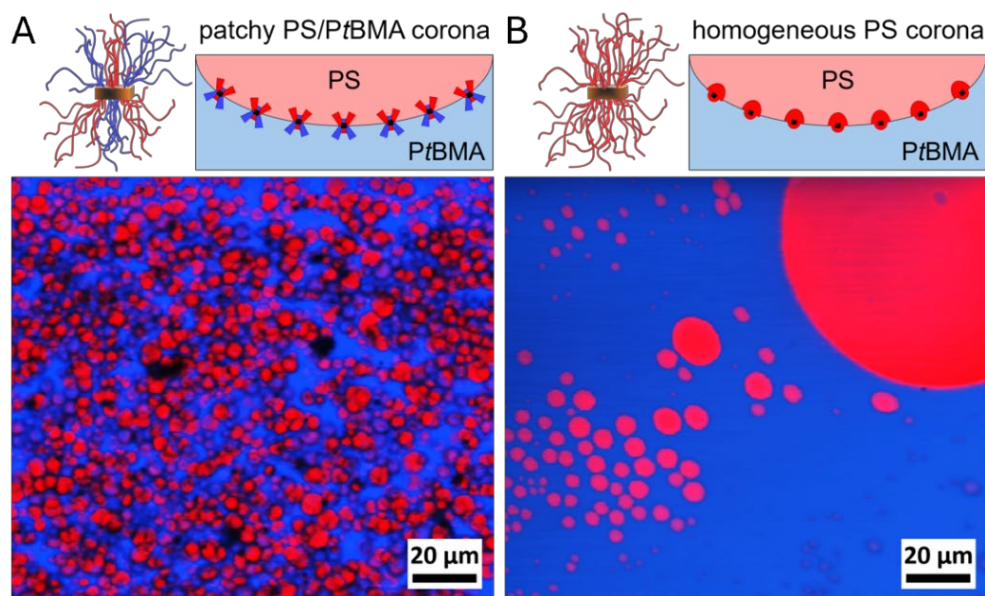


Figure 2.4 Spatial component distributions extracted from Raman imaging for PS/PtBMA (30/70 (w/w)) blends compatibilized with (A) 7 wt% patchy PS-*sc*-PLA-PtBMA micelles and (B) 7 wt% PS-*sc*-PLA-PS micelles with homogeneous PS corona. The domains coloured in red represent PS droplets being dispersed in a continuous PtBMA matrix (depicted in blue). The sketches depict the adaption of the SC micelle corona according to their miscibility/immiscibility with the blend components.

The effect of compatibilizer content on blend homogeneity and PS droplet size was studied by a combination of Raman imaging and scanning electron microscopy (SEM). Raman imaging enables clear phase identification within the blend without the need for contrast enhancement through staining, which is commonly required in electron microscopy and may compromise accurate evaluation. However, SEM remains essential for precise size determination due to an enhanced lateral resolution compared to Raman imaging. The optimum compatibilizer content was 7 wt%, resulting in a homogeneous blend with significantly reduced PS droplet sizes ($D_{PS} = 2.5 \pm 0.9 \mu\text{m}$) (**Figure 2.5**). Although below this concentration macrophase separation was already not observable anymore and the PS droplet size was reduced, a bimodal size distribution of the PS phase persisted. Increasing the compatibilizer content further to 10 wt% did not affect the blend morphology. Notably, when Janus micelles with a PS/PtBMA corona, were used at identical filler content of 7 wt%, the PS droplet size reduction was comparable ($D_{PS} = 2.6 \pm 1.8 \mu\text{m}$), however, only for the patchy SC micelles a homogenous and monomodal size distribution was achieved.

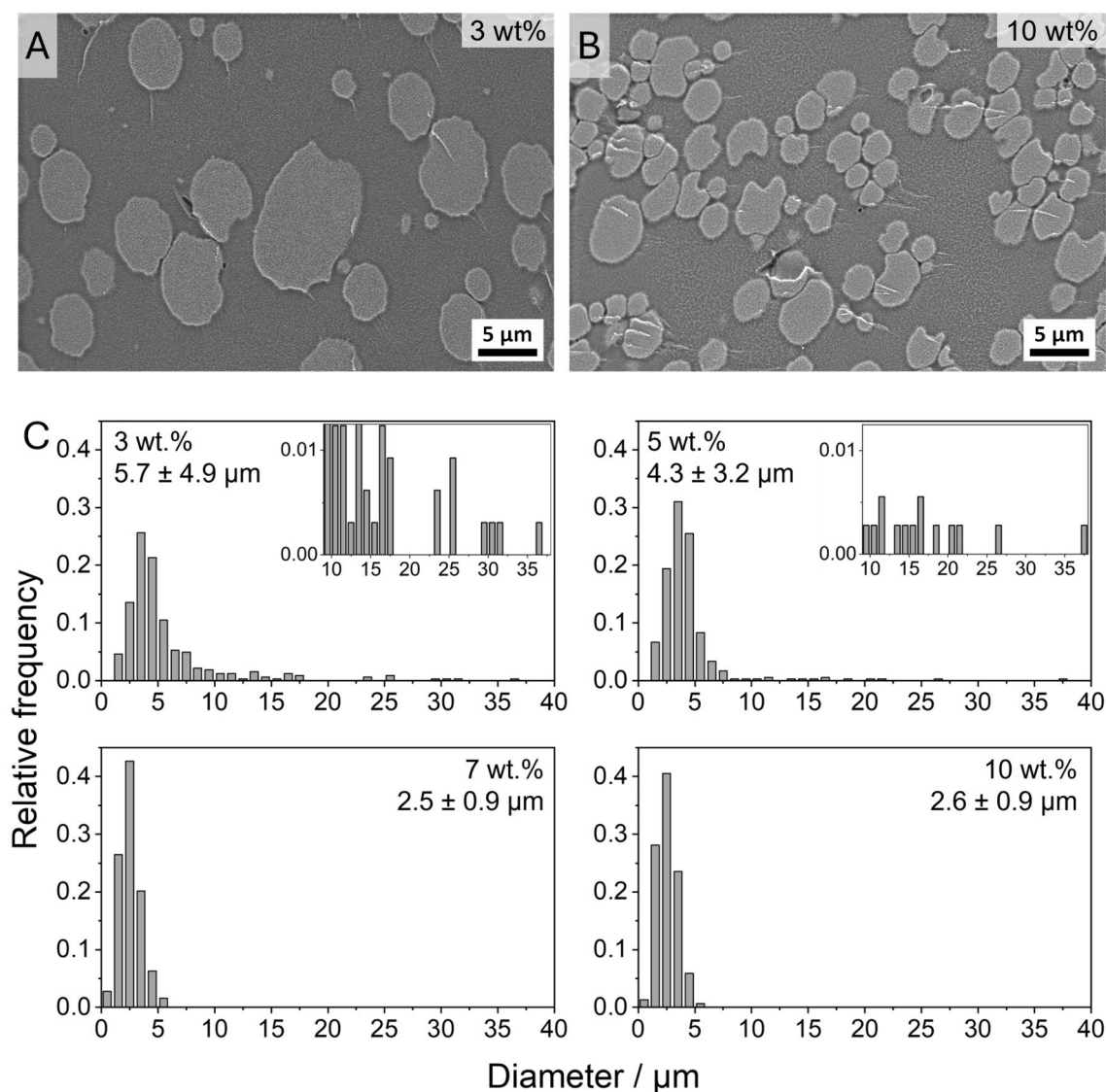


Figure 2.5 SEM images of the fracture surfaces of PS/PtBMA (30/70 (w/w)) blends compatibilized with different amounts of PS-*sc*-PLA-PtBMA micelles: (A) 3 and (B) 10 wt%. The PS domains were selectively stained with RuO₄ vapor to enhance contrast and appear bright. (E) Corresponding histograms of PS droplet diameter distributions.

To verify the presence of patchy SC micelles at the PS/PtBMA interface, confocal scanning fluorescence microscopy (FM) was performed using fluorescently labelled patchy SC micelles. For this purpose, PS-*sc*-PLA-PtBMA micelles were prepared by co-assembling the enantiomeric diblock copolymers with a small amount of sulforhodamine B labelled PDLA₆₂ homopolymer (PDLA₆₂-RB, 10 wt% of the total PDLA content) under the same conditions described above (**Figure 2.6A**). Incorporation of the fluorescently labelled PDLA₆₂-RB did not affect the SCDSA process or the formation of well-defined spherical micelles, as confirmed by DLS and TEM (**Figure 2.6B**). Although the apparent hydrodynamic diameter of the labelled PS-*sc*-PLA-PtBMA_RB micelles ($D_{h,app} = 88 \pm 30 \text{ nm}$) was slightly lower than that of the non-labelled micelles, their overall morphology and patch-like PS/PtBMA corona structure

remained unchanged. Next, a PS/PtBMA (30/70 (w/w)) blend compatibilized with 3 wt% of fluorescently labelled PS-*sc*-PLA-PtBMA_RB micelles was prepared by solvent casting. FM images of the blend clearly show that the patchy SC micelles preferentially accumulate at the PS/PtBMA interface, resulting in a bright rim surrounding the dispersed PS droplets (Figure 2.6C). This was confirmed by TEM, revealing a fringe-like structure at the interface between the two blend phases, characterized by clusters of smaller, dark-appearing patches (Figure 2.6D).

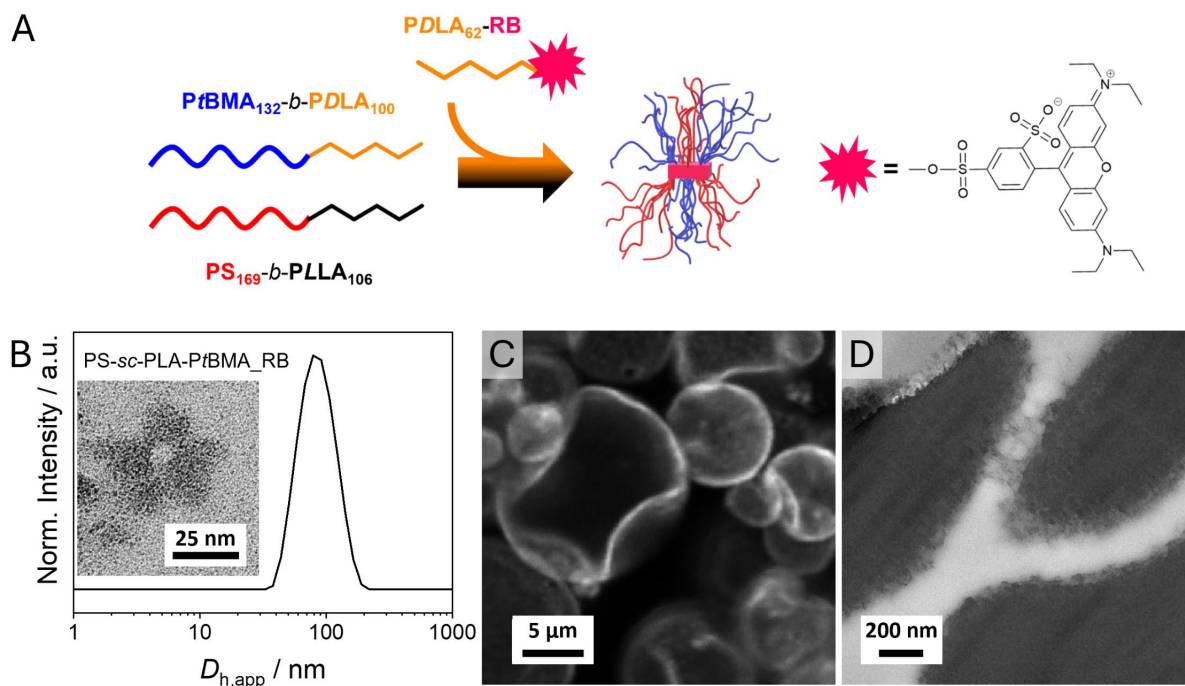


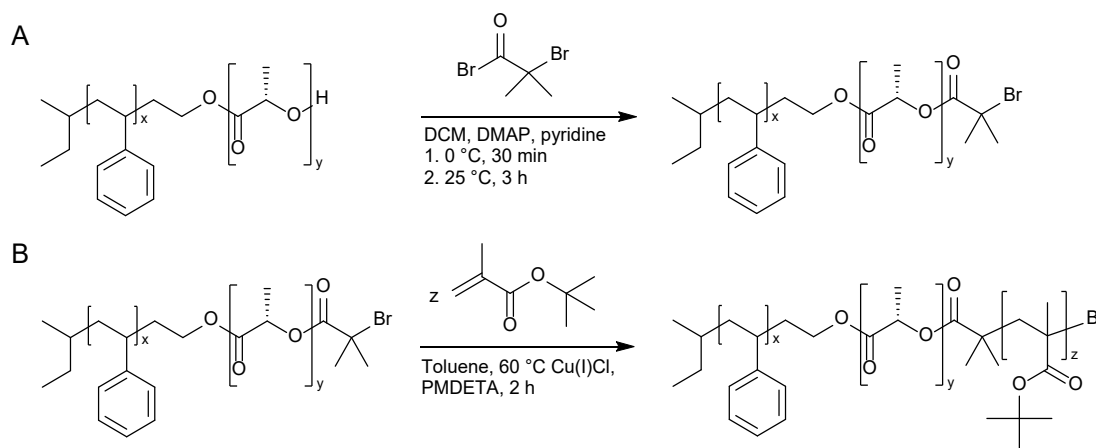
Figure 2.6 (A) Schematic illustration of the preparation of fluorescently labelled PS-*sc*-PLA-PtBMA_RB micelles *via* SCDSA. (B) Hydrodynamic diameter distributions from DLS for fluorescently labelled SC micelles prepared from PS₁₆₉-*b*-PLLA₁₀₆+PtBMA₁₃₂-*b*-PDLA₁₀₀ mixtures with 10 wt% PDLA₆₂-RB ($c = 1 \text{ g L}^{-1}$, CH) and TEM micrograph of the respective micelles. (C) Confocal scanning FM images of a PS/PtBMA (30/70 (w/w)) blend compatibilized with 3 wt% fluorescently labelled PS-*sc*-PLA-PtBMA_RB micelles. (D) TEM micrograph of a PS/PtBMA (30/70 (w/w)) blend compatibilized with 7 wt% patchy PS-*sc*-PLA-PtBMA micelles (stained with RuO₄, PS appears dark).

2.4 From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co-Crystallization-Driven Self-Assembly

This chapter presents CCDSA of PS-*b*-PLLA-*b*-PtBMA (SLT) triblock terpolymers with the corresponding PLLA homopolymer as an alternative route toward patchy platelet-like micelles and their 3D assemblies. The homopolymer proved essential for inducing PLLA crystallization, as otherwise the neat SLT only yields spherical Janus micelles with an amorphous core. The

resulting patchy platelets showed superior interfacial activity compared to spherical patchy SC micelles and effectively stabilized emulsions.

Two SLT triblock terpolymers ($S_{156}L_{82}T_{115}$ and $S_{169}L_{96}T_{200}$) were synthesized by modifying the hydroxy end-group of the respective PS-*b*-PLLA diblock copolymer precursors (**Scheme 2.3A**) with α -bromo-isobutyryl bromide to introduce an ATRP initiating site, followed by ATRP of *tert*-butyl methacrylate (**Scheme 2.4**). In both cases SLT triblock terpolymers with low dispersities ($\bar{D} < 1.2$) were obtained.



Scheme 2.4 Synthesis of (A) PS-*b*-PLLA-Br ATRP-macroinitiator and (B) SLT triblock terpolymer.

Thermal annealing of neat $S_{156}L_{82}T_{115}$ at 45 °C for 2 h in CH, being a selective solvent for the corona blocks, yielded narrowly distributed micelles with an apparent hydrodynamic diameter of $D_{h,app} = 37 \pm 15$ nm as revealed by DLS (**Figure 2.7A**). The TEM micrograph in **Figure 2.7B** shows spherical micelles featuring a bright PLLA core and a surface-compartmentalized PS/*Pt*BMA corona (with the PS domains selectively stained by RuO_4 , appearing dark). Most micelles display a Janus-like corona structure, while a smaller fraction exhibits a patchy corona, which may be related to the relatively short *Pt*BMA block. In comparison, $S_{169}L_{96}T_{200}$, which contains a longer *Pt*BMA block, produced an even higher fraction of Janus micelles, accompanied by a slight increase in micelle size (**Figure 2.7A**). DSC of the freeze-dried micelle dispersion showed that the PLLA core remained amorphous, indicating that PLLA crystallization is strongly suppressed under the applied self-assembly conditions. The formation of Janus spheres was further attributed to the dissolution of the lamella–lamella bulk morphology of SLT. Interestingly, when a solution of SLT in DCM, acting as a good solvent for all blocks, was added to CH (CH/DCM = 9/1 (v/v)), additional cylindrical micelles appeared alongside the spherical micelles. For the cylindrical micelles obtained from $S_{169}L_{96}T_{200}$, a

patch-like corona segregation was observed. Despite several variations in the self-assembly conditions, cylindrical micelles could not be obtained exclusively.

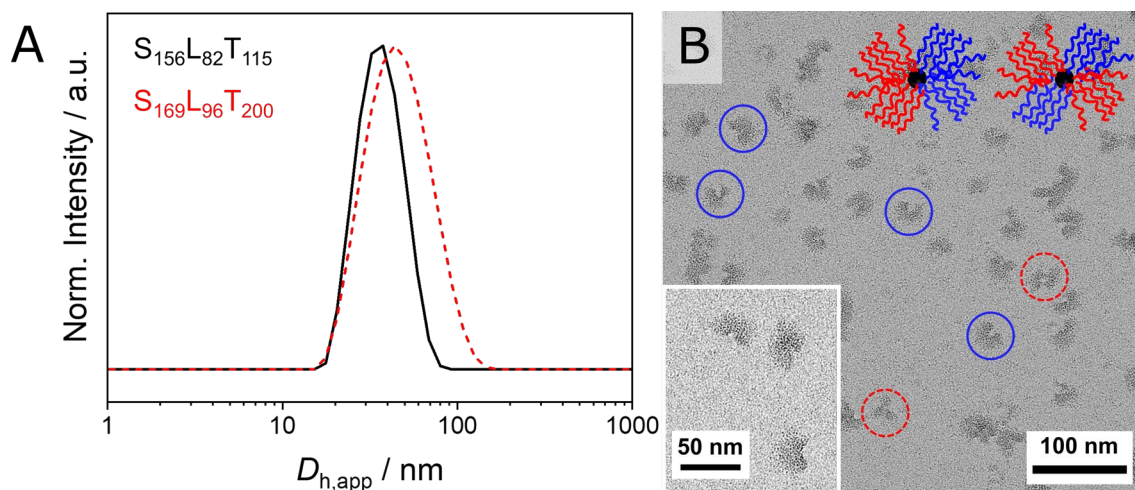


Figure 2.7 (A) Hydrodynamic diameter distribution from DLS for $S_{156}L_{82}T_{115}$ (black) and $S_{169}L_{96}T_{200}$ (red) micelles prepared by thermal annealing at 45 °C and aging in CH ($c = 5 \text{ g L}^{-1}$). (B) TEM micrograph of the corresponding $S_{156}L_{82}T_{115}$ micelles with a Janus-like (left sketch, blue solid circles) or patchy (right sketch, red dashed circles) PS/*Pt*BMA corona. PS was selectively stained with RuO_4 and appears dark.

Hence, the question arose whether the addition of PLLA homopolymer could promote crystallization and alter the resulting morphology, since CCDSA of diblock copolymers with their corresponding homopolymer is known to favour structures of low curvature. To investigate this, solutions of $S_{156}L_{82}T_{115}$ and PLLA_{64} in DCM ($c = 10 \text{ g L}^{-1}$) were mixed in a 1:1 volume ratio and added dropwise to cyclohexane (CH/DCM = 9/1 (v/v)). After five days of aging, the remaining DCM was removed, yielding a dispersion of $S_{156}L_{82}T_{115} + \text{PLLA}_{64}$ (50 wt%) micelles in CH (the content of the PLLA_{64} fraction within the mixture is given in brackets). DLS showed a narrow size distribution with an apparent hydrodynamic diameter of $D_{h,\text{app}} = 1300 \pm 200 \text{ nm}$, confirming the formation of large assemblies. TEM and SEM revealed round, platelet-like micelles, many of which displayed twists and multilayered, step-like features (**Figure 2.8A,B**). A small number of Janus spheres, originating from unassembled $S_{156}L_{82}T_{115}$ unimers, were also detected. Higher-magnification TEM further indicated a non-concentric, stripe-like arrangement of PS (dark) and *Pt*BMA (bright) patches, attributed to the strong incompatibility of the corona-forming blocks. Using $S_{169}L_{96}T_{200}$, featuring a longer *Pt*BMA block, under identical conditions enlarged the spacing between PS domains and the corona appeared brighter in TEM owing to the increased *Pt*BMA content. The observed 3D twisting likely results from screw-dislocation defects and anisotropic stresses at the platelet fold

surfaces. DSC of the freeze-dried micelles showed a melting transition, demonstrating that PLLA crystallization is the primary driving force for platelet formation (**Figure 2.8C**), which was further confirmed by wide angle X-ray scattering. AFM measurements corroborated the twisted platelet morphology (**Figure 2.8D**). The height profile (**Figure 2.8E**) showed an average platelet thickness of 14 – 15 nm. Considering the amorphous PS and P*t*BMA blocks, this suggests that the PLLA block in S₁₅₆L₈₂T₁₁₅ folds once or twice, while PLLA₆₄ folds once, to reach the observed dimensions.

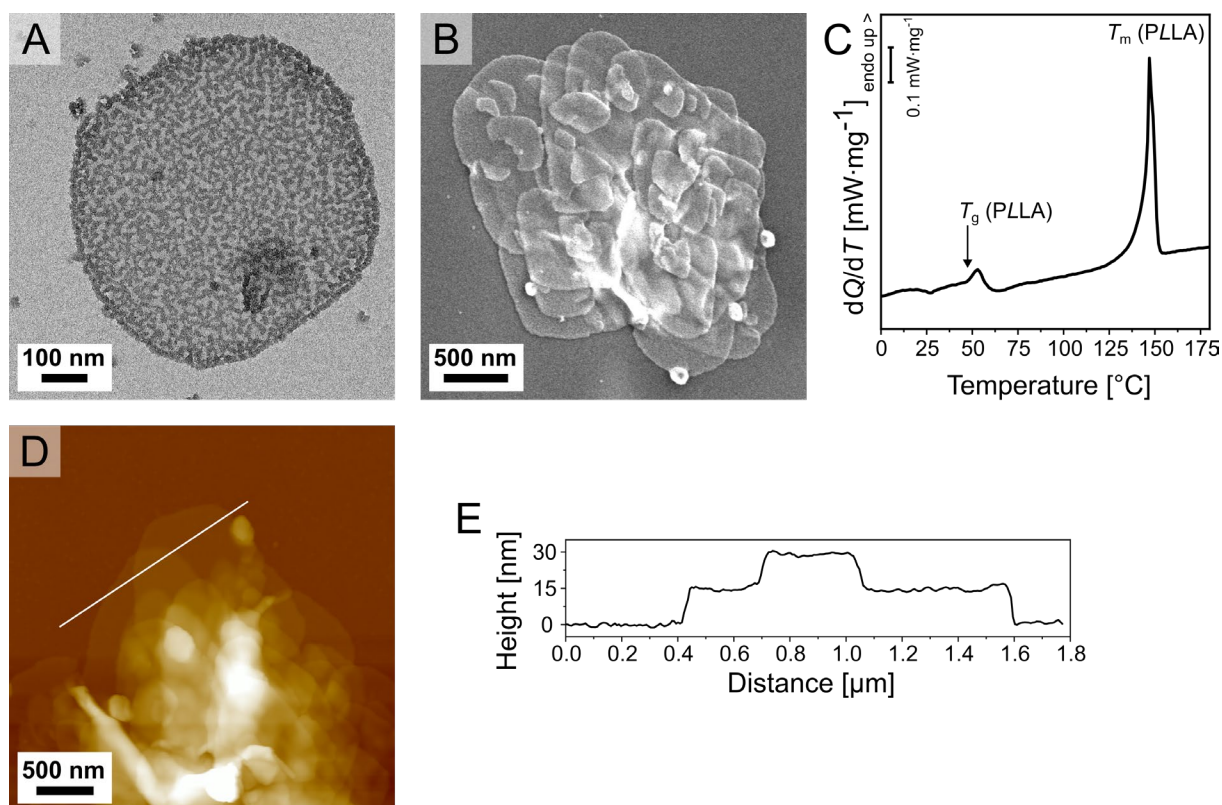


Figure 2.8 (A) TEM micrograph and (B) SEM image of twisted patchy platelet micelles prepared by CCDSA of S₁₅₆L₈₂T₁₁₅ + PLLA₆₄ (50 wt%) in CH. PS was selectively stained with RuO₄ and appears dark in TEM and bright in SEM. (C) DSC 1st heating trace of the freeze-dried micelle dispersion. (D) AFM topography image ($\Delta z = 500$ nm) of a twisted patchy platelet micelle assembly and (E) the corresponding height profile taken at the position indicated by a line in (D).

Next, the fraction of PLLA₆₄ homopolymer was systematically varied between 1 and 60 wt% to investigate the influence on micelle morphology. For PLLA₆₄ contents below 30 wt%, DLS revealed bimodal size distributions with a small population around 35 nm, whose size matches that of the Janus micelles formed by neat S₁₅₆L₈₂T₁₁₅. TEM confirmed that such Janus micelles appear as side products at low PLLA fractions and progressively diminish with increasing PLLA content (**Figure 2.9**). At very low PLLA₆₄ fractions (<10 wt%), co-crystallization of S₁₅₆L₈₂T₁₁₅ and PLLA₆₄ initially produces small platelets that serve as nucleation sites for the epitaxial growth of cylindrical micelles at their edges. As the PLLA₆₄ fraction increases, a larger

portion of the $S_{156}L_{82}T_{115}$ chains becomes involved in this early co-crystallization step, which results in the growth of larger, twisted patchy platelets. At a $PLLA_{64}$ fraction 50 wt%, co-crystallization is complete, and only uniform twisted platelet micelles are formed, with Janus micelles no longer detectable.

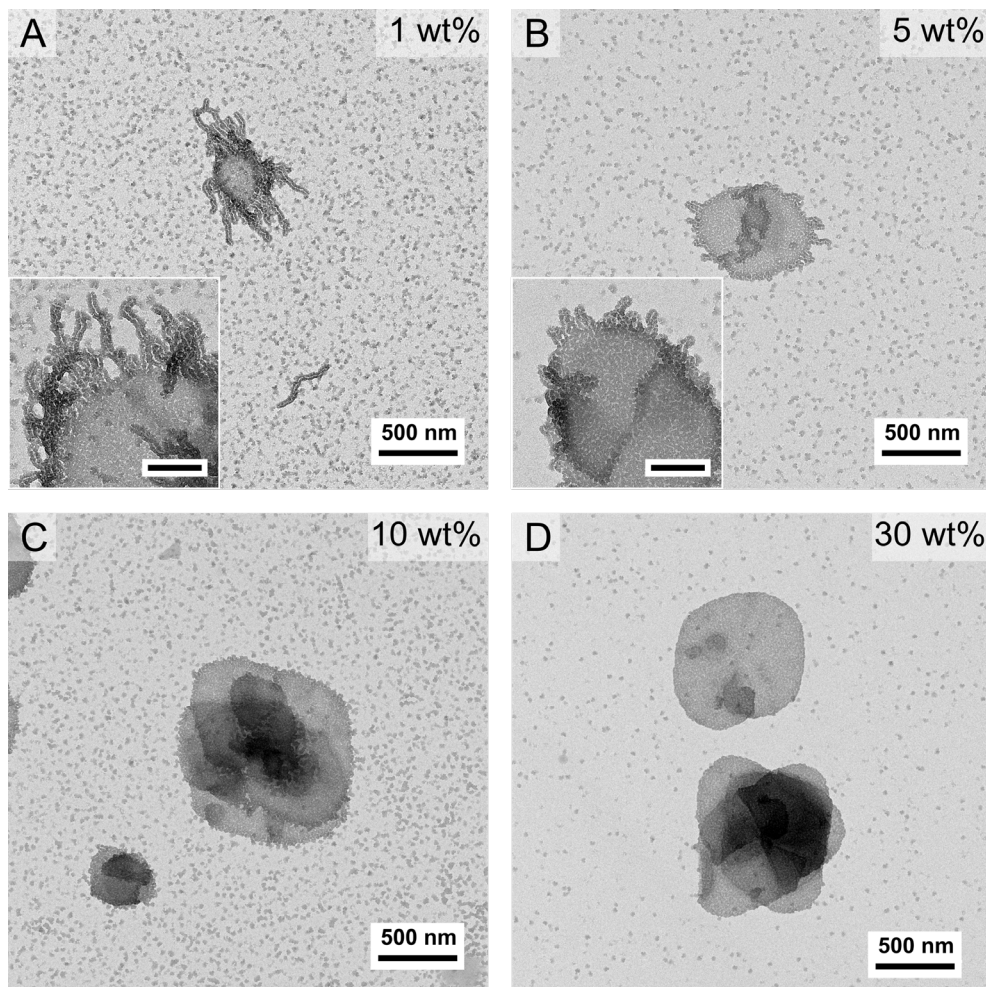


Figure 2.9 TEM micrographs of a $S_{156}L_{82}T_{115}$ + $PLLA_{64}$ micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$) with different fractions of $PLLA_{64}$ in the mixture. (A) 1 wt%, (B) 5 wt%, (C) 10 wt% and (D) 30 wt% (scale bar insets = 200 nm). PS was selectively stained with RuO_4 and appears dark.

Moreover, the crystallization rate was modified by using a shorter $PLLA_{34}$ homopolymer, which exhibits higher solubility and slower crystallization kinetics. CCDSA of $S_{156}L_{82}T_{115}$ with 50 wt% $PLLA_{34}$ under the same conditions as described above resulted in patchy platelets that stack in the z -direction to form well-defined 3D pyramidal structures, as observed by SEM (**Figure 2.10A**). Interestingly, the edges of the platelets are much sharper and the platelets show a more symmetric lozenge-shape compared to the platelets formed when the longer $PLLA_{64}$ was used (**Figure 2.8B**). The higher-magnification TEM micrograph revealed the characteristic patchy surface morphology of the platelets (**Figure 2.10B**). AFM measurements further support these findings, showing 3D particles composed of stacked platelets with an average height of

approximately 14 nm (**Figure 2.10C,D**). As this is comparable to the twisted platelets formed with PLLA₆₄, it is assumed that the PLLA block of S₁₅₆L₈₂T₁₁₅ again folds once or twice and PLLA₃₄ is incorporated in a stretched conformation.

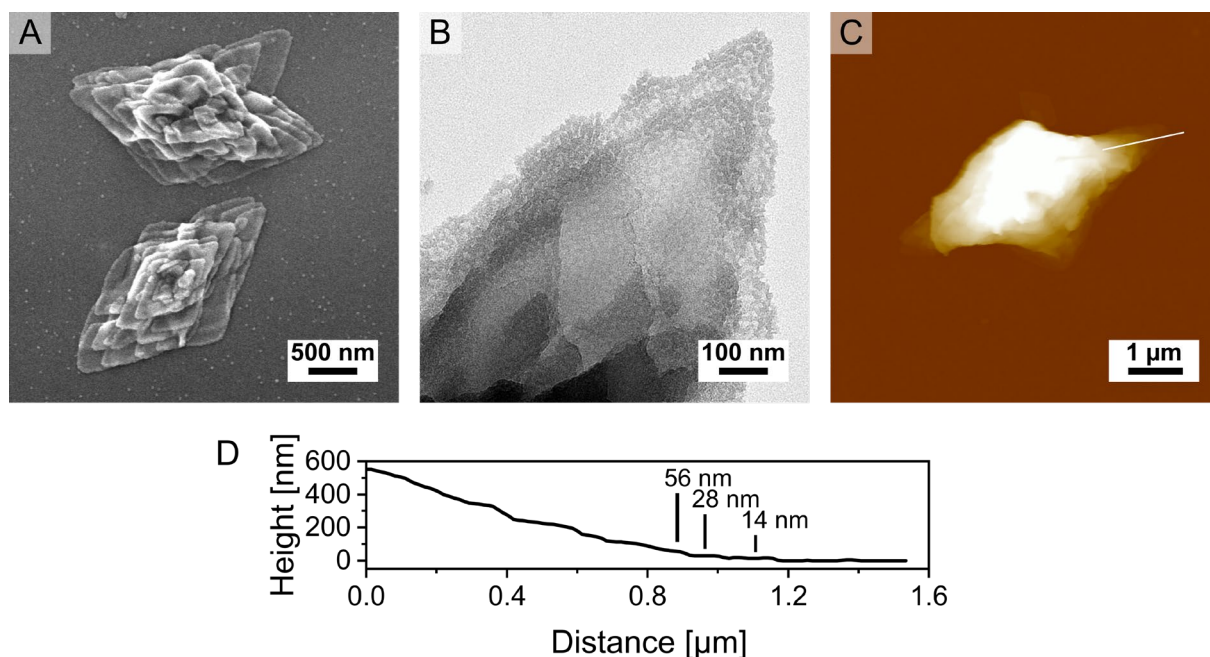


Figure 2.10 (A) SEM image, (B) TEM micrograph and (C) AFM topography image ($\Delta z = 1.6 \mu\text{m}$) of 3D pyramidal structures composed of stacked patchy platelets, which were prepared by CCDSA of S₁₅₆L₈₂T₁₁₅ + PLLA₃₄ (50 wt%) in CH. (D) AFM height profile taken at the position indicated by a line in (C). PS appears bright in SEM and dark in TEM due to selective staining with RuO₄ vapor.

Finally, the twisted patchy platelets were applied in pendant drop measurements to study their interfacial activity at the CH/water interface. Notably, they exhibit a higher interfacial activity with respect to the corresponding spherical patchy SC micelles, as they reduced the interfacial tension to $\gamma = 24.8 \pm 0.1 \text{ mN m}^{-1}$ ($\gamma = 28.0 \pm 0.1 \text{ mN m}^{-1}$ for PS-*sc*-PLA-*Pt*BMA spherical SC micelles, **Figure 2.11A**). This behavior is in contrast to that of Janus particles, as spherical Janus micelles exhibit a significantly higher interfacial activity than Janus discs. Both sides of the patchy platelets are identical, and the amphiphilic Janus structure is formed “in situ” at the liquid-liquid interface by selective collapse/swelling of the respective insoluble and soluble corona patches. This avoids adsorption in unfavourable orientations, commonly observed for Janus discs. The high interfacial activity of the twisted patchy platelets allowed their use in emulsion stabilization, underlining their application potential (**Figure 2.11B**).

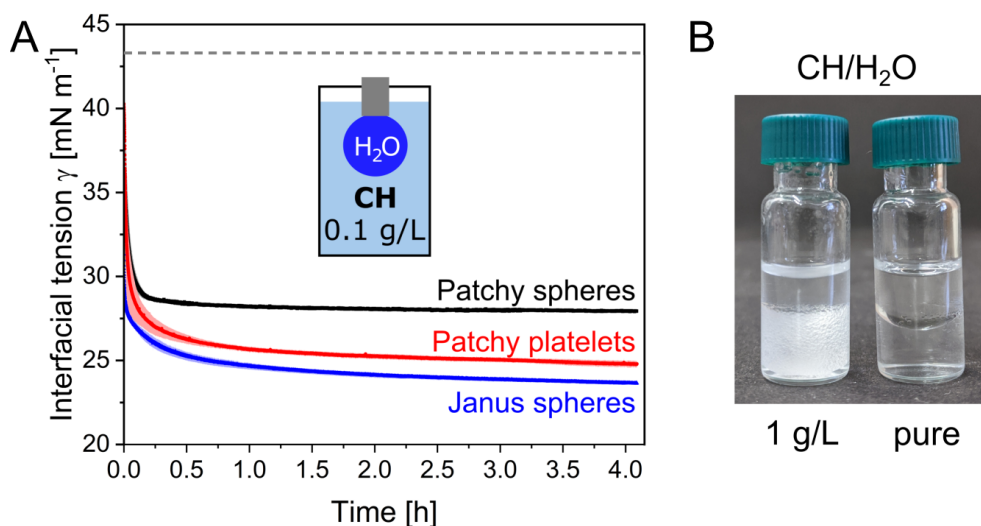
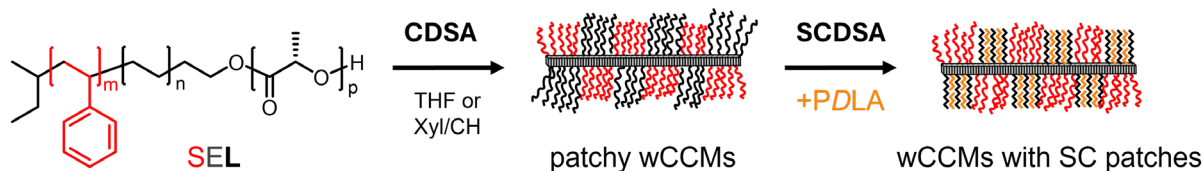


Figure 2.11 (A) Interfacial tension isotherms of spherical patchy micelles formed by SCDSA of PS₁₆₉-*b*-PLLA₁₀₆ and PDLA₁₀₀-*b*-P(BMA)₁₃₂ diblock copolymers, twisted patchy platelet micelles formed by CCDSA of S₁₅₆L₈₂T₁₁₅ + PLLA₆₄ (50 wt%) and spherical S₁₅₆L₈₂T₁₁₅ Janus micelles at the CH/water interface ($c = 0.1 \text{ g L}^{-1}$ in CH). The shown isotherms correspond to the average of three consecutive measurements and the respective standard deviations are displayed as transparent areas (discernable at short measurement times). The dashed grey line is the interfacial tension at the pristine CH/water interface measured as reference. (B) CH/water mixture emulsified with patchy S₁₅₆L₈₂T₁₁₅ + PLLA₆₄ (50 wt%) platelet micelles ($c = 1 \text{ g L}^{-1}$ in CH). The photograph on the right corresponds to the respective pure solvent mixture that separated immediately after shaking.

2.5 Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles

This chapter deals with the question whether CDSA and SCDSA can be combined to selectively address the stereoregular PLLA patches of patchy wCCMs (**Scheme 2.5**). Hereby, CDSA of double crystalline PS-*b*-PE-*b*-PLLA triblock terpolymers (SEL), featuring core-forming PE blocks and additional crystallizable PLLA corona-forming blocks, was examined. SCDSA was utilized to load the patches with PDLA homopolymers and further to incorporate a fluorescent dye within the corona of the micelles.



Scheme 2.5 Schematic illustration of the preparation of patchy wCCMs by CDSA of SEL triblock terpolymers in different solvents. SCDSA with PDLA homopolymer results in the formation of PLLA/PDLA SC patches within the corona.

The triblock terpolymers SEL-1 (S₂₉₆E₅₉₀L₃₆₈) and SEL-2 (S₂₉₆E₅₉₀L₇₈₁) differing in PLLA block length were synthesized by a combination of living anionic polymerization, organo-

catalyzed ROP and catalytic hydrogenation. Briefly, a hydroxy-terminated PS-*b*-PB-OH macroinitiator was prepared by sequential anionic polymerization of styrene and 1,3-butadiene in toluene, followed by end-capping with ethylene oxide. The use of toluene as non-polar solvent in combination with an organolithium initiator is essential to yield a PB block with a high fraction of 1,4-PB repeating units, necessary to obtain a pseudo-PE block after hydrogenation. In the next step, the PS-*b*-PB-*b*-PLLA precursor was synthesized by ROP of *L*-lactide using DBU as a catalyst. Subsequently, the PB middle block was hydrogenated using Wilkinson's catalyst.

CDSA was first studied in THF, a good solvent for both PS and PLLA corona blocks. Micelle dispersions were prepared by a simple heating and cooling protocol. The polymers were dissolved in THF at 65 °C and subsequently cooled to the crystallization temperature of the PE middle block ($T_c(\text{PE}) \approx 30\text{ °C} - 32\text{ °C}$), which was determined from micro-DSC (μ -DSC). After isothermal crystallization for 24 h, the solutions were slowly cooled to -10 °C to enable crystallization of the PE chains with a higher fraction of ethyl branches, that originated from the minor fraction of 1,2-PB repeating units in the precursor polymer. Crystallization of PLLA was not observed, as expected under the employed solvent conditions. TEM analyses revealed the formation of well-defined wCCMs, exemplified by SEL-1, characterized by a bright semi-crystalline PE core surrounded by an amorphous, patchy PS/PLLA corona (PS appearing grey, PLLA bright; **Figure 2.12A**). The apparent size of the PLLA patches may be underestimated due to the known sensitivity of PLLA to electron beam degradation. The patchy SEL wCCMs also show a pronounced tendency to agglomerate, which is considered an artifact arising from TEM sample preparation.

To investigate whether the PLLA blocks in the patchy wCCM corona are able to crystallize, and if crystallization affects the corona structure, CDSA was carried out in solvents of gradually decreasing solvent quality for PLLA. In pure xylene (Xyl), only the PE middle block crystallized for SEL-1, similar to the results obtained in THF, and PLLA remained amorphous. Upon introducing small amounts of CH (20 – 30 vol%), additional weak endotherms appeared in μ DSC heating traces that can be assigned to PLLA melting. However, the corresponding crystallization temperatures and degrees of crystallinity remained significantly reduced ($\alpha < 5\%$), demonstrating the strong confinement imposed by the patchy corona. For SEL-2, the longer PLLA block already yielded detectable PLLA melting in pure xylene, and PLLA crystallization became visible in Xyl/CH mixtures, though still with low crystallinity.

For further CDSA experiments a Xyl/CH = 80/20 (v/v) mixture was selected since for both SEL triblock terpolymers the PLLA blocks are able to crystallize and the PE and PLLA crystallization exotherms are sufficiently separated by 10 °C for SEL-2. The TEM micrograph of the SEL-1 dispersion confirmed the formation of wCCMs. Although the overall morphology of the wCCMs was not altered, the PLLA patches were difficult to distinguish (**Figure 2.12B**). This is likely due to the reduced PLLA solubility causing the patches to collapse near the PE core.

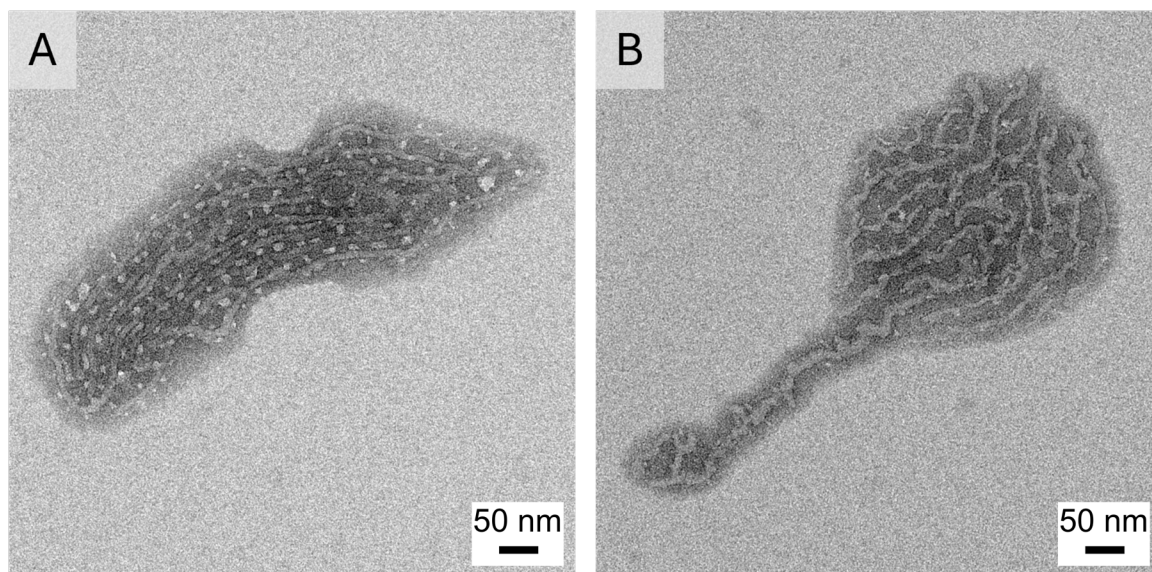


Figure 2.12 TEM micrographs of wCCMs prepared by CDSA of SEL-1 in (A) THF ($c = 10 \text{ g L}^{-1}$, $T_c = 30 \text{ °C}$) or (B) Xyl/CH = 80/20 (v/v) mixture ($c = 10 \text{ g L}^{-1}$, $T_c = 27 \text{ °C}$). PS was selectively stained with RuO_4 and appears dark.

In the next step, the stereoregular PLLA patches of SEL-1 wCCMs in a Xyl/CH = 80/20 (v/v) mixture were selectively loaded with an enantiomeric PDLA₆₂ homopolymers *via* stereocomplexation. To this end, a solution of PDLA₆₂ homopolymer in THF ($c = 10 \text{ g L}^{-1}$) was added to the wCCM dispersion at a ratio of PLLA/PDLA units of 2/1 (w/w). The dispersion was aged for 7 days before the remaining THF was removed by evaporation. In the Xyl/CH = 80/20 (v/v) mixture the solubility of PLLA is reduced, which should promote SC formation. TEM was used to probe the SC formation. From the micrograph, it becomes evident that the overall worm-like structure of the micelles was preserved, with the PE cores again appearing bright (**Figure 2.13A**). In contrast to SEL-1 wCCMs obtained in THF or Xyl/CH = 80/20 (v/v) mixtures, the corona contains noticeably larger, square-like PLLA/PDLA SC patches embedded in the dark PS matrix. TEM image analysis revealed an approximately two-fold increase in patch area ($A = 135 \pm 40 \text{ nm}^2$) compared to that of neat SEL-1 wCCMs in THF ($A = 73 \pm 26 \text{ nm}^2$). This pronounced enlargement strongly indicates the formation of SC domains

within the patchy wCCM corona. Raman spectroscopy further confirms the SC formation, due to a characteristic shift of the carbonyl stretching vibrations from $\tilde{\nu} \approx 1768 \text{ cm}^{-1}$ for PDLA_{62} and neat SEL-1 wCCMs to $\tilde{\nu} \approx 1750 \text{ cm}^{-1}$ for the SEL-1 + PDLA_{62} SC wCCMs. Notably, for SEL-2 the SC formation was not successful, probably due to the reduced solubility of the longer PLLA block hindering the SC formation.

SCDSA was also harnessed to introduce further functionalities in the patchy corona by employing a fluorescently (rhodamine B) labelled PDLA homopolymer ($\text{PDLA}_{62}\text{-RB}$). This enabled the use of fluorescence correlation spectroscopy (FCS) to follow stereocomplexation directly in dispersion. Here, a clear shift of the autocorrelation of intensity data to longer correlation times proved the successful incorporation of the PDLA chains into the larger, slower diffusing wCCMs (**Figure 2.13B**).

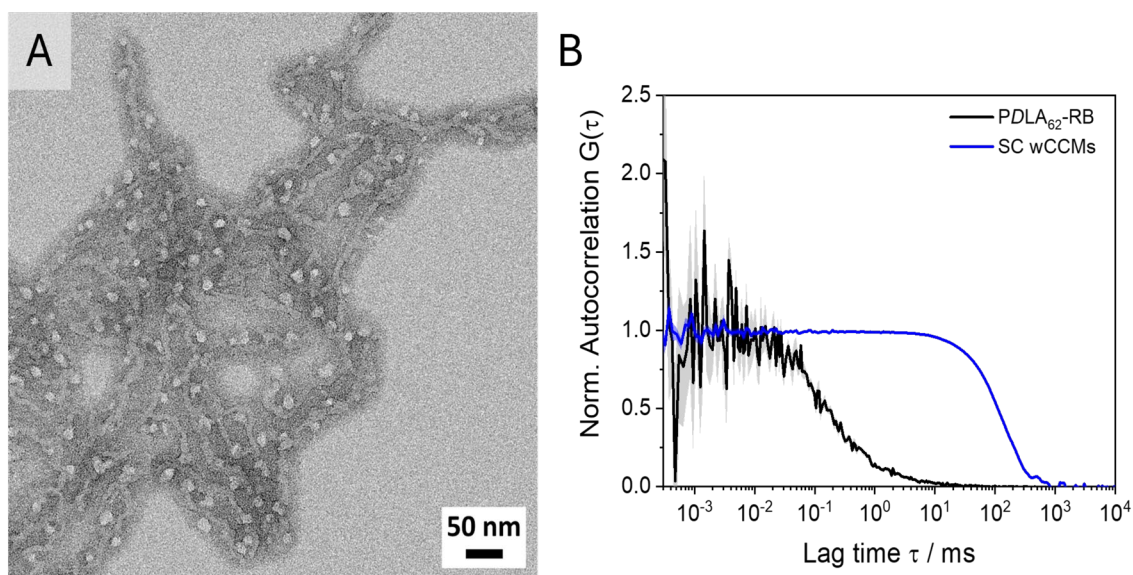


Figure 2.13 (A) TEM micrograph of wCCMs with SC patches prepared by SCDSA of SEL-1 wCCMs with PDLA_{62} homopolymer in a Xyl/CH = 80/20 (v/v) mixture. PS was selectively stained with RuO_4 and appears dark. (B) FCS autocorrelation of intensity data of $\text{PDLA}_{62}\text{-RB}$ homopolymer in THF ($c = 1 \cdot 10^{-8} \text{ g L}^{-1}$) and SEL-1 + $\text{PDLA}_{62}\text{-RB}$ SC wCCMs in Xyl/CH = 80/20 (v/v) ($c = 1 \text{ g L}^{-1}$). Errors are displayed as transparent areas.

2.6 Individual Contributions to Joint Publications

The publications included in this thesis are a collaborative work of several researchers. The individual contributions of all (co-)authors are specified in this section.

Chapter 3 is published in *Macromol. Rapid Commun.* **2023**, *44* (3), 2200682 under the title

Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly

by Roman Schaller, Christian Hils, Matthias Karg and Holger Schmalz

I designed and conducted the main part of the experiments and analytics, including polymer synthesis and characterization, self-assembly experiments, DLS measurements, TEM analyses and pendant drop measurements. I prepared the figures and wrote the manuscript. Christian Hils was involved in preliminary work regarding polymer synthesis. Matthias Karg contributed to scientific discussions on the application of the micelle dispersions and assisted with evaluation of DLS results. Holger Schmalz supervised the project, conducted the Raman spectroscopy measurements, co-designed the experiments, and corrected the manuscript.

Chapter 4 is published in *Polym. Chem.* **2024**, *15* (30), 3100-3112 under the title

Patchy Stereocomplex Micelles as Efficient Compatibilizers for Polymer Blends

by Roman Schaller, Marius Schmidt, Kristian Schweimer and Holger Schmalz

I wrote the manuscript and designed and conducted the main part of the experiments and analytics, including polymer synthesis and characterization, self-assembly experiments, DLS measurements, TEM analyses and polymer blend preparation. I assisted during fluorescence microscopy measurements and analysed the PS size distributions obtained by SEM and Raman imaging. Marius Schmidt conducted the SEM analyses and was involved in scientific discussions. Kristian Schweimer carried out the NOESY NMR measurement and analysed the data. Holger Schmalz supervised the project, performed Raman imaging measurements, co-designed the experiments and corrected the manuscript.

Chapter 5 is published in *Macromolecules* **2026**, 59 (5), 3092–3103 under the title

From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co-Crystallization-Driven Self-Assembly

by Roman Schaller, Marvin Foith, Lisa Maria Günther, Markus Hund, Karsten Busse, Matthias Karg and Holger Schmalz

I designed and conducted all experiments and wrote the manuscript. I synthesized and characterized the polymers, performed the self-assembly experiments, DLS, TEM and pendant drop measurements. Marvin Foith carried out SEM measurements and was involved in scientific discussions. Lisa Maria Günther conducted the fluorescence imaging measurements. Markus Hund carried out AFM measurements and analysed the data. Karsten Busse conducted WAXS measurements and was involved in scientific discussions. Matthias Karg was involved in WAXS measurements and scientific discussions. Holger Schmalz supervised the project, co-designed the experiments and corrected the manuscript.

Chapter 6 is published in *J. Polym. Sci.* **2025**, 63 (10), 2319-2332 under the title

Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles

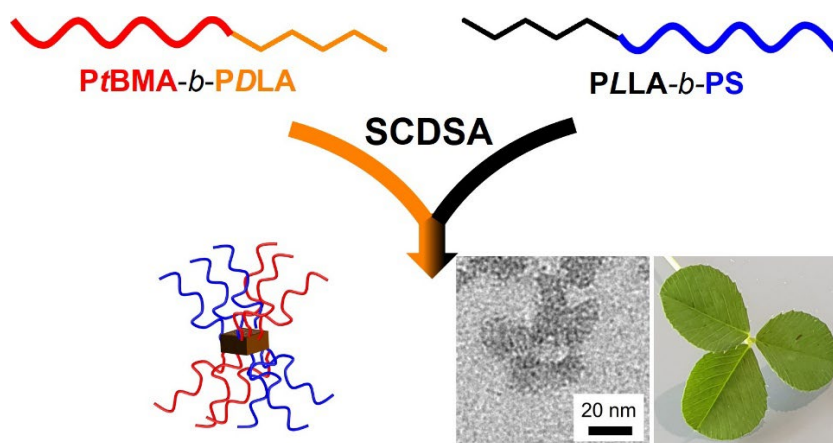
by Roman Schaller, Emma Fuchs, Lisa Maria Günther and Holger Schmalz

Emma Fuchs and I contributed equally to this work. I synthesized and functionalized the PDLA homopolymers, prepared the micelle dispersions, designed and carried out the SCDSA experiments. I conducted TEM analyses and assisted during FCS measurements. I prepared the figures and wrote the main part of the manuscript. Emma Fuchs synthesized and characterized the triblock terpolymers, performed μ -DSC measurements and was involved in preliminary work on the preparation of micelles dispersions. Lisa Maria Günther designed and carried out FCS measurements and wrote the corresponding part of the manuscript. Holger Schmalz performed Raman spectroscopy measurements, co-designed the experiments, supervised the project and was involved in writing and correcting the manuscript.

3 Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly

Roman Schaller,^a Christian Hils,^a Matthias Karg,^b and Holger Schmalz^{a,c,*}

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Published in *Macromol. Rapid Commun.* **2023**, 44 (3), 2200682.

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Abstract

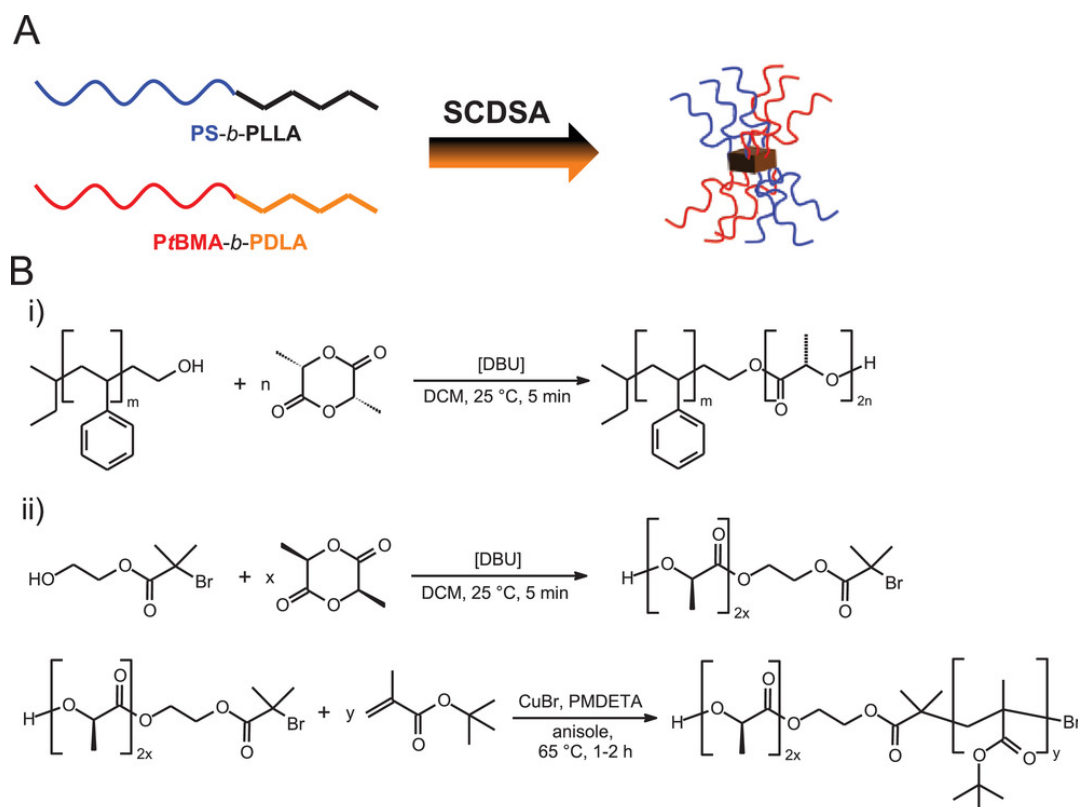
The unique corona structure of surface-compartmentalized micelles (Janus micelles, patchy micelles) opens highly relevant applications, e.g. as efficient particulate surfactants for emulsion stabilization or compatibilization of polymer blends. Here, stereocomplex-driven self-assembly (SCDSA) as a facile route to micelles with a semicrystalline stereocomplex (SC) core and a patch-like microphase separated corona, employing diblock copolymers with enantiomeric poly(*L*-lactide)/poly(*D*-lactide) blocks and highly incompatible corona-forming blocks (polystyrene (PS), poly(*tert*-butyl methacrylate)) is introduced. The spherical patchy SC micelles feature a narrow size distribution and show a compartmentalized, shamrock-like corona structure. Compared to SC micelles with a homogeneous PS corona the patchy micelles have a significantly higher interfacial activity attributable to the synergistic combination of an amphiphilic corona with the Pickering effect of nanoparticles. The patchy micelles are successfully employed in the stabilization of emulsions, underlining their application potential.

Keywords: block copolymers, crystallization-driven self-assembly, particulate surfactants, patchy micelles, stereocomplexes

3.1 Introduction

Surface-compartmentalized micelles are of substantial interest, as their unique corona structure opens a multitude of highly relevant applications, e.g. as efficient stabilizers for emulsions and polymer blends, in catalysis, as optical nanoprobe and biosensors, for self-propulsion, superhydrophobic and anti-ice coatings, and many more.^[1-7] In general, they can be divided into Janus micelles,^[8-13] featuring two opposing faces with different chemistry and/or polarity, and patchy micelles that are characterized by a patch-like microphase-separated corona consisting of several compartments. For the preparation of one-dimensional (cylindrical/worm-like) patchy micelles crystallization-driven self-assembly (CDSA) has proven a highly efficient method.^[14-22] However, other micelle shapes, like spherical patchy micelles, have only scarcely been reported yet. Besides, the formation of semicrystalline stereocomplexes (SC) between block copolymers bearing enantiomeric poly(*L*-lactide) (PLLA) and poly(*D*-lactide) (PDLA) blocks is a strong driving force for the formation of stable micelles (stereocomplex-driven self-assembly (SCDSA)).^[23, 24] SC crystals consist of a parallel packing of PLLA 3_2 and PDLA 3_1 helices and feature an about 50 °C higher melting point compared to that of PLLA/PDLA homopolymers and are insoluble even in the solvents they have been prepared.^[25] The by far most studied SC micelles are based on linear block copolymers (AB-, ABA- and ABC-type), star-shaped block copolymers and graft copolymers with poly(ethylene oxide) (PEO) or poly(oligo(ethylene glycol) methacrylate) blocks rendering the SC micelles water soluble.^[26-29] Alternatively, block copolymers with poly(acrylic acid),^[30, 31] poly(*N,N*-dimethylaminoethyl methacrylate)^[32] or poly(*isoglycerol* methacrylate)^[33] blocks were used. In contrast, only a few reports address SC micelle formation in organic solvents.^[34-36] Up to now there is only one report on SC micelles with a patchy poly(*N-isopropyl* acrylamide) (PNiPAAm)/PEO corona prepared by SCDSA in water.^[37] However, the cloud point of the PNiPAAm block was about 20°C and, thus, the patchy corona structure was induced by a partial collapse of PNiPAAm.

Herein, we report on the preparation of spherical patchy micelles by SCDSA of diblock copolymers bearing enantiomeric PLLA and PDLA core-forming blocks and highly incompatible corona-forming blocks, namely PS-*b*-PLLA and PtBMA-*b*-PDLA (PS = polystyrene, PtBMA = poly(*tert*-butyl methacrylate)), in organic solvents (Scheme 3.1A). Next to the preparation and characterization of the spherical patchy SC micelles also their interfacial activity and potential as particulate surfactants will be addressed.



Scheme 3.1 A) Concept for the preparation of patchy micelles via SCDSA and B) synthesis of diblock copolymers.

3.2 Results and Discussion

3.2.1 SCDSA of Diblock Copolymer Mixtures to Spherical Patchy Micelles

The used PS-*b*-PLLA diblock copolymer ($S_{169}LLA_{119}$, subscripts denote number-averaged degrees of polymerization) was synthesized by organo-catalyzed ring-opening polymerization (ROP) of *L*-lactide starting from a PS-OH macroinitiator prepared by anionic polymerization of styrene and end-capping with ethylene oxide (Scheme 3.1B,i)). For the synthesis of PtBMA-*b*-PDLA ($tBMA_{172}DLA_{114}$) a combination of ROP of *D*-lactide with atom transfer radical polymerization of *t*BMA was employed, utilizing 2-hydroxyethyl 2-bromoisobutyrate as bifunctional initiator (Scheme 3.1B,ii)). Details on synthesis and molecular characterization of the diblock copolymers can be found in the Experimental Section and Supporting Information (Figure S3.1, S3.2 and Table S3.1, Supporting Information). For the preparation of patchy SC micelles the diblock copolymers were first dissolved in dichloromethane (DCM, $c = 10 \text{ g L}^{-1}$) as non-selective solvent, employing a 1/1 (w/w) ratio with respect to the enantiomeric PLA blocks. A PLLA/PDLA ratio of 1/1 (w/w) was chosen to ensure an equimolar ratio of the enantiomeric PLA units for efficient SC formation. Then, the mixture ($V = 300 \mu\text{L}$) was added

drop-wise to an excess of cyclohexane (CH, $V = 3$ mL), a selective solvent for the PS and PtBMA corona-forming blocks, under stirring to induce SC formation and crystallization followed by aging for at least 1 day at ambient conditions (no stirring was applied during aging). This resulted in a dispersion of PS-*sc*-PLA-PtBMA micelles ($c = 0.9$ g L⁻¹ in CH/DCM = 10/1 (v/v)) with an insoluble SC core and a soluble PS/PtBMA corona. Dynamic light scattering (DLS) revealed a narrow size distribution of the SC micelles with an apparent hydrodynamic diameter of $D_{h,app} = 104 \pm 30$ nm (Figure 3.1A). In the beginning, the micelle size increases slightly with time and stays constant after ca. 6 h (Figure 3.1B). The mean diameter and the diameter distribution do not change significantly even after ten weeks of aging. This underlines the stability of the SC micelles in dispersion (Figure S3.3A, Supporting Information). Also the time between preparing the diblock copolymer mixture in DCM and SCDSA in CH has no obvious impact on the size distribution of the micelles (Figure S3.3B, Supporting Information).

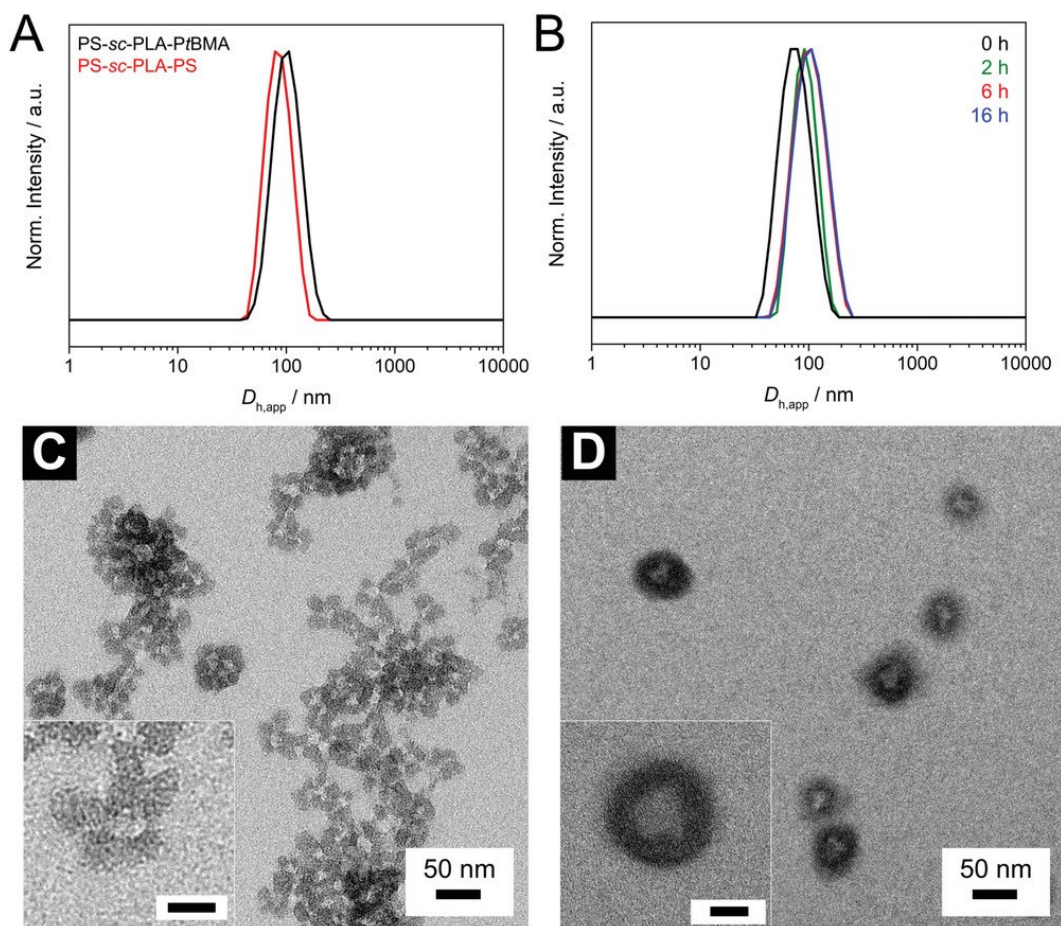


Figure 3.1 Hydrodynamic diameter distributions from DLS for A) SC micelles prepared from PS-*b*-PLLA/PtBMA-*b*-PDLA and PS-*b*-PLLA/PS-*b*-PDLA mixtures, respectively ($c = 0.9$ g L⁻¹, CH/DCM = 10/1 (v/v)), and B) of a PS-*sc*-PLA-PtBMA micelle dispersion after aging for different times as indicated. TEM micrographs (RuO₄ staining, scale bars inset = 20 nm) of the corresponding SC micelles with C) a patchy PS/PtBMA corona and D) a homogeneous PS corona. The small black dots in the PS patches are RuO₂ nanoparticles, which form selectively in the PS domains during the staining process.

From the transmission electron microscopy (TEM) micrograph shown in Figure 3.1C a patch-like microphase-separated corona of the micelles can be clearly deduced. Due to selective staining with RuO₄ vapor PS domains appear dark and the semicrystalline PLA SC core as well as the *Pt*BMA domains in the corona bright. The micelles feature different numbers of PS patches, mostly 3–5, and hence the micelle structure might be described best as a shamrock-like morphology. The patchy corona structure becomes even clearer by comparison with PS-*sc*-PLA-PS micelles prepared by SCDSA of S₁₆₉LLA₁₁₉ and S₁₆₉DLA₁₉₀ under identical conditions. The micelles exhibit a narrow size distribution with a comparable $D_{h,app}$ of 82 ± 25 nm (Figure 3.1A) and from TEM (Figure 3.1D) the difference in corona structure is evident, appearing now homogeneously dark. As DLS shows narrow size distributions the observed agglomeration of the SC micelles on the TEM grid can be attributed to drying artifacts arising from sample preparation. CDSA of the individual diblock copolymers under identical conditions as employed for SCDSA resulted in crystalline-core (PLLA or PDLA) micelles with increased sizes, broader size distributions and mostly cylindrical shapes (Figure S3.4, Supporting Information). This indicates that the formation of spherical patchy micelles from the diblock copolymer mixtures is solely driven by SC formation.

In the Raman spectra of the SC micelles with a patchy PS/*Pt*BMA as well as homogeneous PS corona a shift of the carbonyl stretching vibration from $\approx 1771 - 1773$ cm⁻¹ for the individual diblock copolymers to $\approx 1752 - 1755$ cm⁻¹ is observed (Figure 3.2). This characteristic shift to lower wavenumbers proves that self-assembly is indeed driven by SC formation between the enantiomeric PLLA/PDLA blocks.^[23, 34, 36, 38,39] Nevertheless, the carbonyl band does not shift completely to lower wavenumbers, indicating that some lactide units (probably at the core/corona interface) did not take part in SC formation.

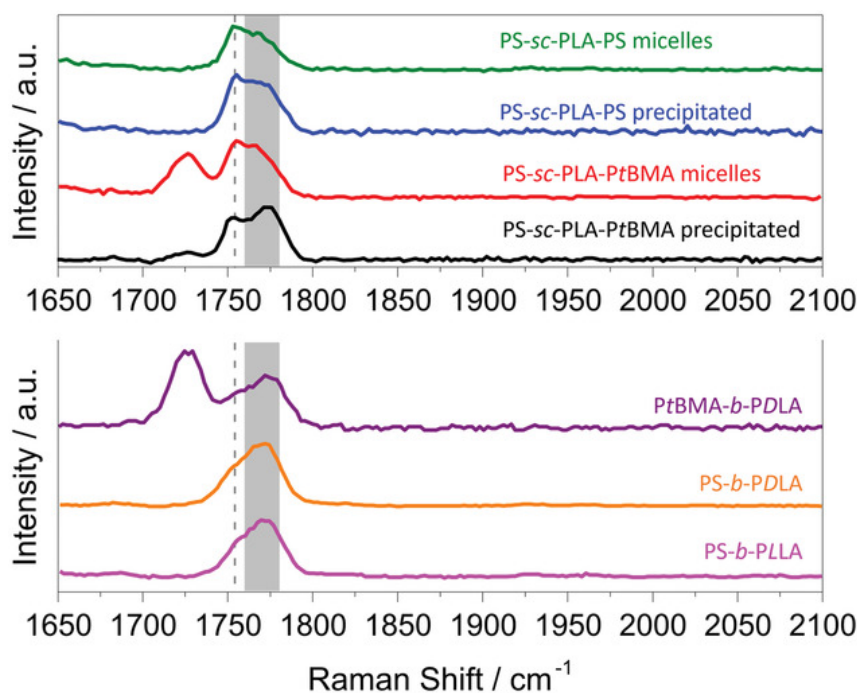


Figure 3.2 Raman spectra of employed diblock copolymers, dried SC micelles, and solid SCs prepared by direct precipitation of the diblock copolymer mixtures in DCM into *n*-pentane. Shown are zoom-ins of the carbonyl stretching vibration regime (dashed line indicates location of SC specific band, full spectra are given in Figure S5, Supporting Information).

As a comparison, the respective diblock copolymer mixtures in DCM were directly precipitated in *n*-pentane, a non-solvent for all blocks. The obtained solids upon precipitation were studied by Raman spectroscopy. Interestingly, for the PS-*sc*-PLA-PtBMA micelles the SC specific band at about 1755 cm^{-1} is more pronounced with respect to the sample prepared by precipitation in *n*-pentane, pointing to a more efficient SC formation upon SCDSA in CH. For PS-*sc*-PLA-PS no significant difference between both methods was observed. These results show that SC formation is a very fast process as even upon direct precipitation SCs are formed. In addition, differential scanning calorimetry revealed significantly higher melting temperatures for the SC micelles ($T_m \approx 200\text{ }^{\circ}\text{C}$) with respect to that observed for the neat PLLA and PDLA homopolymers ($T_m \approx 145\text{ }^{\circ}\text{C}$), further underlining that SC formation and crystallization is the driving force for self-assembly (Figure S3.6, S3.7; Table S3.2, Supporting Information).^[25, 38, 39] It is noted that PLLA or PDLA related melting transitions were not observed for the employed PS-*b*-PLLA and PtBMA-*b*-PDLA diblock copolymers due to confinement effects (Figure S3.6, Supporting Information).^[40] The degree of SC crystallization was determined to $\alpha = 34\%$ for PS-*sc*-PLA-PtBMA and $\alpha = 31\%$ for PS-*sc*-PLA-PS (Table S3.2, Supporting Information), which is in accordance with Raman results revealing the presence of PLLA/PDLA units that did not take part in SC formation. Accordingly, about 70% of the micellar core is still amorphous allowing the PS and PtBMA corona chains to self-

assemble into distinct nanometer-sized patches, as otherwise the parallel packing of PLLA and PDLA blocks in the SC crystal might hamper the segregation of the corona chains for higher degrees of crystallinity.

3.2.2 Effect of Dilution on Micelle Size and Corona Structure

Next, we studied whether dilution has an impact on the structure of the SC micelles, keeping the concentration of the diblock copolymer mixture in DCM constant at $c = 10 \text{ g L}^{-1}$. Accordingly, smaller amounts of the diblock copolymer mixtures ($V = 60$ and $30 \text{ }\mu\text{L}$), prepared in an identical manner as described above, were added in one portion to 3 mL of CH and aged for 1 day. This yielded SC micelle dispersions with a concentration of $c = 0.2 \text{ g L}^{-1}$ in CH/DCM = 50/1 (v/v) and $c = 0.1 \text{ g L}^{-1}$ in CH/DCM = 100/1 (v/v), respectively. DLS again shows narrow size distributions for the formed SC micelles at $c = 0.2 \text{ g L}^{-1}$ (Figure S3.8A, Supporting Information; PS-*sc*-PLA-PtBMA: $D_{\text{h,app}} = 50 \pm 14 \text{ nm}$) as well as $c = 0.1 \text{ g L}^{-1}$ (Figure 3.3A; PS-*sc*-PLA-PtBMA: $D_{\text{h,app}} = 52 \pm 17 \text{ nm}$, PS-*sc*-PLA-PS: $D_{\text{h,app}} = 50 \pm 14 \text{ nm}$), however, being significantly smaller compared to the micelles prepared at lower dilution (Figure 3.1A). The smaller size of the micelles might be attributed to the altered preparation method employed. For higher dilutions (CH/DCM = 50/1 and 100/1 (v/v)) small amounts of the diblock copolymer mixtures in DCM were added in one portion to CH in contrast to the drop-wise addition employed for lower dilution (CH/DCM = 10/1 (v/v)).

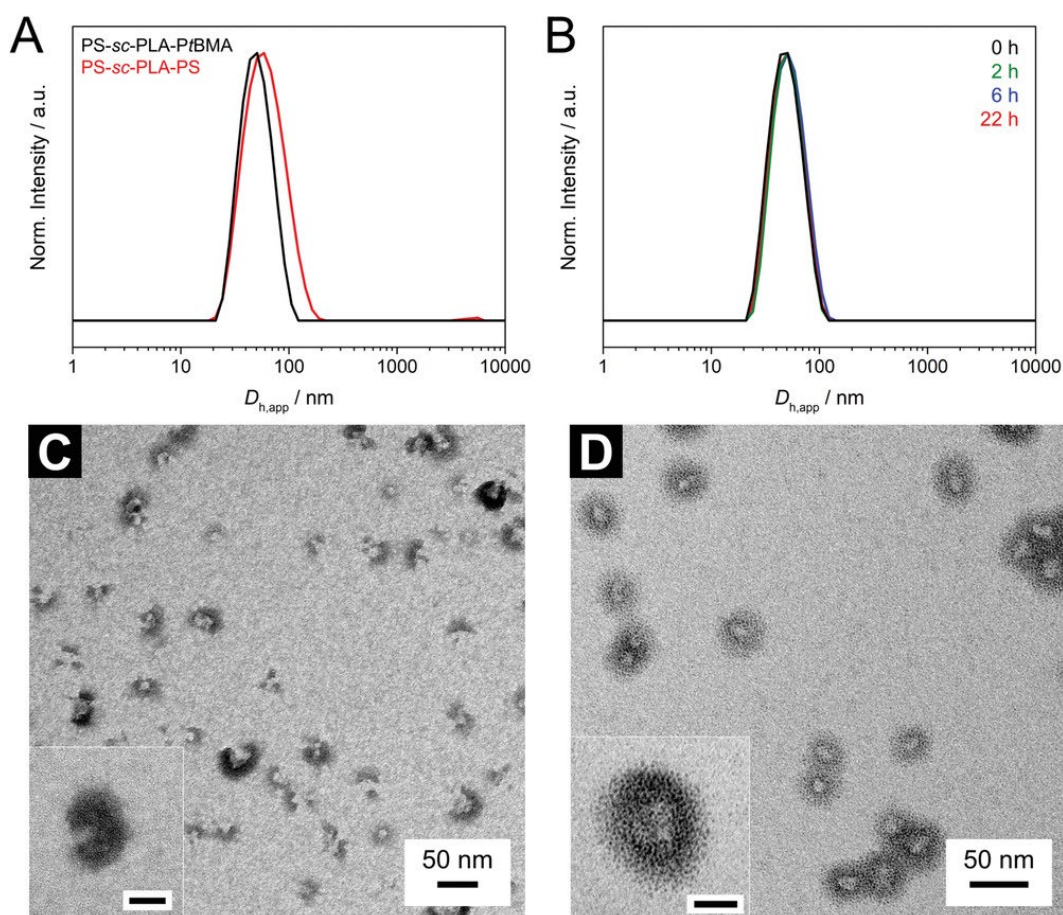


Figure 3.3 Hydrodynamic diameter distributions from DLS for A) SC micelles prepared from PS-*b*-P_{LLA}/PtBMA-*b*-PD_{LA} and PS-*b*-P_{LLA}/PS-*b*-PD_{LA} mixtures, respectively, and B) of a PS-*sc*-PLA-PtBMA micelle dispersion after aging for different times as indicated, employing a higher dilution ($c = 0.1 \text{ g L}^{-1}$, CH/DCM = 100/1 (v/v)). TEM micrographs of the formed SC micelles (RuO₄ staining, scale bars inset = 20 nm) with C) a surface-compartmentalized PS/PtBMA and D) a homogeneous PS corona

Since SC formation is a very fast process, as revealed from the samples prepared by direct precipitation in *n*-pentane (Figure 3.2, S3.7; Table S3.2, Supporting Information), SC micelles are formed instantaneously upon addition of the DCM solution to CH. This is confirmed by the observation that the size distribution of the micelles formed at CH/DCM = 100/1 (v/v) (Figure 3.3B) does not change with time in contrast to the behaviour at lower dilution (CH/DCM = 10/1 (v/v), Figure 3.2B) and that the degree of stereocomplexation as deduced from Raman spectroscopy is comparable (Figure S3.9, Supporting Information). Accordingly, during the drop-wise addition SC micelles are presumably formed instantaneously upon addition of the first drop and micelles grow with time during further addition and subsequent aging. This in turn indicates the presence of a certain amount of unimers in solution that can add to the SC micelles, which might be facilitated by the comparably high DCM content (non-selective solvent) of 9 vol.% for the samples prepared at lower dilution.

Interestingly, the corona of the PS-*sc*-PLA-*Pt*BMA micelles prepared at higher dilutions (Figure S3.8B, Supporting Information: CH/DCM = 50/1 (v/v), Figure 3.3C: CH/DCM = 100/1 (v/v)) exhibits some distinct differences with respect to the quite uniform patchy structure observed before (Figure 3.1C). Here, a mixture of SC micelles with a patchy and a Janus-like corona structure is formed instead, both featuring defined compartments in the corona. If the Janus-type micelles are oriented in a proper way on the carbon-coated copper grid (inset Figure 3.3C), they can be distinguished as micelles with a bright appearing PLA SC core, which is surrounded by a dark PS and a bright *Pt*BMA hemisphere. In contrast, if one side of the micelle is facing the surface of the grid (preferentially the PS face), the micelle corona appears homogeneously dark. The concomitant formation of Janus micelles might be attributed to the significantly lower micelle size, which favors to some extent a separation into two distinct PS and *Pt*BMA faces due to a denser chain packing and, hence, increased segregation strength in the corona. Also the reduced DCM amount in the dispersions prepared at higher dilutions (2 vol.% for CH/DCM = 50/1 (v/v) and 1 vol.% for CH/DCM = 100/1 (v/v), respectively) might induce a somewhat higher incompatibility as DCM is a good solvent for both PS and *Pt*BMA, whereas CH (theta solvent for PS) is a slightly better solvent for *Pt*BMA. The PS-*sc*-PLA-PS micelles show again a homogeneously dark appearing PS corona (Figure 3.3D), being clearly distinguishable from the compartmentalized corona of the PS-*sc*-PLA-*Pt*BMA micelles.

3.2.3 Interfacial activity of spherical patchy stereocomplex micelles

To test the potential of the patchy PS-*sc*-PLA-*Pt*BMA micelles as particulate surfactants the interfacial tension at the CH/water interface was studied. To this end, the micelle dispersions ($c = 0.9 \text{ g L}^{-1}$, CH/DCM = 10/1 (v/v), Figure 3.1) were dialyzed against pure CH prior to the measurement and diluted to $c = 0.1 \text{ g L}^{-1}$. DLS and TEM shows that the size and corona structure of the micelles did not change upon dialysis (Figure S3.10, Supporting Information). Figure 3.4A reveals a significantly higher interfacial activity of the patchy micelles compared to SC micelles with a homogeneous PS corona, resulting in a decrease of the quasi-equilibrium interfacial tension to $\gamma = 25.9 \pm 0.1 \text{ mN m}^{-1}$ ($\gamma = 31.6 \pm 0.1 \text{ mN m}^{-1}$ for PS-*sc*-PLA-PS and $\gamma = 40.3 \pm 0.1 \text{ mN m}^{-1}$ for pristine CH/water interface). Notably, the decrease of interfacial tension in the beginning is steeper for the patchy micelles, which can be attributed to their pronounced interfacial activity promoted by the combination of an amphiphilic corona with the Pickering effect of nanoparticles.

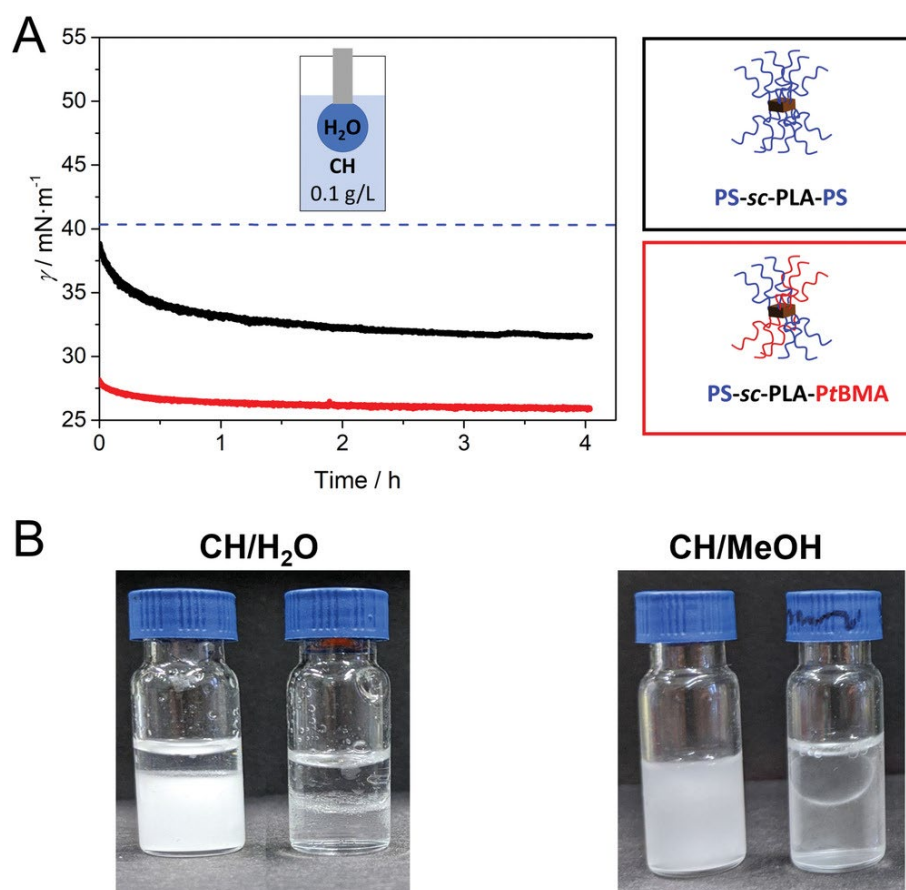


Figure 3.4 A) Interfacial tension isotherms of spherical PS-*sc*-PLA-*Pt*BMA micelles with a patchy corona compared to spherical PS-*sc*-PLA-PS micelles with a homogeneous corona at the CH/water interface. The dashed blue line is the interfacial tension at the pristine CH/water interface measured as reference. B) CH/water and CH/methanol mixtures emulsified with patchy PS-*sc*-PLA-*Pt*BMA micelles ($c = 0.9 \text{ g L}^{-1}$ in CH). The photographs on the right of each mixture correspond to the respective pure solvent mixtures that separated immediately after shaking.

Exemplarily, we have tested the potential of patchy PS-*sc*-PLA-*Pt*BMA micelles as particulate surfactants in the emulsification of CH/water and CH/methanol mixtures (50/50 (v/v)), employing dispersions with a concentration of $c = 0.9 \text{ g·L}^{-1}$ (Figure 3.4B). For the CH/water mixture the emulsion sediments to the bottom of the vial and is overlaid with excess oil (CH) phase. As the density of water is significantly higher compared to that of CH ($\rho = 0.78 \text{ g·cm}^{-3}$) a water-in-oil (w/o) emulsion is formed consequently. This is in accordance with emulsification studies on Janus particles featuring two hydrophobic faces.^[41] In case of CH/methanol mixtures homogeneous emulsions were obtained, which might be attributed to the comparable densities of both solvents ($\rho(\text{MeOH}) = 0.79 \text{ g·cm}^{-3}$) in combination with methanol being a selective solvent for *Pt*BMA. Here, the PS patches are soluble in the CH phase and the *Pt*BMA patches in the methanol phase, respectively, in contrast to CH/water where both patches are insoluble in the water phase. Hence, the amphiphilicity of the patchy micelles for the CH/methanol combination might result in a more efficient emulsification.

3.3 Conclusion

This work shows that stereocomplex-driven self-assembly (SCDSA) of diblock copolymers bearing enantiomeric PLLA and PDLA blocks as well as strongly incompatible, amorphous corona-forming blocks is a facile route toward spherical patchy micelles with excellent interfacial activity. This modular approach allows for an easy variation of corona-forming blocks and, thus, corona chemistries to tune interfacial activity or functionality. This might open interesting applications not only as efficient particulate surfactants/compatibilizers but also in other fields like heterogeneous catalysis or hierarchically structured assemblies.

3.4 Experimental Section and Methods

Materials

All chemicals were used as received unless otherwise noted. Ethylene oxide (Linde, 3.0) was condensed onto calcium hydride (CaH_2) and stirred at 0 °C for 3 h before being transferred into a storage ampoule. Prior to use ethylene oxide was additionally purified over *n*-butyllithium at 0 °C. Styrene (>99%, Sigma-Aldrich) was stirred over di-*n*-butylmagnesium (Bu_2Mg) under nitrogen and condensed into a storage ampoule. Dichloromethane (DCM, $\geq 99.8\%$, analytical reagent grade, Thermo Scientific) used for lactide polymerization was dried by successive distillation over CaH_2 . *n*-Pentane (technical grade) was purified by distillation prior to use. Tetrahydrofuran (THF, 99.9%, Sigma-Aldrich) was dried by successive distillation over CaH_2 and potassium and stored under nitrogen until use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, >98%, TCI) was dried by successive distillation over CaH_2 . *D*- and *L*-lactide ($\geq 99.8\%$, PURASORB® D and L, Corbion, Amsterdam, The Netherlands) were recrystallized from toluene and stored under nitrogen or argon until use. *tert*-Butyl methacrylate (*t*BMA, BASF SE) was passed through a column with basic alumina and *N,N,N',N'',N''*-pentamethyl-diethylenetriamine (PMDETA, 99%, Sigma-Aldrich) was distilled prior to use. Deionized water (filtered through a Millipore Milli-Q Plus system, QPAK® 2 purification cartridge, conductivity: 18.2 M Ω cm), Bu_2Mg (1.0 M in heptane, Sigma-Aldrich), *sec*-butyllithium (*sec*-BuLi, 1.3 M in cyclohexane/hexane, Thermo Scientific), *n*-butyllithium (*n*-BuLi, 1.6 M in hexanes, Thermo Scientific), benzoic acid (p.a., AlppiChem), copper(I) bromide (Cu(I)Br , 98%, Sigma-Aldrich), CaH_2 (Merck), 2-hydroxyethyl 2-bromoisobutyrate (HEBiB, 95%, Sigma-Aldrich), deuterated chloroform (CDCl_3 , 99.8%, Deutero), ruthenium(III) chloride hydrate (ReagentPlus®, Sigma-Aldrich), sodium hypochlorite solution (NaOCl , 10 – 15 wt.% in water, Sigma-Aldrich), hydrochloric acid (HCl , 37 wt.% in water, VWR), cyclohexane (CH_2

$\geq 99.8\%$, analytical reagent grade, Thermo Scientific), anisole ($>99\%$, Solvagreen, TH. Geyer), 1,4-dioxane ($\geq 99.8\%$, analytical reagent grade, Thermo Scientific), methanol (MeOH, $\geq 99.9\%$, analytical reagent grade, Thermo Scientific) and dialysis membrane (Spectra/Por[®] 1, molecular weight cut-off: 6000 – 8000 Dalton).

Synthesis of hydroxy terminated polystyrene macroinitiator (PS-OH)

PS-OH was prepared by anionic polymerization of styrene in THF followed by end-capping with ethylene oxide. Polymerization of styrene was conducted at $-78\text{ }^{\circ}\text{C}$ using *sec*-BuLi as initiator. After complete conversion a five-fold molar excess of ethylene oxide was added for end-capping followed by stirring for 30 min. The polymer was terminated with a mixture of acetic acid/methanol (1/5 (v/v)) and isolated by precipitation from methanol. The product was filtered and dried in vacuo (20×10^{-3} mbar) at $40\text{ }^{\circ}\text{C}$.

Synthesis of *D*-lactide based ATRP macroinitiator

PDLA-ATRP was prepared according to the literature under an inert argon atmosphere.^[42] To *D*-lactide in DCM ($c \approx 150\text{ g L}^{-1}$) a solution of HEBiB (380 μL , 0.41 mmol, $c = 1.07\text{ mol L}^{-1}$ in DCM) was added at room temperature. DBU (4 eq with respect to HEBiB) was added and the reaction mixture was stirred for 5 min. Subsequently, the reaction was stopped by the addition of benzoic acid (equimolar amount to DBU) and the mixture was stirred for 30 min. The product was precipitated from *n*-pentane/MeOH (10/1 (v/v)), filtrated and dried in vacuo (5×10^{-6} mbar).

Synthesis of PS-*b*-PLLA and PS-*b*-PDLA

PS-*b*-PLLA and PS-*b*-PDLA were prepared according to the literature.^[42] To PS-OH in DCM ($c \approx 150\text{ g L}^{-1}$) the respective *L*- or *D*-lactide was added and stirred at room temperature for 10 min under argon. DBU (4 eq with respect to OH end groups) was added and the reaction mixture was stirred for 5 min. Subsequently, benzoic acid (equimolar amount to DBU) was added to stop the reaction and the mixture was stirred for 30 min. The products were precipitated from *n*-pentane/MeOH (10/1 (v/v)), filtrated and dried in vacuo (5×10^{-6} mbar).

Synthesis of PtBMA-*b*-PDLA

PtBMA-*b*-PDLA was prepared according to the literature.^[43,44] PDLA-ATRP (1.0 g), *t*BMA (8.0 mL) and PMDETA (50.9 μL) were mixed together in anisole (15 mL) and degassed with argon for 60 min. The solution was heated to $65\text{ }^{\circ}\text{C}$ and Cu(I)Br (35.0 mg) was added under stirring. The employed molar ratio of macroinitiator/Cu(I)Br/PMDETA was 1/2/2. After 130 min the reaction was quenched by placing the mixture into liquid nitrogen. The reaction

mixture was passed through a neutral alumina column to remove the catalyst. The product was precipitated from H₂O/MeOH (2/1 (v/v)), filtrated and dried in vacuo (5×10^{-6} mbar). Finally, the diblock copolymer was dissolved in 1,4-dioxane and freeze-dried to yield a white powder.

Preparation of PLA stereocomplexes via precipitation

Typically, solutions of PLA homopolymers or PLA based diblock copolymers in DCM ($c = 10 \text{ g L}^{-1}$) were mixed together, employing a 1/1 weight ratio with respect to the enantiomeric PLLA/PDLA blocks. The mixtures were precipitated from *n*-pentane (combination of PLLA-ATRP/PDLA-ATRP, PS-*b*-PLLA/PS-*b*-PDLA) or H₂O/MeOH (2/1 (v/v), combination of PS-*b*-PLLA/PtBMA-*b*-PDLA), respectively. After removal of the solvents by evaporation or separation by centrifugation the obtained white solids were dried in vacuo (5×10^{-6} mbar). These samples prepared by direct precipitation are denoted as PS-*sc*-PLA-PtBMA precipitated or PS-*sc*-PLA-PS precipitated, respectively.

SCDSA of diblock copolymer mixtures

Solutions of PS-*b*-PLLA and PtBMA-*b*-PDLA in DCM ($c = 10 \text{ g L}^{-1}$) were mixed together, employing a 1/1 weight ratio with respect to the enantiomeric PLA blocks. In a 5 mL snap lid vial, equipped with a small magnetic stirring bar, the obtained mixture (300 μL) was added dropwise to CH (3 mL) over 20 sec while stirring (approximately 700 rpm), resulting in a micelle dispersion with a concentration of $c = 0.9 \text{ g L}^{-1}$ and a final solvent ratio of CH/DCM = 10/1 (v/v). Subsequently, the dispersion was stirred for an additional 1 min and then aged at room temperature without stirring for at least one day before DLS and TEM characterization. The same protocol was applied to the combination of PS-*b*-PLLA and PS-*b*-PDLA starting from solutions with concentrations of $c = 10 \text{ g L}^{-1}$. Analogously, micelle dispersions with concentrations of $c = 0.2$ and 0.1 g L^{-1} and final solvent ratios of CH/DCM = 50/1 and 100/1 (v/v), respectively, were prepared by adding smaller amounts of the diblock copolymer mixture in DCM (60 and 30 μL , $c = 10 \text{ g L}^{-1}$) in one portion to the same volume of CH (3 mL) using a micropipette. The dispersion of SC micelles prepared by SCDSA are denoted as PS-*sc*-PLA-PtBMA micelles or PS-*sc*-PLA-PS micelles, respectively.

CDSA of neat diblock copolymers

CDSA of the individual diblock copolymers in CH was conducted the same way as described above for SCDSA of diblock copolymer mixtures, starting from DCM solutions of the diblock copolymers with concentrations of $c = 10 \text{ g L}^{-1}$.

Characterization techniques

The polymers were characterized by proton nuclear magnetic resonance (^1H NMR) spectroscopy using a Bruker Ultrashield-300 spectrometer (300 MHz) at 20 °C. The chemical shift (δ) was determined relatively to the signal of the solvent CDCl_3 (δ (^1H) = 7.26 ppm).

Size exclusion chromatography (SEC) was performed on a SEC 1260 Infinity system (Agilent Technologies, Santa Clara, CA, USA) with two PSS-SDV gel columns (particle size = 5 μm) with porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany). CHCl_3 (HPLC grade) was used as eluent. All samples were dissolved and filtered through a 0.2 μm PTFE filter before analyses. The samples were measured at a flow rate of 0.5 mL min^{-1} at 23 °C, using a refractive index detector (Agilent Technologies, Santa Clara, CA, USA). A calibration with narrowly distributed PS standards (PSS calibration kit) and toluene (HPLC grade) as internal standard were used.

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 FIVE 5.3 software package was employed for Raman measurements. All spectra were acquired with an excitation wavelength of $\lambda = 532$ nm and a 50x long working distance objective (Zeiss LD EC Epiplan-Neofluar Dic 50x, NA = 0.55). Typically, a laser intensity of 20 mW and integration times of 0.5–1 s (grating: 600 g mm^{-1}) were employed and 50 measurements were accumulated for a spectrum. All spectra were corrected for cosmic ray spikes and subjected to a background removal routine. Samples of the micelle dispersions were prepared by dropping small amounts (3×5 μL) of the dispersion onto a glass slide followed by drying in vacuo (3 h, 20 mbar).

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 3⁺ or a Netzsch DSC 204 F1 Phoenix instrument using aluminum crucibles (pierced lid) and nitrogen as protecting gas. The temperature range was selected from –20 °C to 220 °C employing a scanning rate of 10 K min^{-1} .

Dynamic light scattering (DLS) was conducted on a Zetasizer Nano S (Malvern Panalytical, UK) instrument equipped with a red He-Ne laser ($\lambda = 632.8$ nm) and a detector placed at $\theta = 173^\circ$ to the incident radiation. The micelle dispersions were measured without further dilution at 25 °C in quartz glass cuvettes (10.0 mm path length), which were sealed with Teflon tape to prevent solvent evaporation. Data analyses were carried out using the Malvern Zetasizer software (version 7.13). The results are displayed as normalized intensity weighted size distributions and micelle sizes are reported as apparent hydrodynamic diameter ($D_{\text{h,app}}$) determined from the average of three replicate measurements.

Transmission electron microscopy (TEM) was carried out with a Zeiss CEM902 and a Zeiss/LEO EM922 Omega TEM. All microscopes are energy filtering transmission electron microscopes (EFTEMs), operated at an acceleration voltage of 80 kV and 160/200 kV, respectively. Zero-loss filtered micrographs ($\Delta E \approx 0$ eV) were taken with a side mounted CCD camera system (Orius, Gatan) in case of the Zeiss CEM902 and a bottom mounted CCD camera (Ultrascan 1000, Gatan) in case of the Zeiss/LEO EM922 Omega, respectively. The images were processed with a digital image processing software (Digital Micrograph DM 1.9, DM 2.3, Gatan). For TEM analyses of the micelle dispersions, samples were diluted to a concentration of $c = 0.1 \text{ g L}^{-1}$ and stirred for 30 min at room temperature. Subsequently, $10 \mu\text{L}$ of the respective dispersion was applied to a carbon-coated copper grid and residual solvent was removed directly by blotting with a filter paper followed by drying of the coated copper grid under vacuum (24 h, 1×10^{-5} mbar, room temperature). For RuO_4 staining the samples were treated for 7–12 min with RuO_4 vapor, which was formed in situ from RuCl_3 hydrate and NaOCl . After staining, the samples were stored for at least 1 h in a fume hood to ensure that any not reacted RuO_4 was completely removed.

Interfacial tension measurements were performed using a DS25 from Krüss. The interfacial tensions at the CH/water interface were determined with the software “Advanced Drop Shape Analyses” (version 1.3.1.0) and the method “Pendant Drop” employing a droplet volume of $V = 20 \mu\text{L}$ (deionized water). Micellar dispersions were measured at a concentration of $c = 0.1 \text{ g L}^{-1}$. The quasi-equilibrium interfacial tensions were determined as average over the last 30 min of the respective measurement, where the interfacial tension levels off. The interfacial tension of the pristine CH/water interface was determined to $\gamma = 40.3 \text{ mN m}^{-1}$.

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Conflict of Interest

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.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

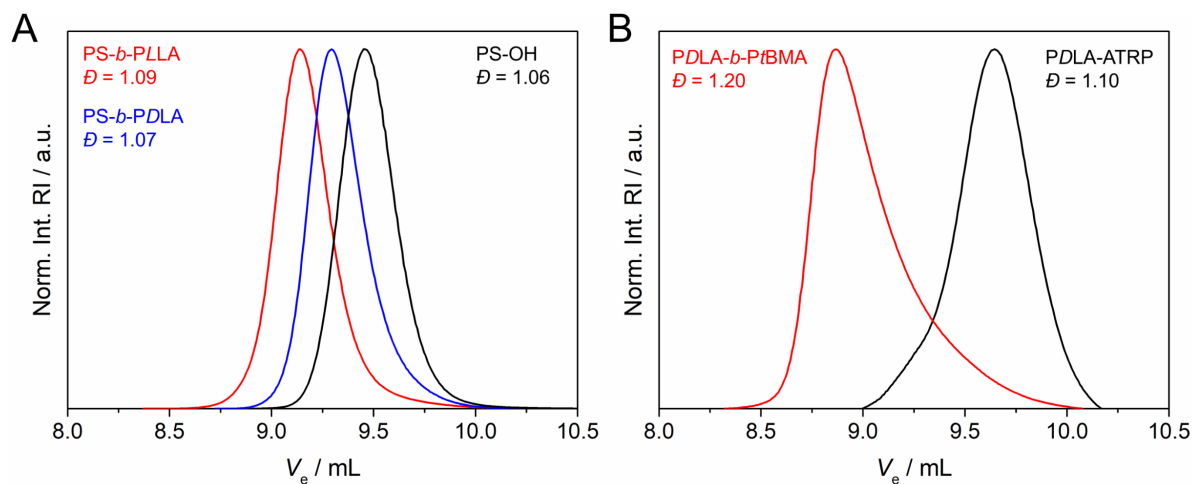


Figure S3.1 SEC traces of A) PS-OH, PS-*b*-PLLA, PS-*b*-PDLA, and B) PDLA-ATRP and PtBMA-*b*-PDLA (CHCl_3 , PS calibration).

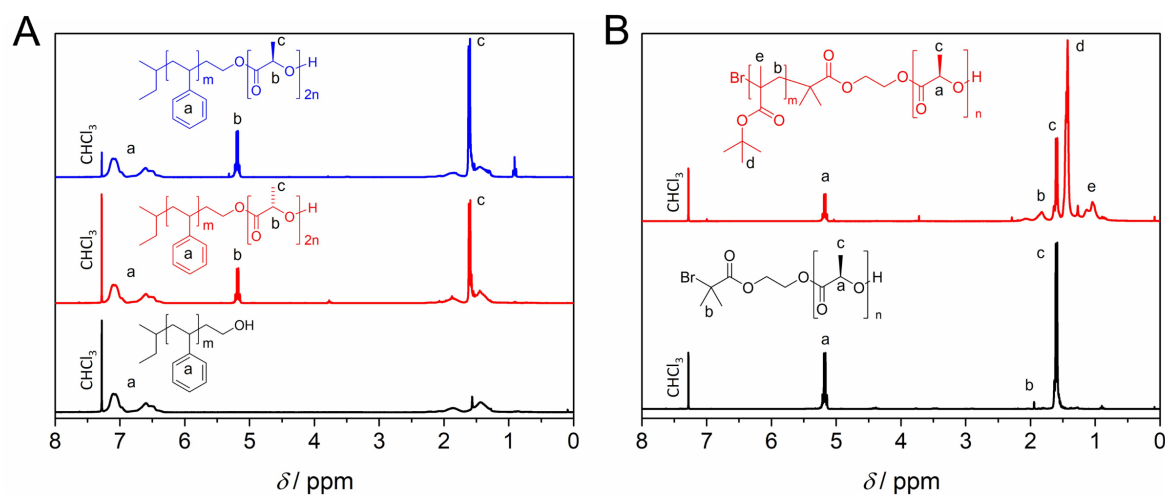


Figure S3.2 ^1H NMR (CDCl_3 , 300 MHz) spectra of A) PS-OH (black), PS-*b*-PLLA (red), PS-*b*-PDLA (blue) and B) PDLA-ATRP (black) and PtBMA-*b*-PDLA (red).

Table S3.1 Molecular characteristics of synthesized polymers.

Sample	Composition (wt.% / DP) ^a	$M_n(\text{NMR})^a$ [g mol ⁻¹]	$M_n(\text{SEC})^b$	$\bar{D}^b$
PS-OH	- / S ₁₆₉	-	17 600	1.06
PLLA-ATRP	- / LLA ₁₁₄	8 200	7 200	1.33
PDLA-ATRP	- / DLA ₁₁₄	8 200	14 200	1.10
PS- <i>b</i> -PLLA	S ₆₅ LLA ₃₅ / S ₁₆₉ LLA ₁₁₉	27 000	30 900	1.09
PS- <i>b</i> -PDLA	S ₅₆ DLA ₄₄ / S ₁₆₉ DLA ₁₉₀	31 000	35 900	1.07
PtBMA- <i>b</i> -PDLA	<i>t</i> BMA ₇₅ DLA ₂₅ / <i>t</i> BMA ₁₇₂ DLA ₁₁₄	32 700	37 500	1.20

a) determined from ¹H NMR (CDCl₃, 300 MHz) using the ATRP end group or M_n of the PS and PDLA precursor polymers for internal signal calibration, respectively

b) determined from SEC (PS-standards; eluent: CHCl₃)

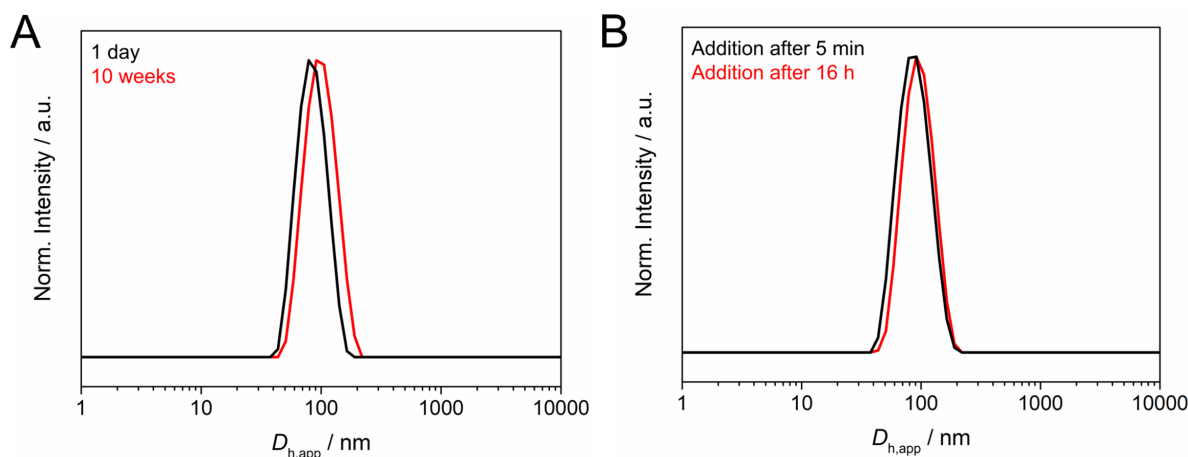


Figure S3.3 A) DLS measurements of a PS-*sc*-PLA-PtBMA micelle dispersion in CH/DCM (10:1 (v/v), $c = 0.45 \text{ g L}^{-1}$) after aging for different times as indicated. The dispersion was prepared by the addition of a mixture of PS-*b*-PLLA and PtBMA-*b*-PDLA in DCM ($V = 300 \mu\text{L}$, $c = 5 \text{ g L}^{-1}$) to cyclohexane ($V = 3 \text{ mL}$). B) DLS measurements of PS-*sc*-PLA-PtBMA micelle dispersions in CH/DCM (10:1 (v/v), $c = 0.45 \text{ g L}^{-1}$) prepared by adding a mixture of PS-*b*-PLLA and PtBMA-*b*-PDLA in DCM ($V = 300 \mu\text{L}$, $c = 5 \text{ g L}^{-1}$) after 5 min ($D_{h,\text{app}} = 86 \pm 21 \text{ nm}$) and 16 h ($D_{h,\text{app}} = 94 \pm 25 \text{ nm}$) to CH ($V = 3 \text{ mL}$), respectively, and subsequent aging for 1 day.

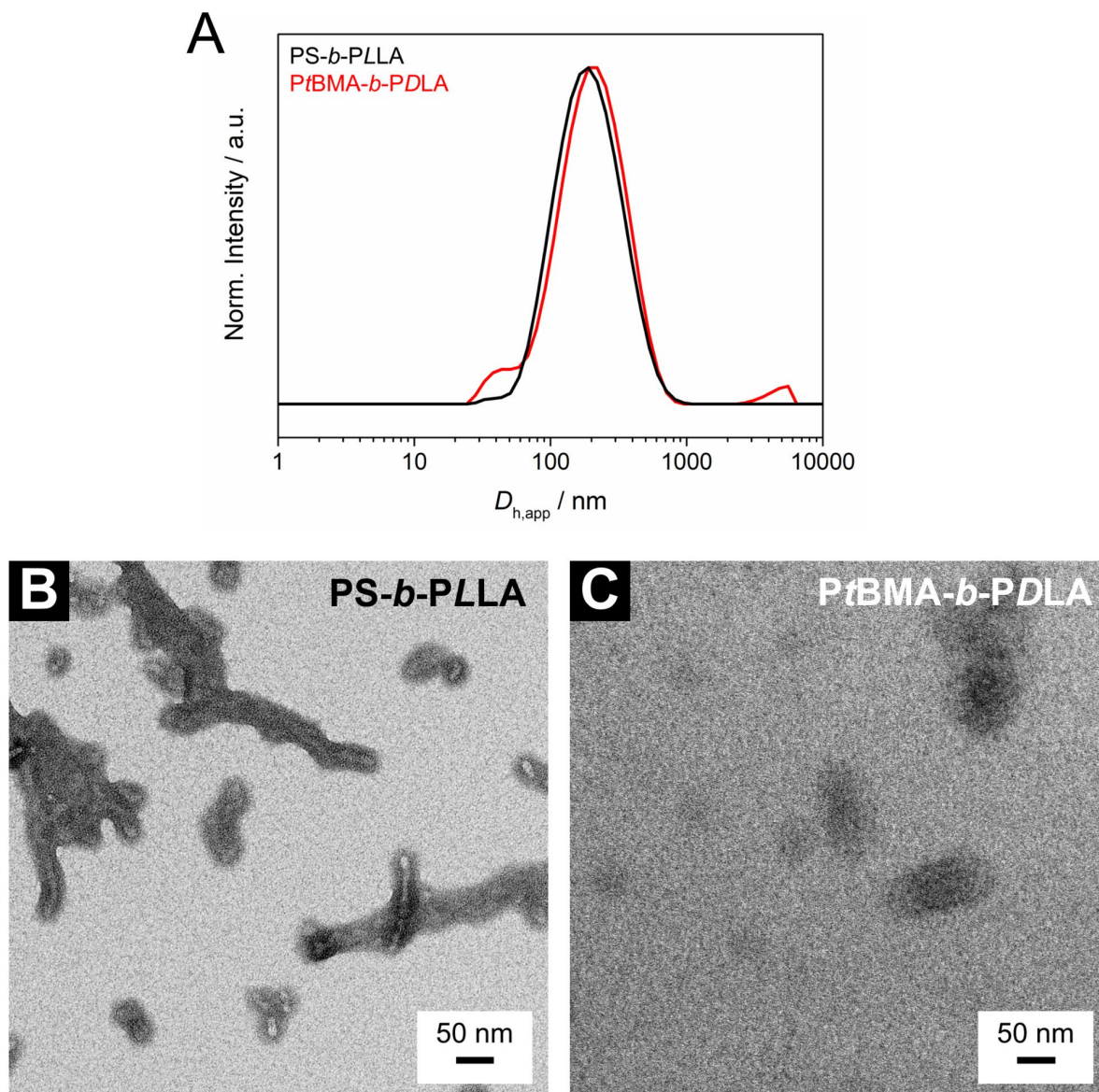


Figure S3.4 A) DLS measurements of PS-*b*-PLLA ($D_{h,app} = 216 \pm 117$ nm) and PtBMA-*b*-PDLA ($D_{h,app} = 227 \pm 112$ nm) micelle dispersions in CH/DCM (10/1 (v/v)) and B, C) TEM micrographs of the respective diblock copolymer micelles. The dispersions ($c = 0.9$ g L⁻¹) were prepared by the addition of PS-*b*-PLLA and PtBMA-*b*-PDLA solutions in DCM ($c = 10$ g L⁻¹) to CH and aging for 1 day, respectively. PS was selectively stained with RuO₄ vapor and appears dark. It is noted that PtBMA-*b*-PDLA micelles are difficult to visualize in TEM due to the pronounced degradation of the PtBMA corona block in the electron beam.

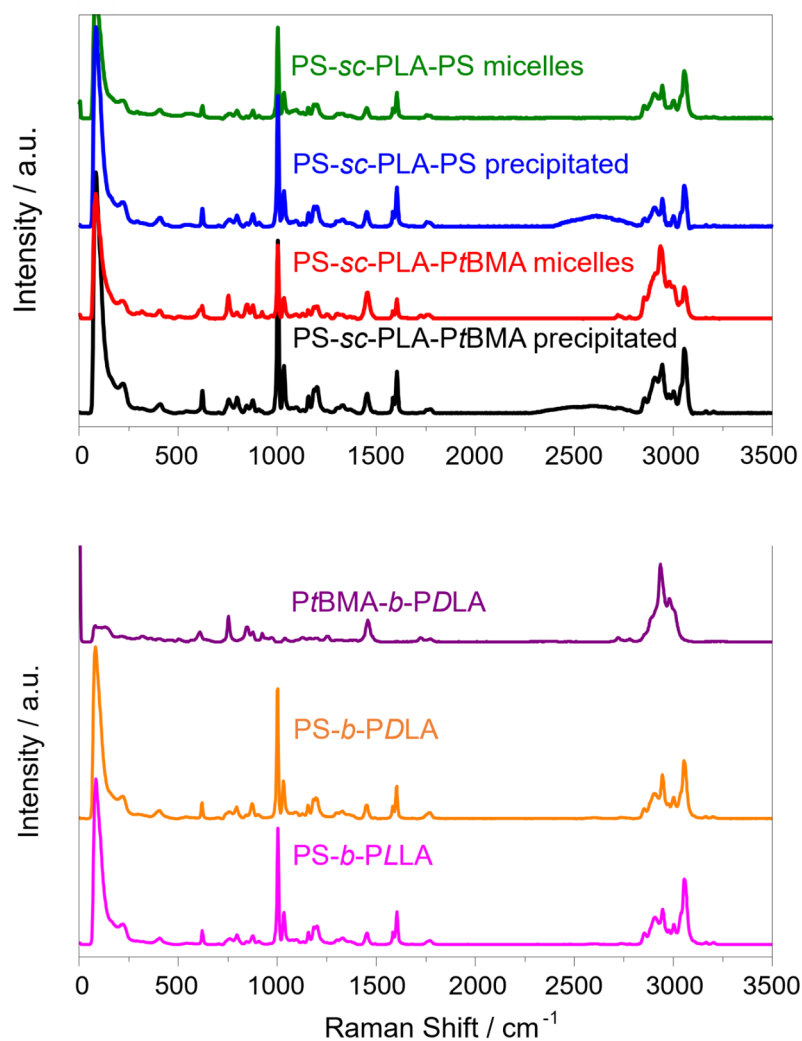


Figure S3.5 Raman spectra of individual diblock copolymers, dried SC micelles and SCs prepared by direct precipitation in *n*-pentane.

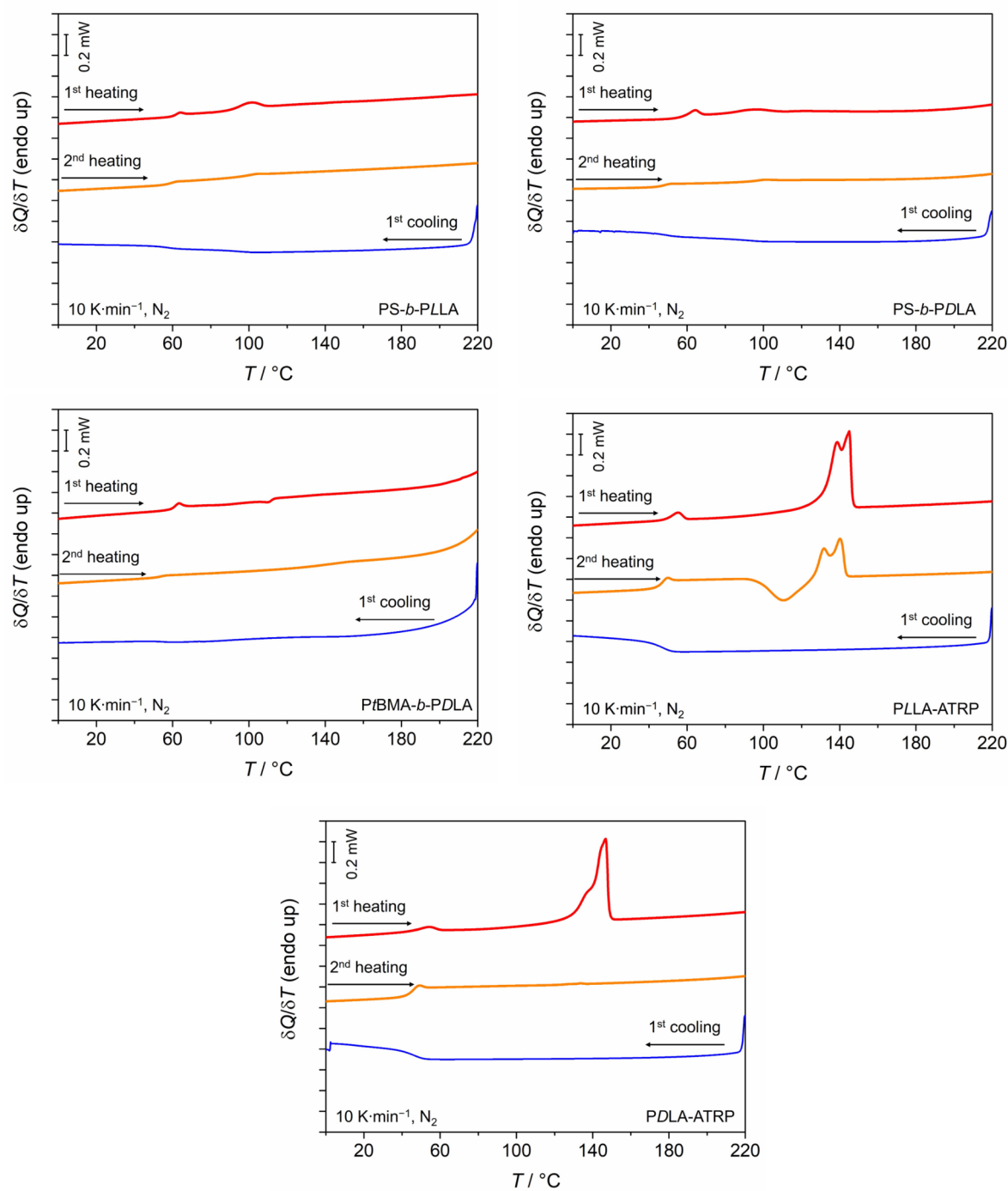


Figure S3.6 DSC measurements of diblock copolymers as well as PLLA- and PDLA-ATRP homopolymers.

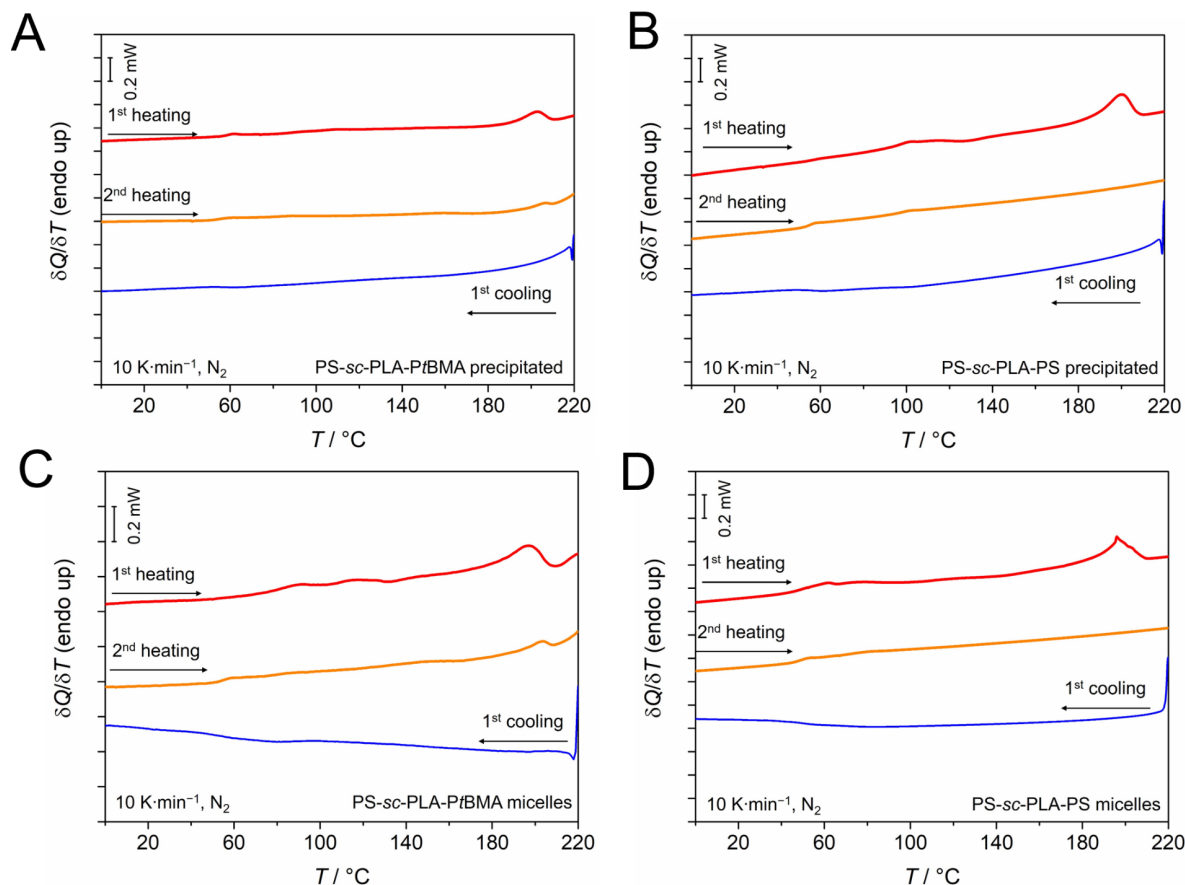


Figure S3.7 DSC measurements of A, B) diblock copolymer stereocomplexes prepared by direct precipitation in *n*-pentane and C, D) dried stereocomplex micelles obtained from freeze drying.

Table S3.2 Thermal properties of PLA based polymers and stereocomplexes.^a

Sample	f_{PLA}	$T_{\text{m},1}$ [°C]	$\Delta H_{\text{m},1}$ [J g ⁻¹]	α [%]	T_{c} [°C]	$\Delta H_{\text{c},1}$ [J g ⁻¹]	T_{g} [°C]	$T_{\text{recryst},2}$ [°C]	$\Delta H_{\text{recryst},2}$ [J g ⁻¹]	$T_{\text{m},2}$ [°C]	$\Delta H_{\text{m},2}$ [J g ⁻¹]
PLLA-ATRP	1	139, 145 ^b	51.3	55	-	-	46	110	-21.3	132, 140 ^b	22.7
PDLA-ATRP	1	146	41.9	45	-	-	45	-	-	-	-
PS- <i>b</i> -PLLA	0.35	-	-	-	-	-	59, 101	-	-	-	-
PS- <i>b</i> -PDLA	0.44	-	-	-	-	-	47, 96	-	-	-	-
PtBMA- <i>b</i> -PDLA	0.25	-	-	-	-	-	54, - ^c	-	-	-	-
<i>sc</i> -PLA (precipitated)	1	194, 206 ^b	54.2	37	101	-18.8	47	87.5	-22.2	192	50.7
PS- <i>sc</i> -PLA-PtBMA (precipitated)	0.29	202	5.1	12	-	-	56, 88, - ^c	-	-	-	-
PS- <i>sc</i> -PLA-PS (precipitated)	0.39	200	17.6	31	-	-	54, 99	-	-	-	-
PS- <i>sc</i> -PLA-PtBMA (dried dispersion)	0.29	197	14.2	34	-	-	55, - ^c , - ^c	-	-	203	1.4
PS- <i>sc</i> -PLA-PS (dried dispersion)	0.39	196	17.7	31	-	-	48, - ^c	-	-	-	-

a) Peak melting (T_{m}), crystallization (T_{c}), recrystallization (T_{recryst}) temperatures and enthalpies of fusion (ΔH). The numbers in the subscript denote the respective heating traces. The degree of crystallization α was determined with equation (1). Glass transition temperatures (T_{g}) were determined from the 2nd heating traces. DSC measurements were conducted at 10 K·min⁻¹ under N₂

b) Several peaks in melting signal

c) T_{g} not detectable

The degree of crystallinity α was determined with the following equation:

$$\alpha = \frac{\Delta H_{\text{m}}}{f_{\text{PLA}} \cdot \Delta H_{\text{m}}^0} \cdot 100\% \quad (1)$$

where ΔH_{m} is the measured enthalpy of fusion, ΔH_{m}^0 is the theoretical enthalpy of fusion of a 100% crystalline PLLA (93 J g⁻¹)^[1] and PLA SC (146 J g⁻¹)^[2] and f_{PLA} is the weight fraction of PLA.

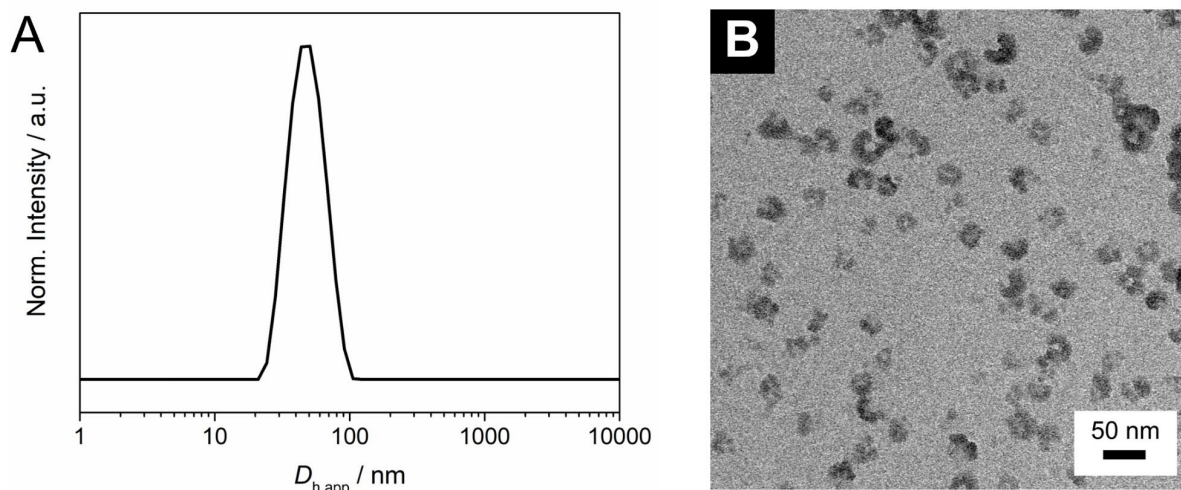


Figure S3.8 A) Hydrodynamic diameter distribution from DLS for SC micelles prepared from PS-*b*-P*LLA*/P*tBMA-b*-P*DLA* employing an intermediate dilution ($c = 0.2 \text{ g L}^{-1}$, CH/DCM = 50/1 (v/v)) and B) TEM micrographs of the formed SC micelles; PS was selectively stained with RuO₄ vapor and appears dark.

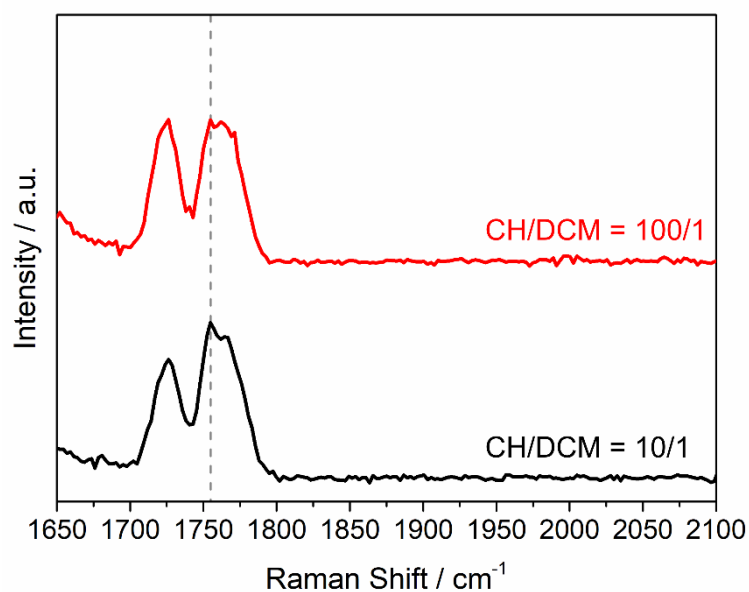


Figure S3.9 Comparison of Raman spectra (zoom-in of the carbonyl stretching vibration regime) of dried PS-*sc*-PLA-P*tBMA* SC micelles prepared at different dilutions, $c = 0.9 \text{ g L}^{-1}$ in CH/DCM = 10/1 (v/v) and $c = 0.1 \text{ g L}^{-1}$ in CH/DCM = 100/1 (v/v), respectively (dashed line indicates location of SC specific band).

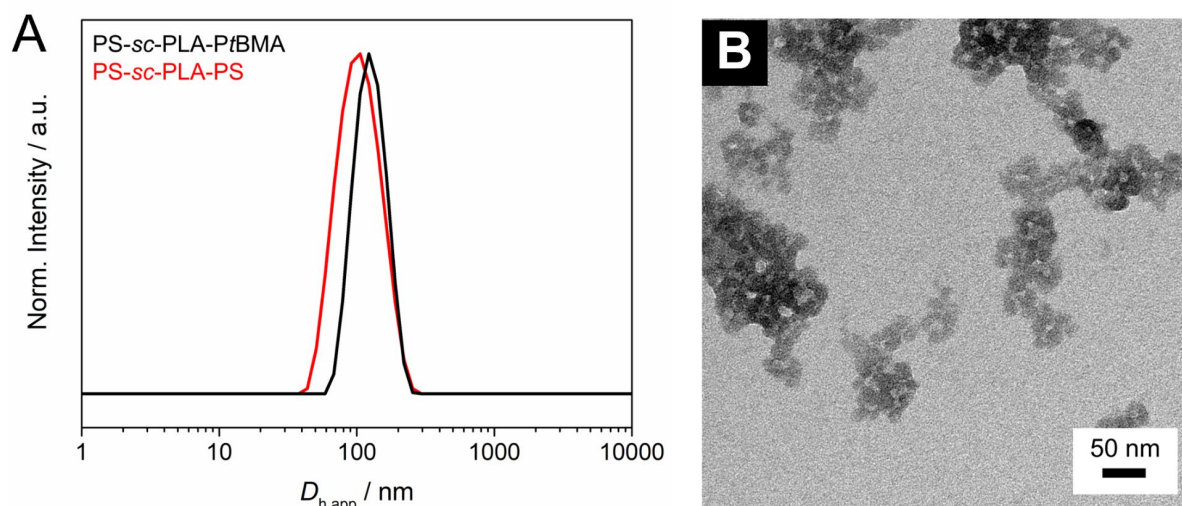


Figure S3.10 A) DLS measurements of stereocomplex micelles after dialysis against pure CH ($c = 0.9 \text{ g L}^{-1}$) and B) TEM micrograph of the PS-*sc*-PLA-PtBMA micelles after dialysis; PS was selectively stained with RuO₄ vapor and appears dark.

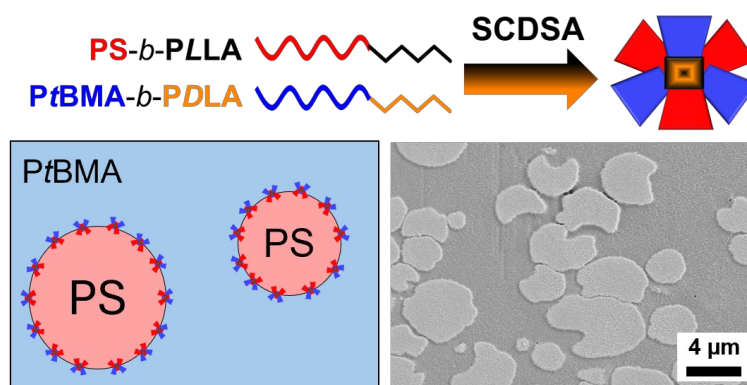
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4 Patchy Stereocomplex Micelles as Efficient Compatibilizers for Polymer Blends

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Abstract

Surface-compartmentalized polymer micelles (Janus and patchy micelles) have gained increasing attention as their unique properties open the way for various applications. While Janus micelles have been extensively studied, *e.g.* as compatibilizers in polymer blends, there are hardly any reports on the use of patchy micelles. In this study, we show that spherical micelles with a polylactide stereocomplex (SC) core and a patch-like microphase separated polystyrene/poly(*tert*-butyl methacrylate) (PS/*Pt*BMA) corona are efficient compatibilizers for highly immiscible PS/*Pt*BMA blends. The patchy SC micelles, prepared by stereocomplex-driven self-assembly (SCDSA) of enantiomeric diblock copolymers, improved the homogeneity of the blends and led to a significant reduction of the PS droplet size. We further employed SCDSA to selectively incorporate a fluorescent dye inside the SC micelle core without changing the shape or chemistry of the patchy corona. This allows the use of confocal scanning fluorescence microscopy to localize the patchy SC micelles, being predominantly assembled at the PS/*Pt*BMA blend interface. Interestingly, the reduction in PS droplet size was comparable for blends compatibilized with patchy SC micelles and Janus micelles, but only for patchy SC micelles a monomodal droplet size distribution could be achieved. The outstanding interfacial activity of the patchy SC micelles can be attributed to their adaptive corona structure, resulting in a selective swelling/collapse of the respective miscible/immiscible corona patches at the blend interface.

4.1 Introduction

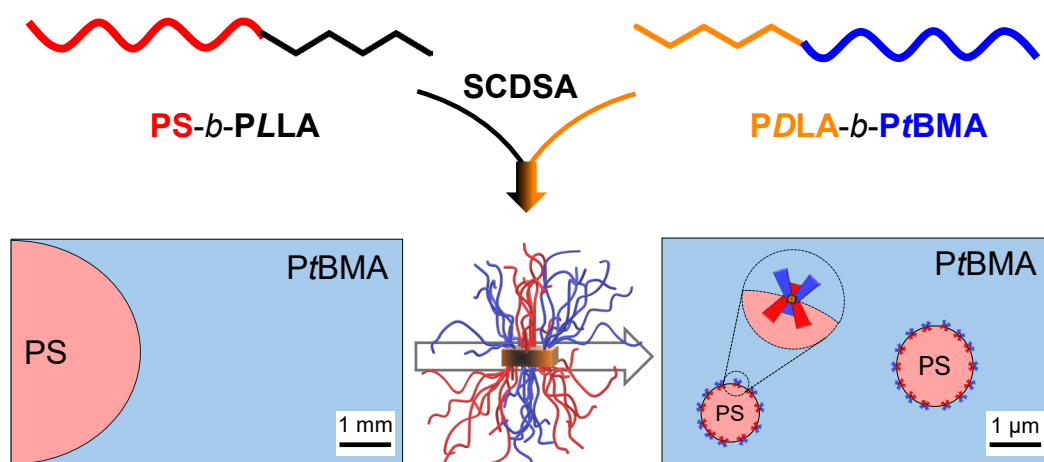
The unique corona structure of surface-compartmentalized polymer micelles (or particles) opens a wide variety of potential applications and, hence, has attracted significant attention in recent years.^{1–10} In general, surface-compartmentalized particles can be divided in Janus or patch-like (patchy) particles. Janus particles and micelles show a stringent biphasic geometry (two separate faces) of distinct chemistry and/or polarity,^{11–17} and have been utilized for various applications, *e.g.* as efficient particulate surfactants for emulsion stabilization,^{18–20} as biosensors and optical nanoprobe,^{21,22} in interfacial catalysis,^{23,24} and for superhydrophobic and anti-ice coatings.^{25,26} Moreover, attributable to their outstanding interfacial activity, Janus micelles have been intensively studied as compatibilizers in polymer blends, even under technologically relevant conditions.^{27–31}

On the other hand, patchy micelles feature a patch-like microphase-separated corona consisting of several compartments with different chemistry and/or polarity.^{1,2,5,32,33} In comparison to Janus micelles, patchy micelles have been considerably less studied with respect to applications and with a strong focus on hierarchical self-assembly.^{34–40} The patchy corona can be harnessed as template for the regioselective incorporation of nanoparticles opening applications in heterogeneous catalysis,^{41–44} or for the construction of hierarchical superstructures when combined with supramolecular self-assembly.^{45,46} Notably, worm-like patchy micelles show a comparable interfacial activity with respect to that of cylindrical Janus micelles.⁴⁷ This is attributed to the ability of the patchy corona to adjust to the interface by selective swelling/collapse of the respective soluble/insoluble surface patches. Despite, there are only a few reports on utilizing patchy micelles or hybrids in the stabilization of emulsions or as compatibilizer in polymer blends.^{48,49} A highly efficient method for the preparation of defined one-dimensional (cylindrical, or worm-like) patchy micelles is crystallization-driven self-assembly (CDSA) or living CDSA,^{50–52} which allows control over length, length distribution, and corona chemistries. This involves commonly the use of ABC triblock terpolymers, featuring amorphous incompatible end blocks and a crystallizable middle block based on polyethylene or polyferrocenyldimethylsilane (PFS).^{32,53–55} Besides, tailoring the self-assembly kinetics or employing synergistic self-seeding gives access to patchy cylindrical micelles employing mixtures of PFS based diblock copolymers.^{56–59} By the latter approaches the use of triblock terpolymers, being more difficult to synthesize, can be circumvented.

We have previously introduced stereocomplex-driven self-assembly (SCDSA) of diblock copolymers bearing enantiomeric poly(*L*-lactide) (PLLA) and poly(*D*-lactide) (PDLA) core-

forming blocks and highly incompatible polystyrene (PS) and poly(*tert*-butyl methacrylate) (PtBMA) corona-forming blocks as alternative and synthetically less demanding route for the preparation of patchy spherical micelles. These patchy stereocomplex (SC) micelles show a high interfacial activity and were applied as particulate surfactants in the stabilization of emulsions.⁴⁹ SCDSA is a versatile method for the preparation of SC micelles with varying shapes and property profiles (*e.g.* enhanced hydrolytic stability), however, mostly SC micelles with a homogeneous corona have been reported so far.^{60–62} Interestingly, SCDSA can give rise to unexpected morphological transitions as reported for mixtures of cylindrical micelles with enantiomeric PLLA and PDLA cores, whereby the solubility of the employed diblock copolymers was found to play a vital role.^{63,64} SCDSA of block or graft copolymers with chemically different coil (amorphous) blocks has only scarcely been investigated and was employed for example for the preparation of non-covalent block copolymers or micelles with a mixed, thermo-responsive corona, respectively.^{65–68}

Herein, we report on the application of patchy spherical SC micelles as efficient compatibilizers in immiscible PS/PtBMA polymer blends (Scheme 4.1). The improvement and up-scaling of the preparation method for the patchy SC micelle dispersions as well as the influence of corona chemistry (patchy *vs.* homogeneous corona) of the employed SC micelles and the compatibilizer content on the blend morphology will be addressed. Moreover, fluorescence labelling is introduced as an elegant method to localize the patchy SC micelles at the PS/PtBMA blend interfaces. Finally, the compatibilization efficiency of the patchy SC micelles is compared to that of Janus micelles.



Scheme 4.1 Schematic illustration of the preparation of patchy stereocomplex (SC) micelles *via* SCDSA of PS-*b*-PLLA and PDLA-*b*-PtBMA diblock copolymers and their application as compatibilizers in immiscible PS/PtBMA blends.

4.2 Experimental

4.2.1 Materials

All chemicals were used as received unless otherwise noted. Ethylene oxide (Linde, 3.0) was stirred over calcium hydride (CaH_2) at 0 °C for 3 h before being transferred into a storage ampoule. Prior to use ethylene oxide was additionally purified over *n*-butyllithium (*n*-BuLi) at 0 °C. Styrene (>99%, Sigma-Aldrich) was stirred over di-*n*-butylmagnesium (Bu_2Mg) under nitrogen and condensed into a storage ampoule. Dichloromethane (DCM, $\geq 99.8\%$ stabilized with amylene, analytical reagent grade, Thermo Scientific) used for lactide polymerization was dried by distillation over CaH_2 . Tetrahydrofuran (THF, 99.9%, Sigma-Aldrich) was dried by successive distillation over CaH_2 and potassium and stored under nitrogen until use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, >98%, TCI) was dried by distillation over CaH_2 . d- and l-lactide ($\geq 99.8\%$, PURASORB® d and l, Corbion, Amsterdam, The Netherlands) were recrystallized from toluene and stored under nitrogen or argon until use. *tert*-Butyl methacrylate (*t*BMA, 98%, TCI) was passed through a column with basic aluminum oxide for ATRP or stirred over trioctylaluminum under nitrogen and condensed into a storage ampoule for anionic polymerization, respectively. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich) was distilled prior to use. *n*-Pentane (technical) and isopropanol (technical) were purified by distillation. Copper(i) bromide (Cu(i)Br , 98%, Alfa Aesar) and copper(i) chloride (Cu(i)Cl , 99%, Sigma-Aldrich) were stirred in glacial acetic acid for 6 h, washed with glacial acetic acid and ethanol and dried *in vacuo* for 24 h. 1,1-Diphenylethylene (DPE, >98%, TCI) was stirred with *sec*-butyllithium (*sec*-BuLi) under argon atmosphere, distilled under vacuum and stored under argon until use. Pyridine (>99%, Carl Roth) was dried successively over KOH and CaH_2 and distilled prior to use. Trioctylaluminum (25 wt% in hexane, Sigma-Aldrich), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, HPLC grade, Sigma-Aldrich), silver trifluoroacetate (AgTFA , >99.9%, Sigma-Aldrich), sodium trifluoroacetate (NaTFA , $\geq 99.5\%$, Fluka), sulforhodamine B acid chloride (pure, Thermo Scientific), Bu_2Mg (1.0 M in heptane, Sigma-Aldrich), *sec*-BuLi (1.3 M in cyclohexane/hexane, Thermo Scientific), *n*-BuLi (1.6 M in hexanes, Thermo Scientific), α -bromoisobutyryl bromide (98%, Sigma-Aldrich), benzoic acid (p.a., AlppiChem), 4-dimethylaminopyridine (DMAP, 99%, Sigma-Aldrich), CaH_2 (Merck), 2-hydroxyethyl 2-bromoisobutyrate (HEBiB, 95%, Sigma-Aldrich), deuterated chloroform (CDCl_3 , 99.8%, Deutero), deuterated cyclohexane ($\text{CH-}d_{12}$, 99.5%, Deutero), deuterated dichloromethane ($\text{DCM-}d_2$, 99.6%, Deutero), trimethylsilyl chloride (>98%, Sigma-Aldrich), ruthenium(iii) chloride hydrate (ReagentPlus®, Sigma-Aldrich), sodium hypochlorite solution (NaOCl , 10–

15 wt% in water, Sigma-Aldrich), chloroform (CHCl_3 , $\geq 99.8\%$, analytical reagent grade, Thermo Scientific), cyclohexane (CH_2 , $\geq 99.8\%$, analytical reagent grade, Thermo Scientific), toluene ($\geq 99.5\%$, AnalaR NORMAPUR ACS, Reag. Ph. Eur., VWR chemicals) and methanol (MeOH , $\geq 99.9\%$, analytical reagent grade, Thermo Scientific).

4.2.2 Polymer syntheses

Polystyrene (PS) homopolymer PS was prepared by living anionic polymerization of styrene in THF at -70°C employing *sec*-BuLi as initiator. The reaction was terminated after 5 min by the addition of degassed MeOH and the product was precipitated from isopropanol. The product was filtered and dried *in vacuo* (2×10^{-2} mbar) at 40°C .

Poly(*tert*-butyl methacrylate) (PtBMA) homopolymer PtBMA was synthesized by living anionic polymerization of *t*BMA in THF. 1,1-Diphenyl-3-methylpentyllithium, prepared *in situ* by the reaction of *sec*-BuLi with DPE (5 eq. with respect to *sec*-BuLi) at -70°C , was employed as initiator. *t*BMA was added to the initiator at -70°C and the reaction was slowly heated to -40°C . After 2 h the reaction was stopped by the addition of degassed MeOH and the product was isolated by precipitation from H_2O . The product was filtered and dried *in vacuo* (2×10^{-2} mbar) at 40°C .

Hydroxy terminated polystyrene macroinitiator (PS-OH) PS-OH was prepared by living anionic polymerization of styrene in THF followed by end-capping with ethylene oxide. Polymerization of styrene was conducted at -70°C using *sec*-BuLi as initiator. After complete conversion a 5-fold molar excess of ethylene oxide was added for end-capping followed by stirring for 30 min. The polymer was terminated with a mixture of acetic acid/methanol (1/5 (v/v)) and isolated by precipitation from methanol. The product was filtered and dried *in vacuo* (2×10^{-2} mbar) at 40°C .

D-Lactide based ATRP macroinitiator (PDLA-Br) PDLA-Br was prepared according to the literature under an inert argon atmosphere.⁶⁹ To *D*-lactide in DCM ($c \approx 150 \text{ g L}^{-1}$) a solution of HEBiB (380 μL , 0.41 mmol, $c = 1.07 \text{ mol L}^{-1}$ in DCM) was added at 25°C . DBU (1 eq. with respect to HEBiB) was added and the reaction mixture was stirred for 5 min at 25°C . Subsequently, the reaction was stopped by the addition of benzoic acid (equimolar amount to DBU) and the mixture was stirred for 5 min. The product was precipitated from *n*-pentane/MeOH (10/1 (v/v)), filtered and dried *in vacuo* (1×10^{-5} mbar). For additional purification, the product was redissolved in THF, precipitated from MeOH, filtered and dried *in vacuo* (1×10^{-5} mbar).

PS-*b*-PLLA and PS-*b*-PDLA PS-*b*-PLLA and PS-*b*-PDLA diblock copolymers were prepared according to the literature.⁶⁹ To PS-OH in DCM ($c \approx 150 \text{ g L}^{-1}$) the respective *L*- or *D*-lactide was added and stirred at 25 °C for 10 min under argon. DBU (3 eq. with respect to OH end groups) was added and the reaction mixture was stirred for 5 min at 25 °C. Subsequently, benzoic acid (equimolar amount to DBU) was added to stop the reaction and the mixture was stirred for 5 min. The products were precipitated from *n*-pentane/MeOH (10/1 (v/v)), filtered and dried *in vacuo* (1×10^{-5} mbar).

PDLA-*b*-PtBMA The PDLA-*b*-PtBMA diblock copolymer was prepared according to the literature.^{70,71} PDLA₁₀₀-Br (1.0 g) and *t*BMA (8.0 mL) were mixed together in anisole (22 mL), degassed with argon for 60 min and the solution was heated to 65 °C. In a second flask PMDETA (53.2 μL) in anisole (2 mL) was degassed with argon for 20 min before Cu(i)Br (36.5 mg) was added under stirring. After 20 min the catalysator complex was added to the reaction mixture under stirring. The employed molar ratio of macroinitiator/Cu(i)Br/PMDETA was 1/2/2. After 210 min the reaction was quenched by placing the mixture into liquid nitrogen. The product was precipitated from *n*-pentane and dissolved in THF. The solution was passed through a neutral aluminum oxide column to remove the catalyst. The product was precipitated from H₂O/MeOH (2 : 1 (v/v)), filtered and dried *in vacuo* (1×10^{-5} mbar).

PS-*b*-PLLA based ATRP macroinitiator PS-*b*-PLLA -Br was prepared according to the literature.⁷² To PS-*b*-PLLA (2 g, 1 eq.) in DCM (10 mL) pyridine (68 μL, 8 eq.) and DMAP (1 mg, 0.1 eq.) were added and the reaction mixture was cooled to 0 °C while stirring. After 35 min α-bromoisobutyryl bromide (19 μL, 2 eq.) was added and stirred for 3 h at 25 °C. The product was precipitated from MeOH and centrifuged. The product was dissolved in CHCl₃, precipitated from MeOH, filtered and dried *in vacuo* (2×10^{-2} mbar) at 40 °C.

PS-*b*-PLLA-*b*-PtBMA PS-*b*-PLLA-*b*-PtBMA was prepared according to the literature.^{70,71} PS-*b*-PLLA-Br (400 mg, 1 eq.) and *t*BMA (1.6 mL, 605 eq.) were mixed together in toluene (4 mL) and degassed with argon for 60 min. Cu(i)Cl (1.9 mg, 1.2 eq.) was added and the solution was heated to 60 °C. Subsequently, PMDETA (195 μL, $c = 0.1 \text{ mol L}^{-1}$ in toluene, 1.2 eq.) was added and the polymerization was allowed to proceed for 120 min before being quenched by placing the mixture into liquid nitrogen. The product was precipitated from *n*-pentane and dissolved in THF. The solution was passed through a neutral alumina column to remove the catalyst. The product was precipitated from H₂O/MeOH (2 : 1 (v/v)), filtered and dried *in vacuo* (2×10^{-2} mbar) at 40 °C.

Fluorescently labelled PDLA homopolymer (PDLA₆₂-RB) PDLA₆₂-RB was prepared according to the literature.⁷² To PdLA₆₂-Br (100 mg, 1 eq.) in DCM (2 mL) pyridine (30 μ L, 8.5 eq.) was added and the reaction mixture was cooled to 0 °C while stirring. After 20 min sulforhodamine B acid chloride (25.1 mg, 2 eq.) was added and stirred for 24 h in the dark. The product was precipitated from MeOH and centrifuged. Afterwards, the product was dissolved in DCM, precipitated from MeOH and centrifuged three more times until the residual solvent was colorless. After drying *in vacuo* (2×10^{-2} mbar) at 40 °C the product was obtained as pink powder.

SCDSA of diblock copolymer mixtures

Solutions of PS-*b*-PLLA and P*t*BMA-*b*-PDLA in DCM ($c = 50 \text{ g L}^{-1}$) were mixed together, employing a 1 : 1 weight ratio with respect to the enantiomeric PLA blocks. In a 50 mL round bottom flask, equipped with a magnetic stirring bar, the obtained mixture (2 mL) was added dropwise to CH (18 mL) over 2 min while stirring (approximately 350 rpm), resulting in a micelle dispersion with a concentration of $c = 5.0 \text{ g L}^{-1}$ and a final solvent ratio of CH/DCM = 9/1 (v/v). Subsequently, the dispersion was stirred for an additional 1 min and then aged at room temperature without stirring for at least one day. The dispersion was opened to air to evaporate the DCM over three days. To the remaining dispersion CH was added to restore the initial concentration before use. The same protocol was applied to the combination of PS-*b*-PLLA and PS-*b*-PDLA starting from solutions with concentrations of $c = 50 \text{ g L}^{-1}$. The dispersions of SC micelles in CH prepared by SCDSA are denoted as PS-*sc*-PLA-P*t*BMA micelles or PS-*sc*-PLA-PS micelles, respectively.

Fluorescently labelled PS-*sc*-PLA-P*t*BMA micelles Solutions of PS-*b*-PLLA, PDLA-*b*-P*t*BMA and PDLA₆₂-RB (10 wt% of total PDLA content in the mixture) in DCM ($c = 10 \text{ g L}^{-1}$) were mixed together, employing a 1 : 1 weight ratio with respect to the enantiomeric PLA blocks. The dispersion of fluorescently labelled SC micelles was prepared the same way as described above and is denoted as PS-*sc*-PLA-P*t*BMA_RB micelles.

Preparation of polymer blends

In a hydrophobized snap lid vial (by reacting with trimethylsilyl chloride) PS and P*t*BMA were dissolved in CH or a SC micelle dispersion ($c = 5 \text{ g L}^{-1}$ in CH) with an overall polymer concentration of $c = 100 \text{ g L}^{-1}$. The amount of micelles was varied from 0, 1, 3, 5, 7 to 10 wt% while the ratio of PS/P*t*BMA was kept constant at 30/70 (w/w). The samples were shaken at 45 °C (200 rpm, thermo shaker HLC MKR-13, Ditabis) for 16 h to ensure complete dissolution of the polymers. Then, the solvent was allowed to evaporate slowly over 1 week while shaking

gently (200 rpm) at 45 °C. The films were obtained by smashing the vial after freezing in liquid nitrogen, followed by drying *in vacuo* (2×10^{-2} mbar). For the blend compatibilized with 7 wt% Janus micelles, which were formed by self-assembly of the PS-*b*-PLLA-*b*-PtBMA triblock terpolymer in CH, the same procedure as described for blends with SC micelles as compatibilizers was employed.

4.2.3 Methodes

Proton nuclear magnetic resonance (^1H NMR) spectroscopy was conducted with a Bruker Ultrashield-300 spectrometer (300 MHz) at 20 °C. The chemical shift (δ) was determined relatively to the residual solvent signal of CDCl_3 (δ (^1H) = 7.26 ppm).

$2\text{D}^1\text{H}$ NMR nuclear Overhauser effect spectroscopy (NOESY). ^1H NMR spectra of the patchy SC micelle dispersion in CH-d_{12} ($c = 5 \text{ g L}^{-1}$) were recorded at 298 K on a Bruker Avance IIIHD 600 MHz spectrometer. The 2D ^1H NOESY spectrum (mixing time 250 ms) was recorded with 96 scans and 2048×128 complex data points. The spectral width was 12 kHz and the recycle delay 2 s. The patchy SC micelle dispersion was prepared as described above using deuterated solvents for SCDSA.

Size exclusion chromatography (SEC) was carried out on SEC 1200/1260 Infinity systems (Agilent Technologies, Santa Clara, CA, USA) equipped with a SDV gel precolumn (particle size = 5 μm , PSS, Mainz, Germany). CHCl_3 -SEC was performed with a SDV linear XL gel column (particle size = 5 μm) with porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany) using CHCl_3 (HPLC grade) as eluent. The samples were measured at a flow rate of 0.5 mL min^{-1} at 23 °C, employing a refractive index (RI) detector (Agilent Technologies, Santa Clara, CA, USA). THF-SEC was performed with four SDV gel columns (particle size = 5 μm) with porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany). THF (HPLC grade) was used as eluent and the samples were measured at a flow rate of 1.0 mL min^{-1} at 40 °C. For detection a RI detector (Agilent Technologies, Santa Clara, CA, USA) or a variable wave-length detector (VWD, Agilent Technologies, Santa Clara, CA, USA) were used. All samples were dissolved and filtered through a 0.2 μm PTFE filter before analyses. A calibration with narrowly distributed PS standards (PSS calibration kit) and toluene (HPLC grade) as internal standard were used in all cases.

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 $50\times$ long working distance objective (Zeiss LD EC Epiplan-Neofluar Dic $50\times$, numerical aperture $\text{NA} = 0.55$) and a step size of $0.5 \mu\text{m pixel}^{-1}$ were used. Raman imaging with a $100\times$ objective (Zeiss EC Epiplan-Neofluar Dic $100\times$, $\text{NA} = 0.9$, 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. The spatial distribution of PS and PtBMA was determined using the True Component Analysis tool of the WITec Project SIX 6.1 software. The sizes of the PS domains were determined with the software Fiji by evaluating at least 100 PS droplets from multiple positions.⁷³ Samples of the micelle dispersions were prepared by dropping small amounts ($3 \times 10 \mu\text{L}$) of the dispersion onto a glass slide followed by drying *in vacuo* (3 h, 20 mbar). Raman spectra of the dried SC micelle dispersions were acquired with the $100\times$ objective employing a laser intensity of 20 mW and integration times of 0.5–1 s (100 accumulations).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) was carried out with a Bruker Daltonics autoflex maX (Bruker, Germany) equipped with a smartbeam-II solid state laser and operating in linear mode. The samples were prepared by the dried droplet method, employing DCTB as matrix and AgTFA in the case of PS and NaTFA in the case of PtBMA as ionization agents. All components were dissolved in THF (HPLC grade) at a concentration of $c = 10 \text{ g L}^{-1}$ and mixed together in a volumetric ratio of matrix/sample/ionization agent = 20/3/1.

Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 Phoenix instrument using aluminum crucibles (pierced lid) and nitrogen as protecting gas. The temperature range was selected from 0°C to 220°C employing a scanning rate of 10 K min^{-1} .

Dynamic light scattering (DLS) was performed using a Zetasizer Nano S (Malvern Panalytical, UK) instrument equipped with a He–Ne laser ($\lambda = 632.8 \text{ nm}$) and a detector placed at $\theta = 173^\circ$. Unless otherwise noted, the micelle dispersions were diluted to a concentration of $c = 0.5 \text{ g L}^{-1}$ and measured at 25°C in quartz glass cuvettes (10.0 mm path length), which were sealed with Teflon caps to prevent solvent evaporation. The samples measured at 45°C were equilibrated for 30 min inside the measurement chamber to assure constant temperature. The data were evaluated using the Malvern Zetasizer software (version 7.13) and the implemented distribution analysis fit option. The results are displayed as normalized intensity weighted size distributions, and the micelle sizes are reported as apparent hydrodynamic diameter ($D_{\text{h,app}}$) determined from the average of three replicate measurements.

Transmission electron microscopy (TEM) was carried out with a Zeiss/LEO EM922 Omega and a JEOL JEM-2200FS field emission TEM. All microscopes are energy filtering transmission electron microscopes (EFTEMs), operated at an acceleration voltage of 160 kV and 200 kV, respectively. Zero-loss filtered micrographs ($\Delta E \approx 0$ eV) were taken with a bottom mounted CCD camera (Ultrascan 1000, Gatan) in case of the Zeiss/LEO EM922 Omega and a bottom mounted CMOS camera system (OneView, Gatan) for the JEOL JEM-2200FS. The images were processed with a digital image processing software (Digital Micrograph DM 2.3 and 3.11, Gatan). For TEM analyses of the micelle dispersions, samples were diluted to a concentration of $c = 0.1 \text{ g L}^{-1}$ and stirred for 30 min at room temperature. Subsequently, 10 μL of the respective dispersion was applied to a carbon-coated copper grid and residual solvent was removed directly by blotting with a filter paper followed by drying of the coated copper grid *in vacuo* (24 h, 1×10^{-5} mbar). For TEM investigation of the polymer blend, the sample was cut into ultrathin sections (cut thickness: 50–60 nm) under cryogenic conditions ($T = -140^\circ\text{C}$) using a Leica UC7 ultramicrotome together with a EM FC7 cryochamber (Leica, Wetzlar, Germany). For RuO_4 staining the samples were treated for 7 min with RuO_4 vapor, which was formed *in situ* from RuCl_3 hydrate and an aqueous NaOCl solution. After staining, the samples were stored for at least 1 h in a fume hood to ensure that any not reacted RuO_4 was completely removed.

Scanning electron microscopy (SEM) measurements were done with a Zeiss Ultra Plus at an acceleration voltage of 1–3 kV and with SE2 and backscattered electron (BSE) detectors. Prior to analyses the samples were stained for 15 min with RuO_4 vapor, following the same procedure as described for TEM. The manually fractured surfaces were fixed on an aluminum stub *via* electrically conductive tape and sputtered with a thin layer of platinum of around 2 nm with a Cressington sputter coater 208HR. The sizes of the PS domains were determined with the software Fiji.⁷³ To this end, the area of at least 200 PS droplets from multiple positions were measured using the free hand selection tool and converted to the respective equivalent diameter assuming a perfect spherical cross-section.

A commercial optical microscope MicroTime 200 (PicoQuant) was used for the *fluorescence experiments*. The setup contained a laser diode operated in pulsed mode with a repetition rate of 20 MHz and an excitation wavelength of $\lambda = 560 \text{ nm}$ (LDH-d-TA-560B, PicoQuant). The excitation intensities were adjusted to approximately 1 μW . Radiation from the laser was directed through a single-mode optical fiber into the main optical unit, reflected by a dichroic mirror (ZT488/561rpc, AHF/Croma) into an inverted confocal optical microscope, and focused onto the sample using a super-apochromatic water immersion objective (UPLSAPO60XW, NA

= 1.2, Olympus). Fluorescence images were acquired by scanning the focal spot over $250\ \mu\text{m} \times 250\ \mu\text{m}$ on the sample using a galvo scanner (FLIMbee unit, PicoQuant). The signal from the sample was transmitted to the dichroic mirror and passed through a long pass filter (561 LP Edge Basic, Semrock). The signal was detected by a single-photon counting avalanche diode (SPCM-AQRH-14-TR, Excelitas) and a time-correlated single-photon counting unit (TCSPC TimeHarp 260 PICO Dual, PicoQuant, temporal resolution of 250 ps) was used to collect fluorescence data. The fluorescence images were evaluated using the commercial software SymPhoTime 64 (Picoquant). The PS/*Pt*BMA (30/70 (w/w)) blend sample (3 wt% compatibilizer) was prepared as described above using a PS-*sc*-PLA-*Pt*BMA_RB micelle dispersion.

4.3 Results and Discussion

4.3.1 Up-scaling of patchy micelle preparation via SCDSA

Well-defined and long-term stable patchy micelles with a shamrock-like microphase-separated PS/*Pt*BMA corona were prepared by SCDSA of diblock copolymers with enantiomeric PLLA and PDLA blocks and highly incompatible corona-forming PS and *Pt*BMA blocks (Scheme 4.1). For the use as blend compatibilizers the preparation of patchy SC micelles had to be scaled up, as in our previous work the maximum concentration achieved was only $c = 1\ \text{g L}^{-1}$ in cyclohexane (CH), being impractical for the preparation of blends by solvent casting.⁴⁹ The employed PS-*b*-PLLA ($S_{169}LLA_{106}$) and PS-*b*-PDLA ($S_{156}DLA_{106}$) diblock copolymers (subscripts denote number-average degrees of polymerization) were synthesized by organo-catalyzed ring-opening polymerization (ROP) of the respective enantiomeric lactide with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) starting from PS-OH macroinitiators, which were prepared by living anionic polymerization of styrene followed by end-capping with ethylene oxide (Scheme S4.1A and B†). For the synthesis of PDLA-*b*-*Pt*BMA ($DLA_{100}tBMA_{132}$) a combination of ROP of *D*-lactide and atom transfer radical polymerization (ATRP) of *t*BMA was employed, utilizing 2-hydroxyethyl 2-bromoisobutyrate as bifunctional initiator (Scheme S4.1C†). The success of the diblock copolymer syntheses was followed by a combination of proton nuclear magnetic resonance (¹H NMR) spectroscopy (Fig. S4.1†) and size exclusion chromatography (SEC), whereby monomodal distributions and low dispersities ($D < 1.2$) were obtained in all cases (Fig. 4.1). The syntheses are described in detail in the Experimental section and additional characterization is provided in the ESI (Fig. S4.2 and Table S4.1†).

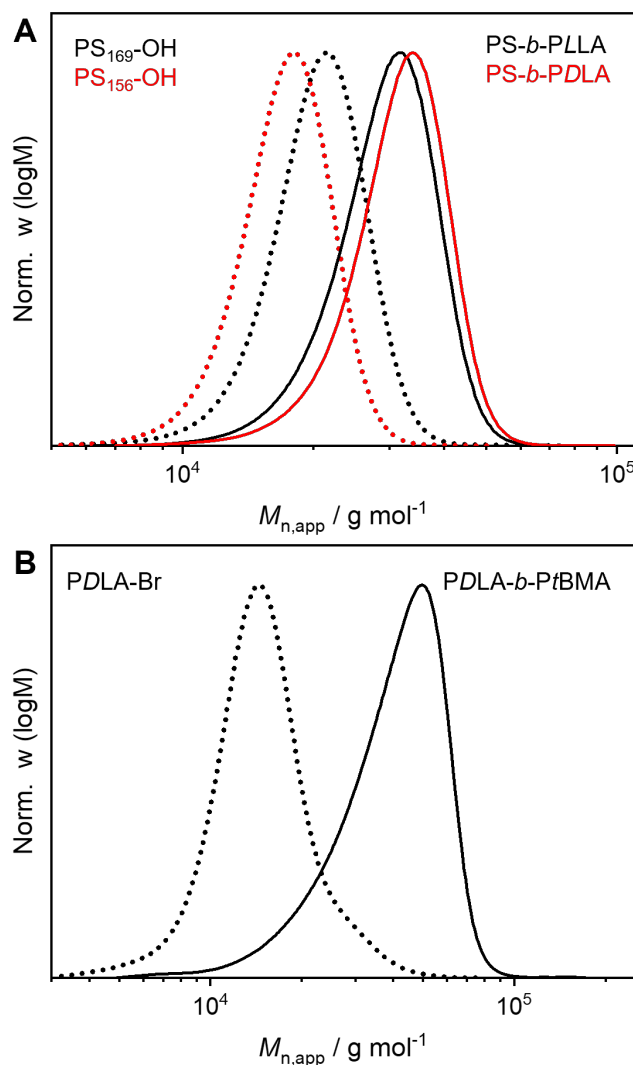


Figure 4.1 Apparent molecular weight distributions of (A) PS-*b*-PLLA (black, solid line) with PS₁₆₉-OH (black, dotted line) precursor, PS-*b*-PDLA (red, solid line) with PS₁₅₆-OH (red, dotted line) precursor and (B) PDLA-*b*-PtBMA (solid line) with PDLA-Br (dotted line) precursor (CHCl₃-SEC, PS calibration).

For SCDSA a mixture of the enantiomeric diblock copolymers (PS-*b*-PLLA and PDLA-*b*-PtBMA, 1/1 (w/w) with respect to the enantiomeric PLLA/PDLA blocks) in DCM was added drop-wise to an excess of CH, a selective solvent for the corona forming PS and PtBMA blocks. This resulted in a dispersion of spherical PS-*sc*-PLA-PtBMA micelles with an insoluble PLLA / PDLA SC core and a soluble, patchy PS/PtBMA corona. As shown before, the corona structure of the PS-*sc*-PLA-PtBMA micelles is influenced by the final CH/DCM ratio in the dispersion and, hence, the extend of dilution upon micelle formation.⁴⁹ SC micelles with a well-defined patchy corona were obtained at a volume ratio of CH/DCM = 9/1 and a final concentration of $c = 1 \text{ g L}^{-1}$, whereby at higher dilution a mixture of Janus and patchy micelles was obtained. Accordingly, the ratio was kept at CH/DCM = 9/1 (v/v) in this study and the desired higher concentration of the SC micelle dispersion was achieved by increasing the concentration of the

initial diblock copolymer mixture in DCM from $c = 10 \text{ g L}^{-1}$ to 50 g L^{-1} ($V = 2 \text{ mL}$). After aging for one day under ambient conditions the remaining DCM was allowed to slowly evaporate over 3 days. Since DCM is a good solvent for all blocks its removal is essential for complete SC formation and also enhances corona segregation. After refilling with CH to compensate the simultaneous loss of CH during DCM evaporation 20 mL of the final PS-*sc*-PLA-*Pt*BMA micelle dispersion with a concentration of $c = 5 \text{ g L}^{-1}$ were obtained (100 mg SC micelles per batch). Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were used to prove that the increase in concentration does not compromise the formation of well-defined, spherical patchy SC micelles. DLS shows a monomodal size distribution of the SC micelles with an apparent hydrodynamic diameter of $D_{h,app} = 103 \pm 40 \text{ nm}$, and the dispersion was stable even for 8 months with no signs of agglomeration as would be indicated by a shift or substantial broadening of the size distribution (Fig. 4.2A, respective autocorrelation functions are shown in Fig. S4.3†). The size of the SC micelles is comparable to the size obtained in our previous study employing a lower concentration of $c = 1 \text{ g L}^{-1}$ ($D_h = 104 \pm 30 \text{ nm}$) and enantiomeric diblock copolymers with comparable block lengths.⁴⁹ This supports the conclusion that an increase in concentration does not significantly alter the SCDSA behaviour of the diblock copolymers. No significant shift of the size distribution to lower values was observed upon diluting the SC micelle dispersion from $c = 5 \text{ g L}^{-1}$ to $c = 0.1 \text{ g L}^{-1}$ (Fig. S4.4†), which is also consistent with the presence of single SC micelles. The dispersion was also stable after thermal annealing at $T = 45 \text{ }^{\circ}\text{C}$ for 30 min, showing only a slight increase of the hydrodynamic diameter ($D_{h,app} = 119 \pm 41 \text{ nm}$). This is important, as the blends were cast at $45 \text{ }^{\circ}\text{C}$ to ensure proper solubility of PS and *Pt*BMA during film formation. The increased micelle size can be attributed to an increased solubility and stretching of the PS chains, since CH is a theta-solvent for PS with a theta temperature of $T_{\theta} = 34 \text{ }^{\circ}\text{C}$.⁷⁵

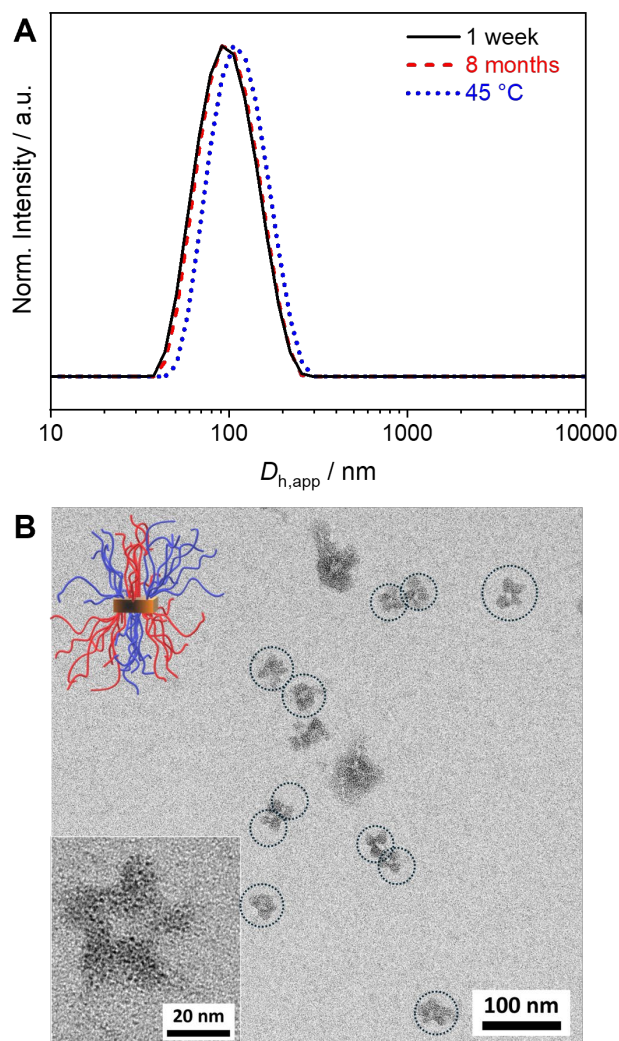


Figure 4.2 (A) Hydrodynamic diameter distributions from DLS for SC micelles prepared from PS-*b*-PLLA/ PDLA-*b*-PtBMA mixtures ($c = 5 \text{ g L}^{-1}$, CH) after aging for 1 week, 8 months, and at 45 °C. (B) TEM micrographs of the micelles with a patchy PS/PtBMA corona (PS selectively stained with RuO₄). The dimensions of the single micelles in the partially aggregated structures are indicated by dotted circles for means of clarity and the sketch illustrates the patchy structure of the corona.

The TEM micrograph shown in Fig. 4.2B confirms the formation of spherical SC micelles with a patch-like microphase separated corona. The PS domains in the corona appear dark due to selective staining with RuO₄ vapor, whereas the semicrystalline SC core as well as the PtBMA domains in the corona appear bright. The micelles tend to form small aggregates on the carbon-coated TEM grid. This is a drying artifact from sample preparation, as DLS shows a monomodal size distribution (Fig. 4.2A), and is typically observed for patchy micelles.⁷⁵

To prove the microphase separation within the corona in solution a 2D ¹H nuclear Overhauser effect spectroscopy (NOESY) experiment was conducted on the PS-*sc*-PLA-PtBMA micelles prepared in CH-*d*₁₂. No cross-peaks were observed between ¹H NMR signals of PS [$\delta = 7.5\text{--}6.5 \text{ ppm}$ (aromatic protons)] and PtBMA [$\delta = 0.9 \text{ ppm}$ (methyl group, polymer backbone)], confirming that the PS and PtBMA chains are demixed in the corona (Fig. S4.5†). In case of a

mixed corona the close proximity of PS and *Pt*BMA units would give rise to cross-polarization and the appearance of respective cross-peaks in the 2D ^1H NOESY spectrum.

Dispersions of PS-*sc*-PLA-PS micelles with a homogeneous PS corona used as reference in the blend compatibilization studies were prepared analogously to the method described above for the patchy SC micelles. In comparison, the PS-*sc*-PLA-PS micelles also show a narrow size distribution with comparable $D_{\text{h,app}} = 126 \pm 44$ nm, however, in TEM the PS corona now appears homogeneously dark (Fig. S4.6†). The observable agglomeration on the TEM grid can again be attributed to drying artifacts arising from sample preparation, as DLS shows a narrow size distribution.

To prove that self-assembly is indeed driven by SC formation between the enantiomeric PLLA/PDLA blocks Raman spectroscopy on the dried PS-*sc*-PLA-*Pt*BMA and PS-*sc*-PLA-PS micelle dispersions was conducted. A characteristic shift of the carbonyl stretching vibration from $\tilde{\nu} \approx 1770\text{--}1773$ cm^{-1} for the individual diblock copolymers to lower wavenumbers ($\tilde{\nu} \approx 1750\text{--}1752$ cm^{-1}) was observed, confirming SC formation (Fig. S4.7†).^{62,76} In addition, differential scanning calorimetry (DSC) on the freeze-dried PS-*sc*-PLA-*Pt*BMA micelle dispersion shows a melting temperature of $T_{\text{m}} = 203$ °C (Fig. S4.8†), which is typical for polylactide stereocomplexes.^{61,65,66}

4.3.2 Patchy SC micelles as compatibilizers in PS/*Pt*BMA blends

After the successful scale-up of the preparation method, the efficiency of the patchy SC micelles as compatibilizers in immiscible PS/*Pt*BMA blends was tested. This blend system was chosen not only because of the matching chemistry with the corona blocks of the patchy SC micelles, but rather because of the high incompatibility of the two polymers (Flory–Huggins interaction parameter for PS/*Pt*BMA: $\chi = 0.08\text{--}0.10$).⁷⁷ Hence, PS/*Pt*BMA blends are an ideal model system to study the performance of patchy SC micelles, as differences in interfacial activity (*e.g.* patchy *vs.* homogeneous corona) will result in distinctly altered blend morphologies. The used homopolymers were synthesized by living anionic polymerization and have molecular weights of M_{n} (PS) = 39 400 g mol^{-1} and M_{n} (*Pt*BMA) = 93 700 g mol^{-1} as determined by matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-ToF MS). Details on the syntheses procedures and molecular weight characterization can be found in the ESI (Scheme S4.2, Fig. S4.1, S4.2, S4.9 and Table S4.1†). All blends were cast from CH at $T = 45$ °C under gentle shaking to ensure proper solubility of the polymers upon film formation. At lower temperatures a demixing of the phases during the evaporation process was observed due to the comparably high theta temperature of PS in CH of $T_{\theta} = 34$ °C.⁷⁴ The respective neat

PS/*Pt*BMA (30/70 (w/w)) blend showed macrophase separation into millimeter sized PS and *Pt*BMA regions, as revealed by a combination of optical microscopy and Raman spectroscopy (Fig. 4.3), manifesting the high incompatibility of this blend system.

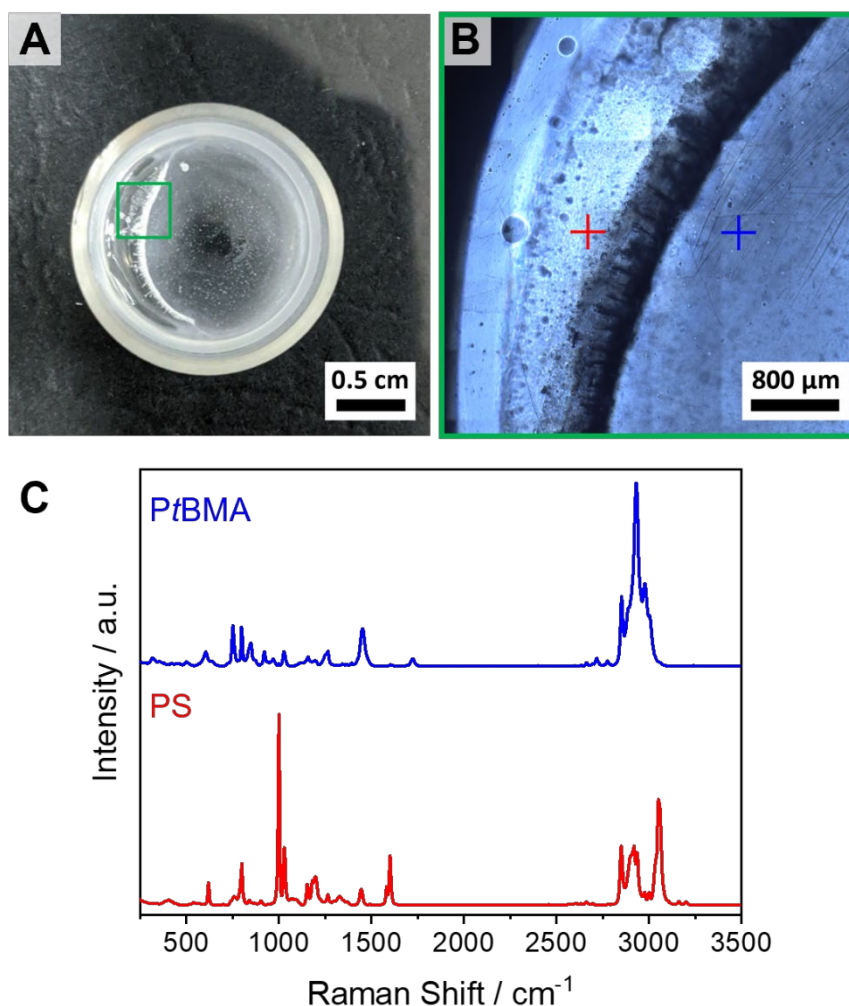


Figure 4.3 (A) Optical image of the neat PS/*Pt*BMA (30/70 (w/w)) blend. (B) Optical microscopy image taken at the area depicted in green in (A). (C) Raman spectra of the *Pt*BMA (blue) and PS (red) phases taken at the respective positions indicated in (B).

First, the influence of the corona chemistry of the SC micelles on their compatibilization efficiency was studied. Fig. 4.4 shows the component distributions extracted from Raman imaging for a PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 7 wt% patchy PS-*sc*-PLA-*Pt*BMA micelles and of the respective blend with 7 wt% PS-*sc*-PLA-PS micelles having a homogeneous PS corona. As both SC micelles have comparable hydrodynamic diameters in CH (PS-*sc*-PLA-*Pt*BMA: $D_{h,app} = 103 \pm 40$ nm; PS-*sc*-PLA-PS: $D_{h,app} = 126 \pm 44$ nm) an influence of micelle size on the blend morphology can be ruled out.

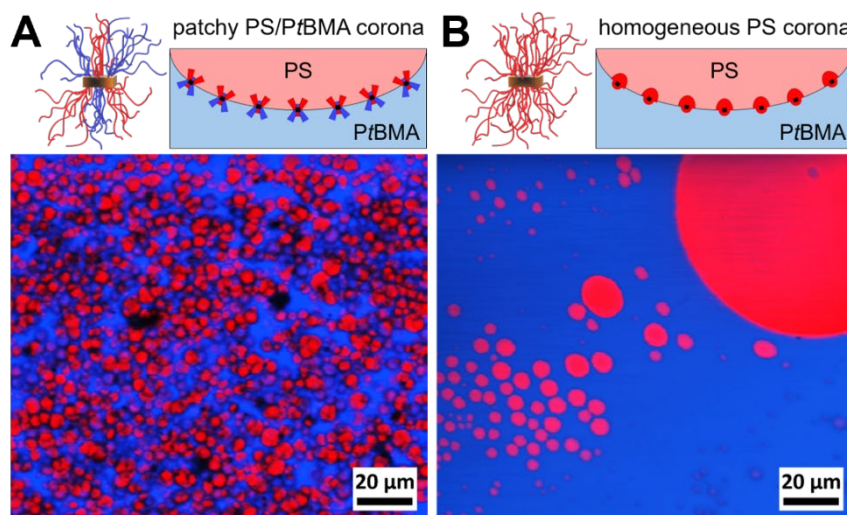


Figure 4.4 Spatial component distributions extracted from Raman imaging for PS/*PtBMA* (30/70 (w/w)) blends compatibilized with (A) 7 wt% patchy PS-*sc*-PLA-*PtBMA* micelles and (B) 7 wt% PS-*sc*-PLA-PS micelles with homogeneous PS corona. The domains colored in red represent PS droplets being dispersed in a continuous *PtBMA* matrix (depicted in blue). The sketches depict the adaption of the SC micelle corona according to their miscibility/immiscibility with the blend components.

In both blends the PS phase (depicted in red in Fig. 4.4) is dispersed as droplets in a continuous *PtBMA* matrix, as might have been expected from the asymmetric blend composition with PS being the minority phase. However, the blend compatibilized with patchy SC micelles shows a more homogeneous dispersion of the PS droplets in the *PtBMA* matrix (Fig. 4.4). Notably, statistical evaluation of the PS droplet sizes (Fig. S4.10A and E†) revealed that the size of the PS droplets is significantly smaller and their size distribution narrower ($D_{\text{PS}} = 3.9 \pm 1.3 \mu\text{m}$) as compared to the blend containing SC micelles with a homogeneous PS corona ($D_{\text{PS}} = 46.8 \pm 66.4 \mu\text{m}$). This higher compatibilization efficiency can be attributed to the ability of the patchy PS/*PtBMA* corona to adapt to the PS/*PtBMA* blend interface by expansion/collapse of the respective miscible/immiscible corona blocks, as indicated in the insets of Fig. 4.4. Hence, the amphiphilicity of the patchy corona in combination with the Pickering effect of nanoparticles is decisive for the observed high interfacial activity, leading to a decrease in interfacial tension and accordingly PS droplet size. In contrast, for the SC micelles with a homogeneous PS corona only the Pickering effect contributes to the stabilization, which makes them considerably less effective.

Next, the content of patchy PS-*sc*-PLA-*PtBMA* micelles in the blend was systematically varied from 1–10 wt% to find the optimum content with respect to blend homogeneity and reduction in PS droplet size. At a filler content of 1 wt% already no macrophase separation of the two blend components was visible anymore in the component distribution extracted from Raman imaging. However, the blend still showed a bimodal PS droplet size distribution with rather

large PS droplets having diameters up to $D_{PS} \approx 100 \mu\text{m}$ (Fig. 4.5A and Fig. S4.10B†). With increasing amount of patchy micelles as compatibilizer the PS droplet size decreased but the size distributions were still comparably broad and bimodal up to a content of 5 wt% (Fig. 4.5B and C, histograms in Fig. S4.10C and D†). Starting with 7 wt% a monomodal size distribution of the dispersed PS domains within the P*t*BMA matrix was obtained, and the average PS droplet diameter decreased substantially to $D_{PS} = 3.9 \pm 1.3 \mu\text{m}$ (Fig. 4.5D and Fig. S4.10E†). Increasing the amount of patchy micelles to 10 wt% did not result in a further decrease in PS droplet size (Fig. 4.5E and Fig. S4.10F†), indicating that 7 wt% is the optimum compatibilizer content for the investigated PS/P*t*BMA (30/70 (w/w)) blends. In the Raman images of the blends with 7 and 10 wt% patchy SC micelles acquired at smaller step sizes the homogeneous dispersion of the PS droplets is also clearly visible (Fig. S4.11†).

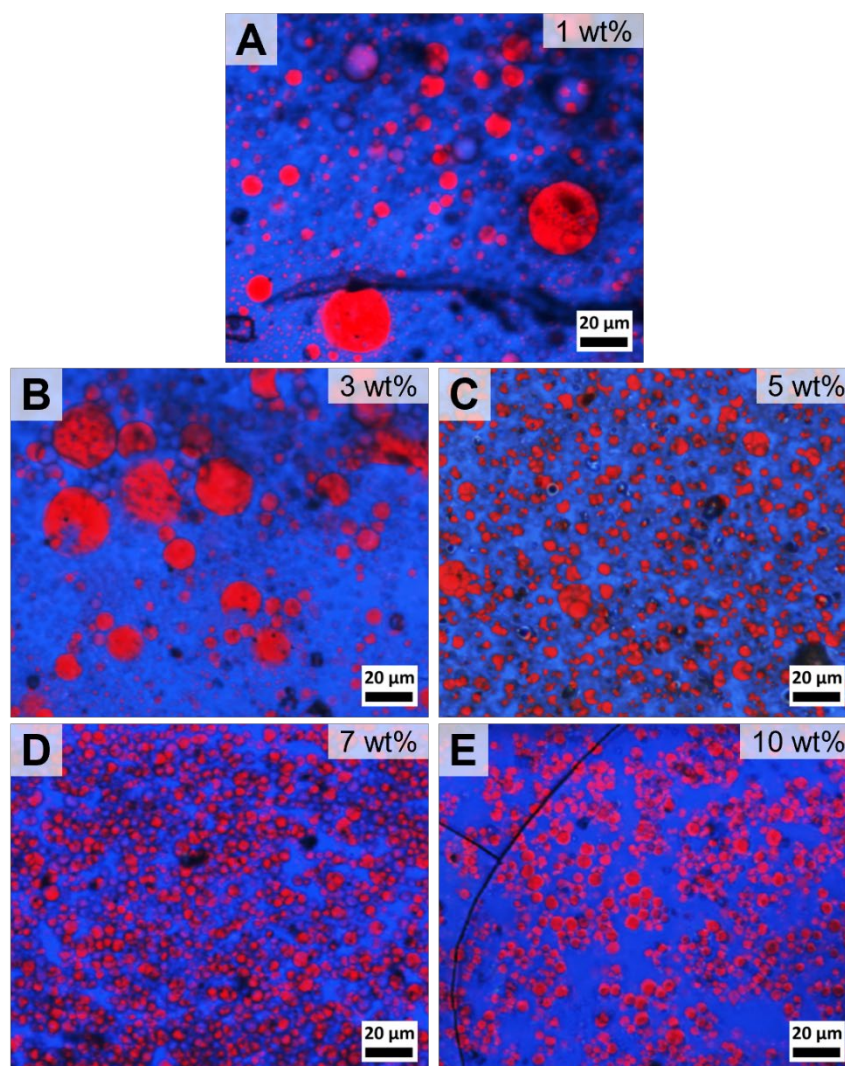


Figure 4.5 Spatial component distribution extracted from Raman imaging for PS/P*t*BMA (30/70 (w/w)) blends compatibilized with patchy PS-*sc*-PLA-P*t*BMA micelles with various concentrations: (A) 1, (B) 3, (C) 5, (D) 7 and (E) 10 wt%. The domains colored in red represent PS droplets being dispersed in a continuous P*t*BMA matrix (depicted in blue).

The blends with 3–10 wt% patchy micelles were further characterized by scanning electron microscopy (SEM) to determine the exact size and size distribution of the dispersed PS droplets in the PS/*Pt*BMA (30/70 (w/w)) blends (Fig. 4.6). Confocal Raman imaging gives direct laterally resolved chemical information, enabling a clear assignment of the blend phases without the need of contrast enhancement by staining as commonly necessary for electron microscopy. However, lateral resolution is restricted by the wavelength of the used laser (here $\lambda = 532$ nm) and the characteristics of the employed objective, resulting in a maximum resolution of *ca.* 0.3–0.4 μm for a 100 $\times$ objective (NA = 0.9). Accordingly, especially for the blends with higher contents of patchy micelles the size of the PS droplets is in the μm -range and might probably be overestimated by Raman imaging. Moreover, with SEM it is more convenient to scan larger areas, which is necessary to evaluate the size and size distribution of the larger PS droplets in blends with a bimodal size distribution. For SEM measurements the samples were stained with RuO₄ to enhance contrast between the dispersed PS droplets (appear bright) and the surrounding *Pt*BMA matrix, and for size evaluation at least 200 PS droplets from different positions were counted. SEM confirms the conclusions drawn from Raman imaging that with increasing amount of patchy micelles the PS droplet size decreases and the size distribution becomes monomodal for micelle contents ≥ 7 wt%. Especially in the overview SEM images shown in Fig. S4.12† the bimodal PS droplet size distribution for the blend with 3 and 5 wt% patchy micelles becomes more obvious. The large PS droplets partially feature droplet-like *Pt*BMA inclusions that were less obvious in the respective Raman images (Fig. 4.5B and C). For the blends with higher micelle contents (7 and 10 wt%) no inclusions within the considerably smaller PS droplets were observed. In good accordance with Raman imaging the strongest reduction in PS droplet size and the narrowest size distribution was observed for a micelle content of 7 wt%, yielding an average PS droplet diameter of $D_{\text{PS}} = 2.5 \pm 0.9 \mu\text{m}$ (Fig. 4.6C and E). Again, no further change in size and size distribution was noticeable upon further increasing the micelle content to 10 wt% ($D_{\text{PS}} = 2.6 \pm 0.9 \mu\text{m}$, Fig. 4.6D and E). Notably, the sizes determined from SEM are systematically lower as compared to that determined by Raman imaging, which is attributed to the aforementioned limited lateral resolution for Raman imaging. Hence, Raman and SEM analyses reveal the same trend, that is a reduction in size and a narrowing in size distribution with increasing content of patchy SC micelles as compatibilizer. Nevertheless, a combination of both methods is recommended to ensure a proper phase assignment, as staining procedures employed for electron microscopy studies might give rise to artifacts in case staining is not sufficiently selective for one of the blend components and might vary from sample to sample and method used.

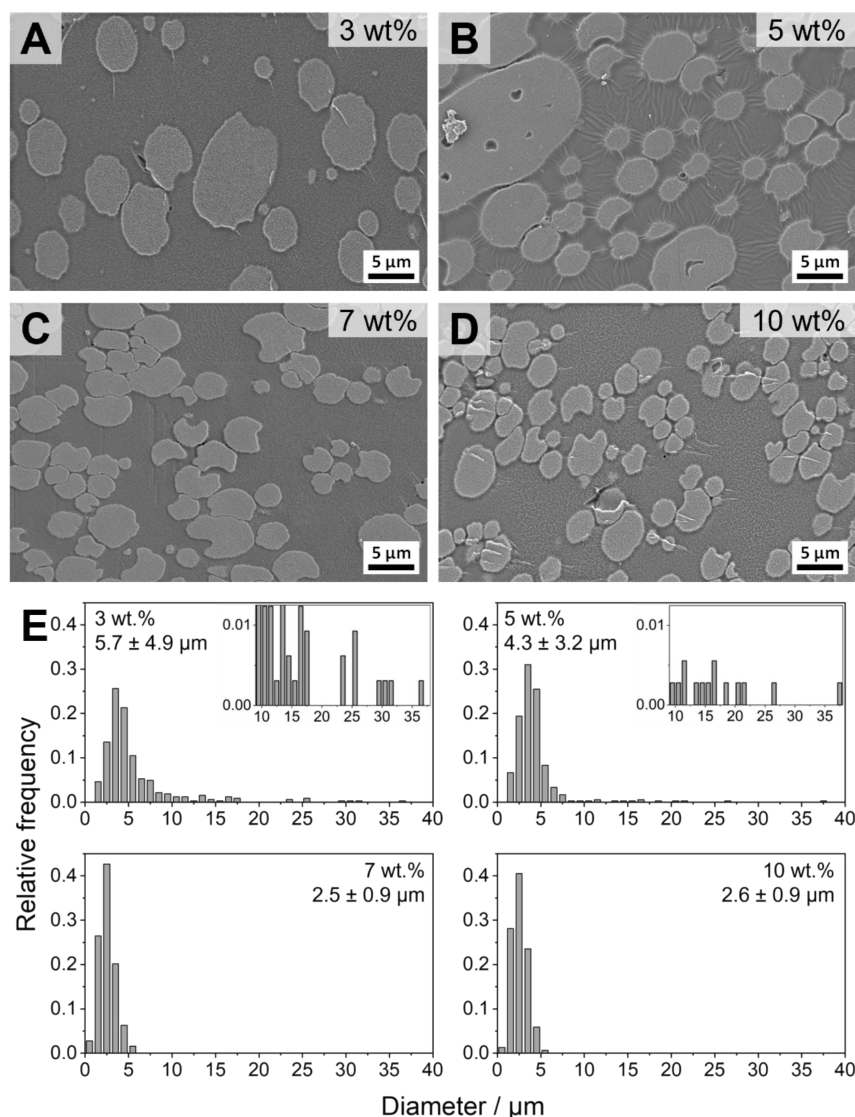


Figure 4.6 SEM images of the fracture surfaces of PS/PtBMA (30/70 (w/w)) blends compatibilized with different amounts of PS-*sc*-PLA-PtBMA micelles: (A) 3, (B) 5, (C) 7 and (D) 10 wt%. The PS domains were selectively stained with RuO₄ vapor to enhance contrast and appear bright. (E) Corresponding histograms of PS droplet diameter distributions.

4.3.3 Localizing patchy micelles at the blend interface

The excellent compatibilization efficiency of the patchy SC micelles is attributed to their high interfacial activity resulting in an accumulation at the PS/PtBMA blend interfaces and, hence, reducing the interfacial tension and accordingly the PS droplet size. In order to prove the presence of patchy SC micelles at the PS/PtBMA interface, confocal scanning fluorescence microscopy (FM) was performed employing fluorescently labelled patchy SC micelles. For fluorescence labelling the PS-*sc*-PLA-PtBMA micelles were prepared by co-assembly of the enantiomeric diblock copolymers with a small amount of a sulforhodamine B labelled PDLA₆₂ homopolymer (PDLA₆₂-RB, Fig. 4.7A). Details on synthesis and molecular characterization of PDLA₆₂-RB are provided in the Experimental section and ESI (Scheme S4.3, Fig. S4.13 and

Table S4.1†). The incorporation of the fluorescently labelled $PDLA_{62}$ -RB homopolymer does not affect the SCDSA to well-defined spherical micelles as DLS shows a monomodal size distribution for the PS-*sc*-PLA-*Pt*BMA_RB micelles with an apparent hydrodynamic diameter of $D_{h,app} = 88 \pm 30$ nm (Fig. S4.14A,† respective autocorrelation function is depicted in Fig. S4.14B†), being slightly lower compared to that of the non-labelled micelles ($D_{h,app} = 103 \pm 40$ nm, Fig. 4.2A). In addition, the overall morphology and patch-like compartmentalized PS/*Pt*BMA corona of the micelles are not altered as revealed by TEM (Fig. S4.14C†). This underpins the potential of SCDSA to selectively incorporate different guest molecules inside the SC core of the micelles, without changing the shape and chemistry of the micelle corona.

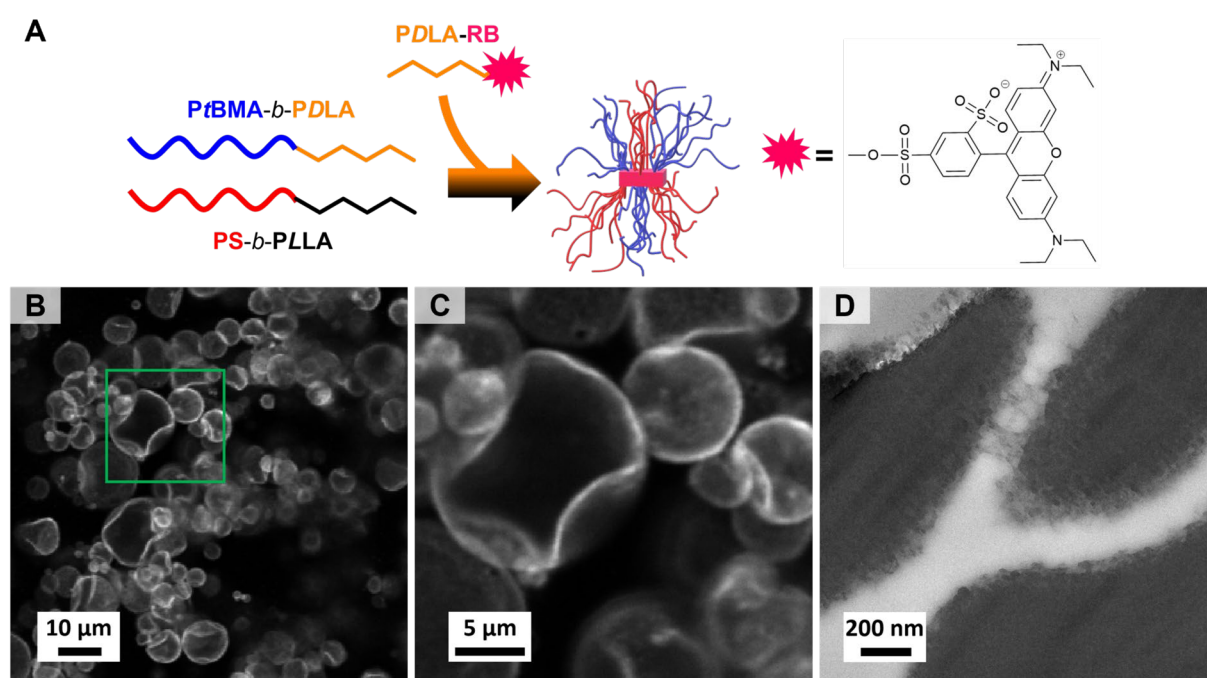


Figure 4.7 (A) Schematic illustration of the preparation of fluorescently labelled PS-*sc*-PLA-*Pt*BMA_RB micelles *via* SCDSA. (B and C) Confocal scanning FM images of a PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 3 wt% fluorescently labelled PS-*sc*-PLA-*Pt*BMA_RB micelles. (D) TEM micrograph of a PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 7 wt% patchy PS-*sc*-PLA-*Pt*BMA micelles (PS selectively stained with RuO_4).

Fig. 4.7B and C show the confocal scanning FM images of a respective PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 3 wt% of fluorescently labeled PS-*sc*-PLA-*Pt*BMA_RB micelles, prepared by solvent casting. The low compatibilizer content of 3 wt% was deliberately chosen as larger PS droplets are expected to form, which makes it easier to visualize the interface. From the confocal FM image it can be clearly deduced that the patchy SC micelles are preferentially located at the PS/*Pt*BMA interface, resulting in a bright appearing rim around the dispersed PS droplets.

In addition, TEM was used to visualize the patchy SC micelles at the PS/*Pt*BMA interface. Accordingly, ultrathin slices were cryo-cut from a PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 7 wt% patchy PS-*sc*-PLA-*Pt*BMA micelles, followed by selective staining of the PS droplets/patches with RuO₄ vapor. Hence, the PS droplets appear dark and are embedded in the bright appearing *Pt*BMA matrix, as shown in Fig. 4.7D (additional TEM micrographs are presented in Fig. S15†). The interface between the two blend phases shows a fringe-like structure with clusters of smaller, dark appearing patches. In contrast, for a neat (without compatibilizer) PS/*Pt*BMA blend sharp interfaces would be expected in order to reduce energetically unfavorable interactions between the highly incompatible blend components. Hence, the observed dark appearing clusters resemble the patchy SC micelles being assembled at the PS/*Pt*BMA interface. Nonetheless, it is stressed that the conclusion drawn from TEM was only possible in combination with the results from confocal FM. From the TEM results alone it is not possible to unambiguously attribute the fringe-like structure at the interface to the presence of patchy SC micelles.

4.3.4 Comparison with Janus-type micelles

As pointed out in the introduction, mainly Janus-type micelles have been studied so far for the compatibilization of polymer blends. Hence, the question arises whether the compatibilization efficiency of the spherical patchy SC micelles is comparable or might even be better with respect to spherical Janus micelles. To address this point, we have synthesized a PS-*b*-PLLA-*b*-*Pt*BMA triblock terpolymer that forms spherical Janus-type micelles upon self-assembly in CH. The triblock terpolymer was synthesized starting from a S₁₆₉LLA₉₆ diblock copolymer by end-functionalization with an ATRP initiator moiety (2-bromoisobutyryl group) followed by ATRP of *t*BMA in toluene (Scheme S4.4†), resulting in a narrowly distributed S₁₆₉LLA₉₆T₂₀₀ triblock terpolymer ($\bar{D} = 1.18$, Table S4.1†). The SEC traces of the PS-*b*-PLLA-Br diblock copolymer precursor and the PS-*b*-PLLA-*b*-*Pt*BMA triblock terpolymer as well as the respective ¹H NMR spectra can be found in the Supplementary Information (Fig. S4.16†).

The Janus-type PS-*b*-PILA-*b*-*Pt*BMA micelles were prepared by a simple heating and cooling protocol in CH ($c = 5 \text{ g L}^{-1}$). The dispersion was annealed for 2 h at 45 °C followed by cooling to 25 °C. DLS (Fig. 4.8A) shows that the obtained micelles are smaller ($D_{\text{h,app}} = 50 \pm 20 \text{ nm}$, respective autocorrelation functions are shown in Fig. S4.17†) with respect to the patchy PS-*sc*-PLA-*Pt*BMA micelles prepared by SCDSA ($D_{\text{h,app}} = 103 \pm 40 \text{ nm}$). From the TEM micrograph in Fig. 4.8B it becomes obvious that the morphology of the micelle corona has changed, showing predominantly a Janus-type structure with a dark appearing PS hemisphere

(selectively stained with RuO_4 vapor). The *Pt*BMA hemisphere is hardly recognizable due to insufficient contrast to the carbon layer on the TEM grid combined with partial electron beam induced degradation. The PLLA core of the micelles again appears bright. It is noted that the Janus structure of the micelles is only visible when the micelles have been deposited on the carbon-coated grid in the proper orientation. In case the PS (or *Pt*BMA) hemisphere points to the surface of the grid the Janus structure will not be visible.

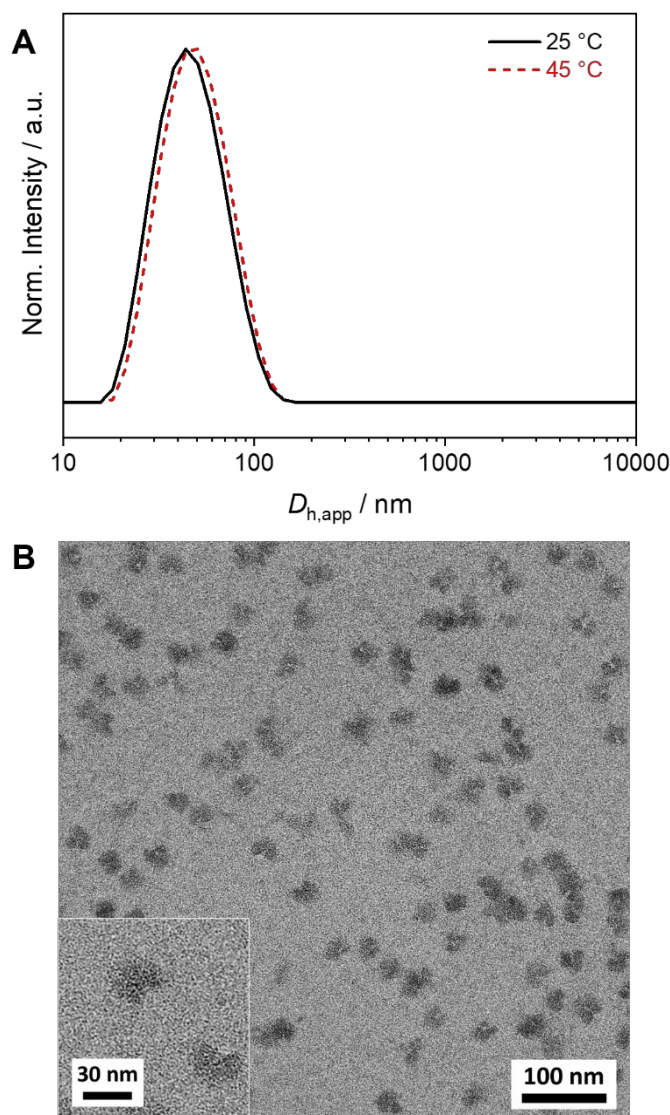


Figure 4.8 (A) Hydrodynamic diameter distributions from DLS for $\text{S}_{169}\text{LLA}_{96}\text{T}_{200}$ triblock terpolymer micelles ($c = 5 \text{ g L}^{-1}$, CH). (B) TEM micrographs of the micelles with a Janus-type corona made of dark appearing PS and bright appearing *Pt*BMA hemispheres (PS selectively stained with RuO_4).

Fig. 4.9A and B show the component distribution extracted from Raman imaging and the respective SEM micrograph for a PS/*Pt*BMA (30/70 (w/w)) blend compatibilized with 7 wt% PS-*b*-PLLA-*b*-*Pt*BMA Janus micelles. The average PS droplet size of $D_{\text{PS}} = 2.6 \pm 1.8 \text{ }\mu\text{m}$ is comparable to that obtained when employing the same amount of patchy PS-*sc*-PLA-*Pt*BMA micelles ($D_{\text{PS}} = 2.5 \pm 0.9 \text{ }\mu\text{m}$). However, the size distribution is significantly broader and

bimodal for the Janus micelles compatibilized blend (Fig. 4.9C). The latter becomes obvious both in the Raman imaging data as well as the SEM micrograph by the presence of significantly larger PS droplets with diameters up to $D_{PS} \approx 10\text{--}15\text{ }\mu\text{m}$, which were not observed for the blend compatibilized with patchy SC micelles (Fig. 4.5D, 4.6C and E). Hence, patchy micelles seem to be superior with respect to achieving a homogeneous size distribution of the dispersed PS droplets, whereby the size reduction of the dispersed PS droplets is comparable.

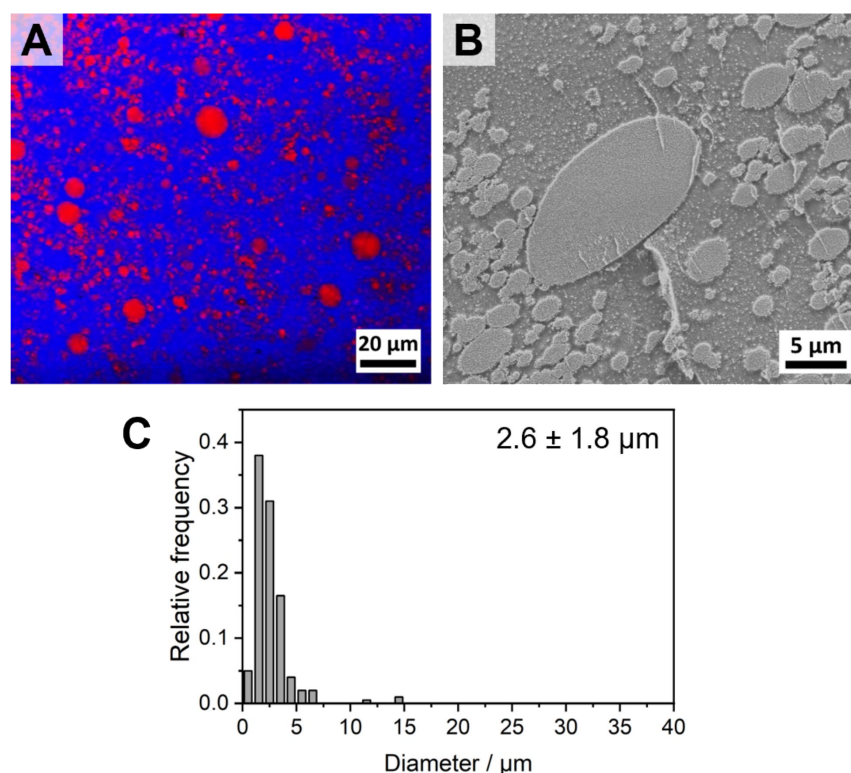


Figure 4.9 (A) Spatial component distribution extracted from Raman imaging (PS droplets are depicted in red and the continuous *PtBMA* matrix in blue) and (B) SEM micrograph for a PS/*PtBMA* (30/70 (w/w)) blend compatibilized with 7 wt% PS-*b*-PLLA-*b*-*PtBMA* Janus micelles. (C) Corresponding histogram of PS droplet diameter distribution.

4.4 Conclusions

This work demonstrates that SCDSA of enantiomeric PLA-based diblock copolymers to well-defined and long-term stable patchy spherical micelles can be scaled-up without compromising their properties, allowing their application as compatibilizers in solvent-cast polymer blends. The patchy stereocomplex (SC) micelles feature a patch-like compartmentalized PS/*PtBMA* corona and have proven highly efficient in the compatibilization of strongly immiscible PS/*PtBMA* blends. With an increasing compatibilizer content the homogeneity of the blends increased and concomitantly the size of the dispersed PS droplets, being embedded in the

PtBMA matrix, was significantly reduced. This is attributed to the unique corona structure of the patchy SC micelles, being capable to adapt to their surrounding by selective collapse/expansion of the respective miscible/immiscible corona patches. SCDSA also opens the way to incorporate different guest molecules inside the SC core of the micelles (exemplary shown for a fluorescence dye), without changing the shape and chemistry of the micelle corona. This makes SCDSA highly valuable for the construction of surface-compartmentalized micelles with tailored functionalities. The modularity of the SCDSA approach allows an easy variation of the corona-forming blocks, which might open the use of patchy SC micelles as compatibilizers in various polymer blend systems. To this end, alternative large-scale preparation methods need to be developed in future.

Data availability statement

All data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no conflict of interest.

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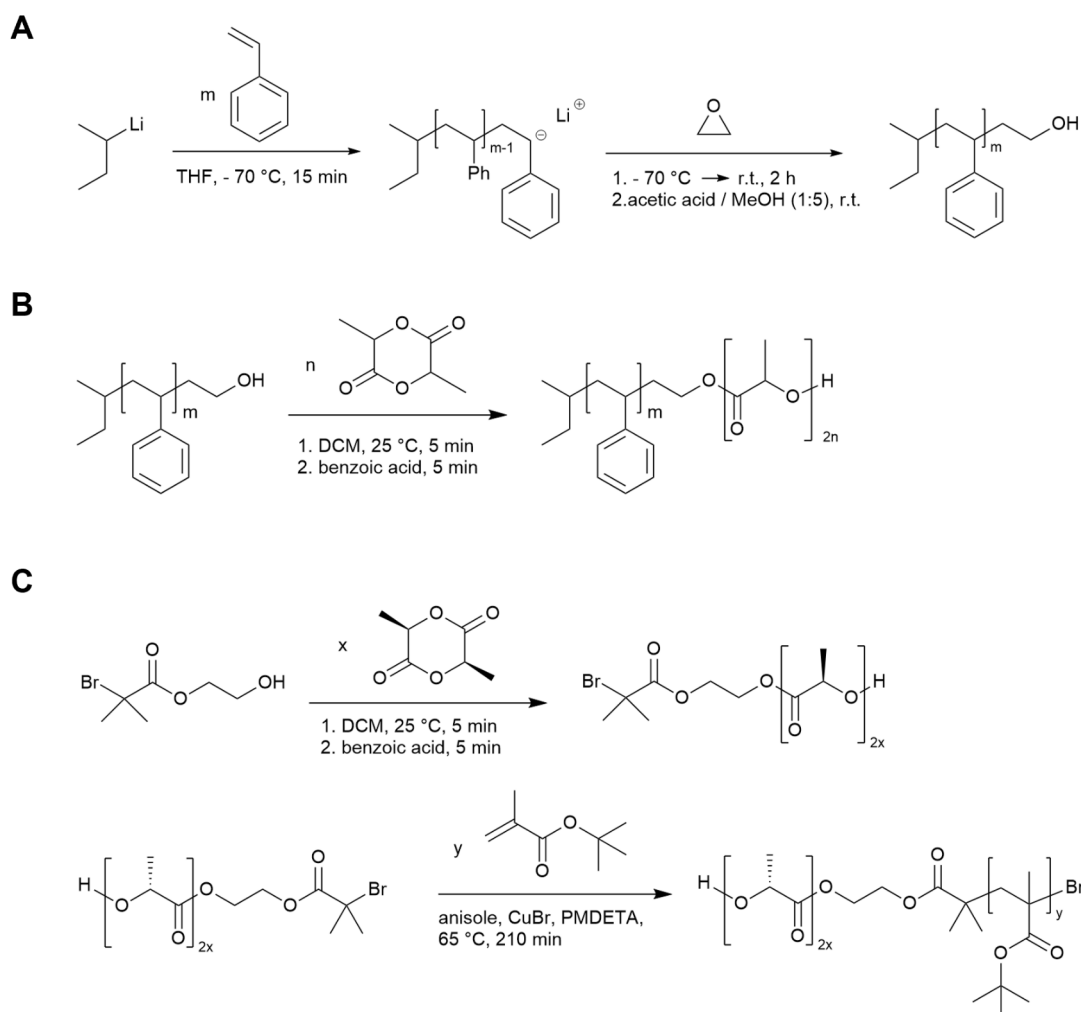
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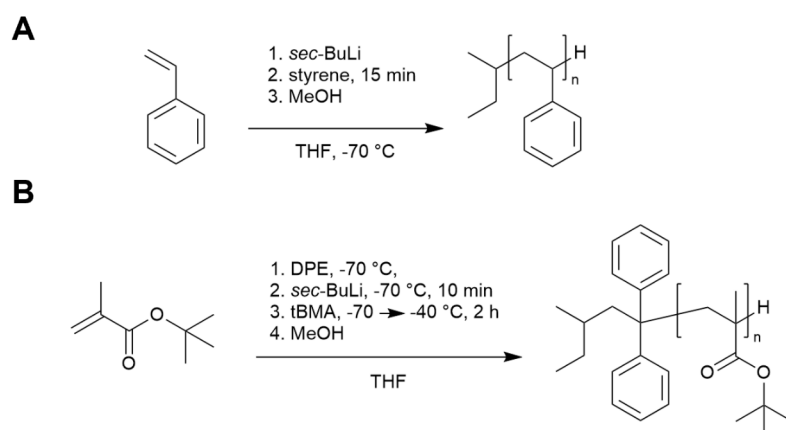
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Supplementary Information



Scheme S4.1 Synthesis of A) PS-OH, B) PS-*b*-PLLA or PS-*b*-PDLA and C) PDLA-*b*-PtBMA diblock copolymers.



Scheme S4.2 Synthesis of A) PS and B) PtBMA homopolymers by living anionic polymerization.

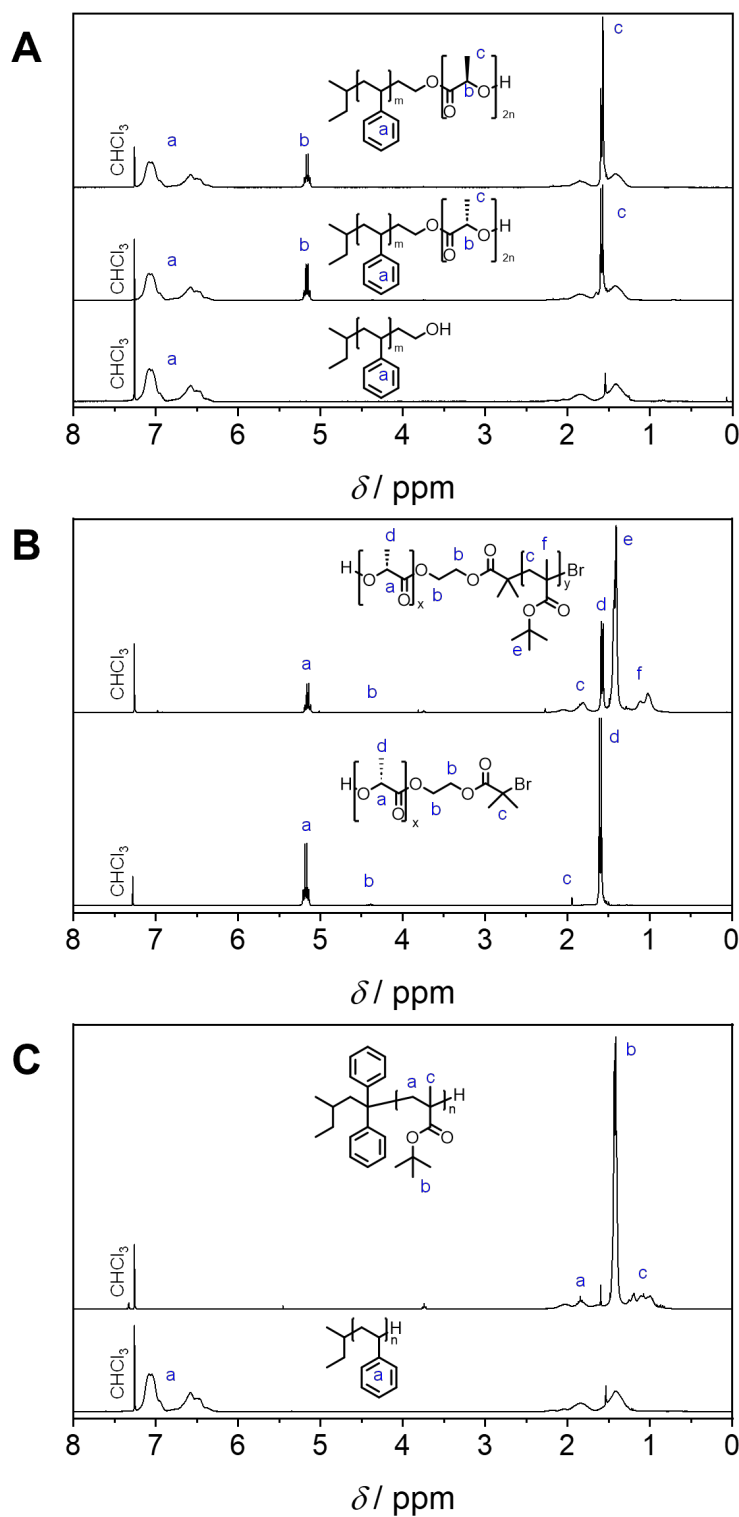


Fig. S4.1 ^1H NMR (CDCl_3 , 300 MHz) spectra of A) PS-OH, PS-*b*-PLLA, PS-*b*-PDLA, B) PDLA-Br, PDLA-*b*-PtBMA and C) PS, PtBMA.

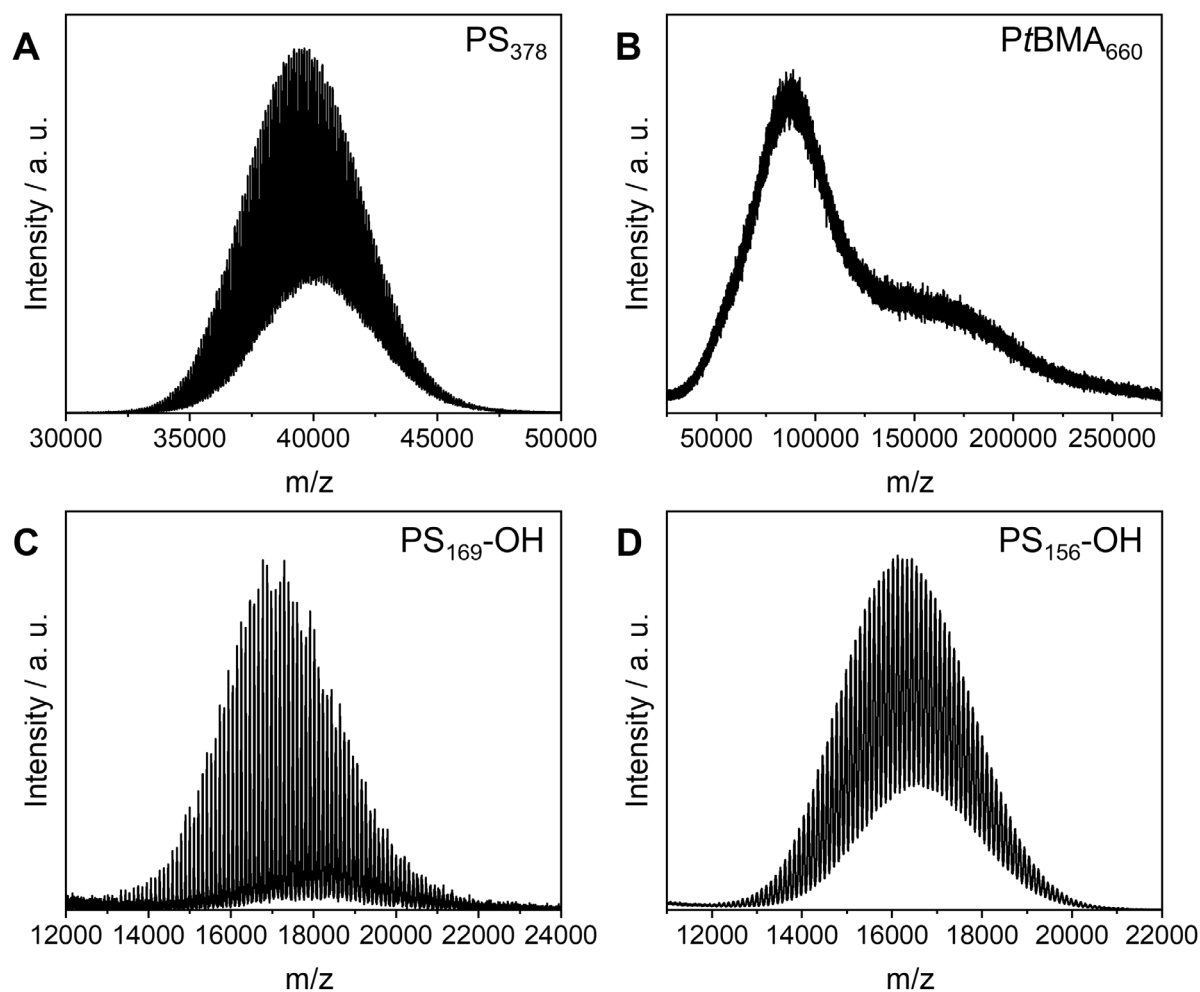


Fig. S4.2 MALDI-ToF MS spectra of A) PS, B) PtBMA (the shoulder at higher molecular weights is an artifact arising from the combination of two polymer chains with one cation), C) PS₁₆₉-OH and D) PS₁₅₆-OH (PS samples: DCTB, AgTFA; PtBMA: DCTB, NaTFA).

Table S4.1 Molecular characteristics of synthesized polymers.

Sample	Composition (wt% / <i>DP</i>) ^a	<i>M_n</i> (NMR) ^a [g mol ⁻¹]	<i>M_n</i> (SEC) ^b	<i>Đ</i> ^b	<i>M_n</i> (MS) ^c [g mol ⁻¹]	<i>Đ</i> ^c
PS	- / S ₃₇₈	-	41 500	1.05	39 400	1.0
PtBMA	- / tBMA ₆₆₀	-	87 000	1.06	93 700	1.06
PS ₁₆₉ -OH	- / S ₁₆₉ EO ₁	-	19 600	1.06	17 600	1.0
PS ₁₅₆ -OH	- / S ₁₅₆ EO ₁	-	16 600	1.06	16 300	1.0
PDLA ₁₀₀ -Br	- / DLA ₁₀₀	7 500	13 500	1.16		
PDLA ₆₂ -Br	- / DLA ₆₂	4 600	6 300 ^d	1.09 ^d		
PDLA ₆₂ -RB	- / DLA ₆₂ RB ₁	5 200	6 700 ^d	1.10 ^d		
PS- <i>b</i> -PLLA	S ₇₀ LLA ₃₀ / S ₁₆₉ LLA ₁₀₆	25 300	27 900	1.08		
PS- <i>b</i> -PDLA	S ₆₈ DLA ₃₂ / S ₁₅₆ DLA ₁₀₆	24 000	30 000	1.07		
PS- <i>b</i> -PLLA-Br	S ₇₂ LLA ₂₈ / S ₁₆₉ LLA ₉₆	24 500	27 900	1.10		
PDLA- <i>b</i> -PtBMA	DLA ₂₈ tBMA ₇₂ / DLA ₁₀₀ tBMA ₁₃₂	26 200	35 100	1.19		
PS- <i>b</i> -PLLA- <i>b</i> - PtBMA	S ₃₃ LLA ₁₃ T ₅₄ / S ₁₆₉ LLA ₉₆ T ₂₀₀	52 600	42 200	1.18		

a) determined from ¹H NMR (CDCl₃, 300 MHz) using the ATRP end group or absolute *M_n* of the PS and PDLA precursor polymers (determined by MALDI-ToF MS or ¹H NMR spectroscopy) for internal signal calibration, respectively (*DP* = degree of polymerization)

b) determined from CHCl₃-SEC (PS calibration), *Đ* = molar mass dispersity

c) determined from MALDI-ToF MS

d) determined from THF-SEC (PS calibration)

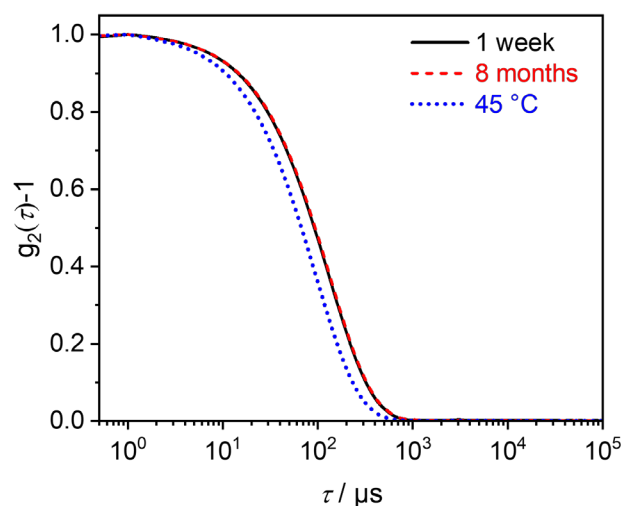


Fig. S4.3 Autocorrelation functions from DLS for SC micelles prepared from PS-*b*-PLLA/PDLA-*b*-PtBMA mixtures ($c = 5 \text{ g L}^{-1}$, CH) after aging for 1 week, 8 months, and at 45 °C.

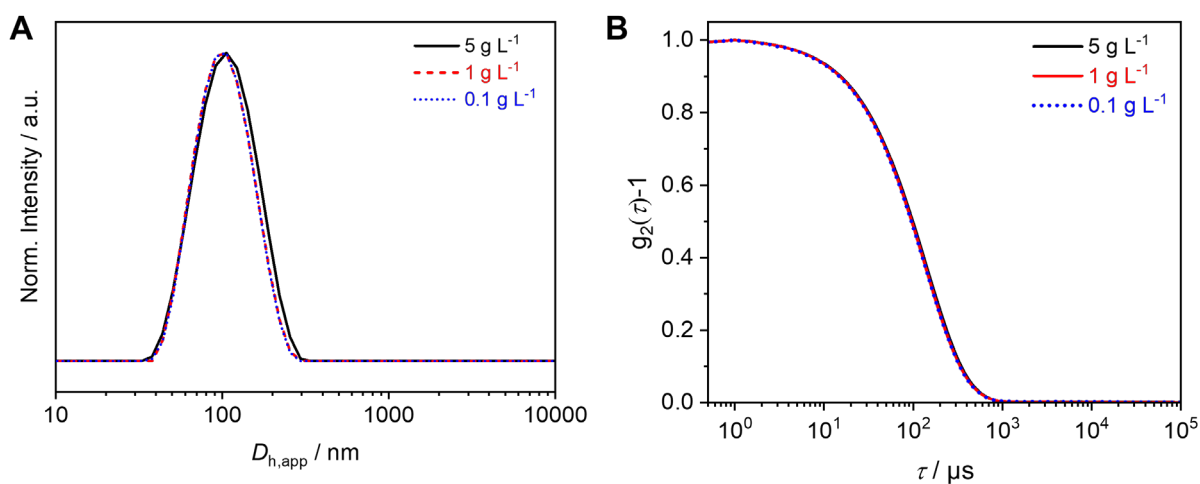


Fig. S4.4 DLS measurements of SC micelles in CH prepared from PS-*b*-PLLA/PDLA-*b*-PtBMA mixtures with a concentration of $c = 5 \text{ g L}^{-1}$ and upon further dilution to $c = 1$ and 0.1 g L^{-1} . A) Hydrodynamic diameter distributions and B) autocorrelation functions.

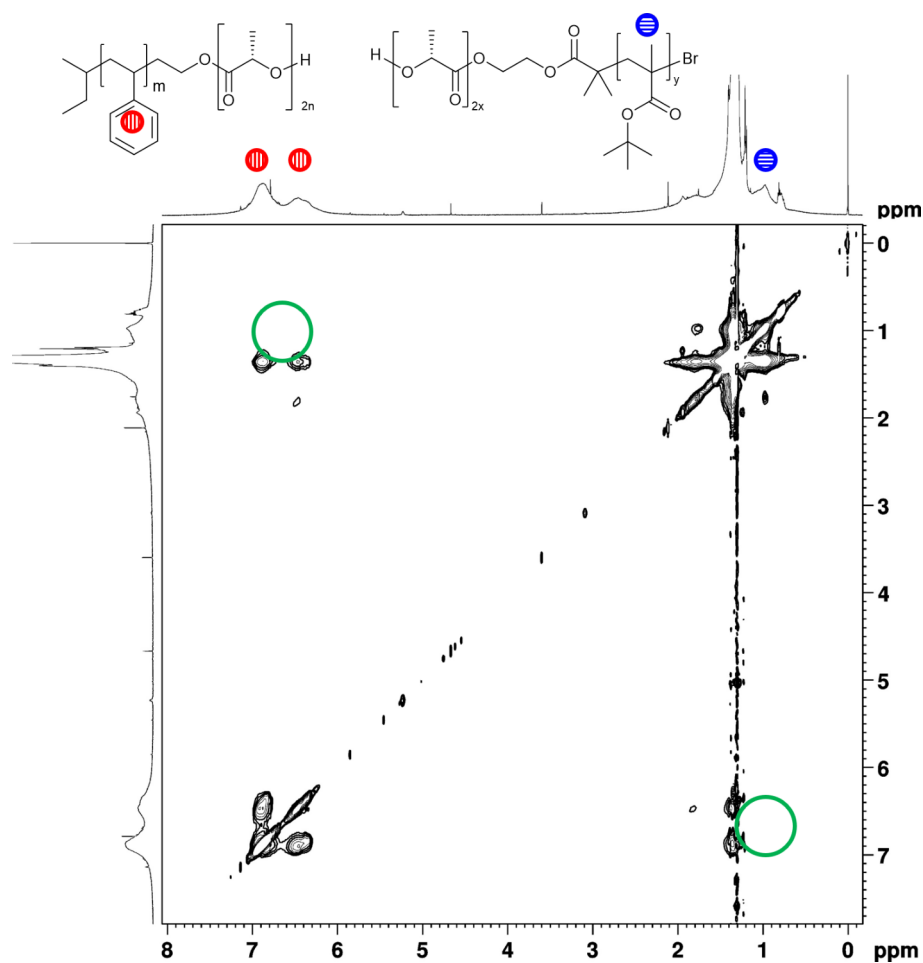


Fig. S4.5 Contour plot of a 2D ^1H NOESY experiment on a SC micelle dispersion prepared from PS-*b*-PLLA/PDLA-*b*-PtBMA mixtures ($c = 5 \text{ g L}^{-1}$, CH_2D_2). The green circles indicate the positions where cross-peaks would be expected in case of a mixed PS/PtBMA corona. In a mixed corona, the PS and PtBMA segments would be in close proximity, giving rise to magnetization transfer by cross-relaxation. Hence, the absence of those cross-peaks confirms that the microphase separation within the PS/PtBMA corona of the SC micelles is present already in the dispersed state.

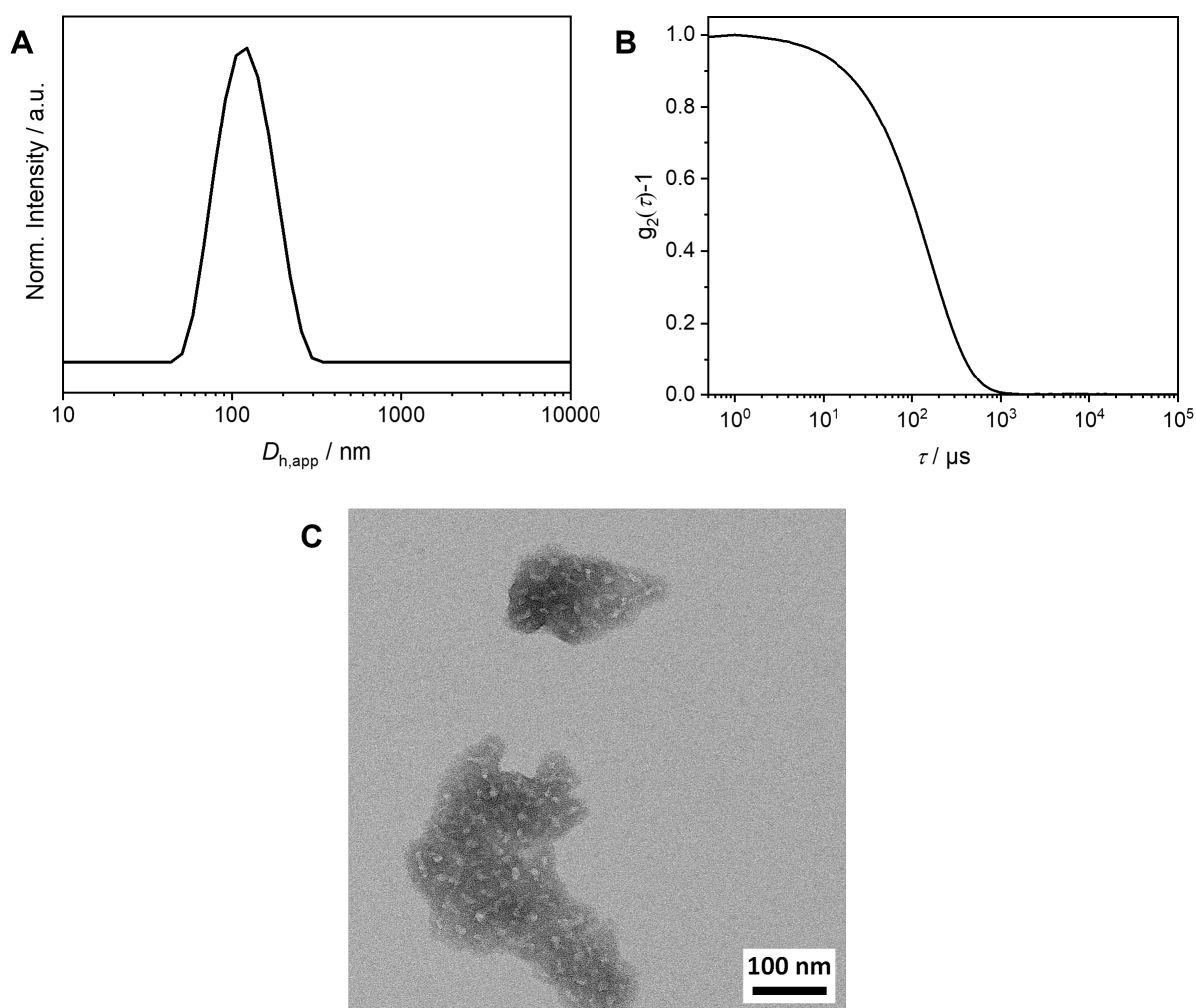


Fig. S4.6 A) Hydrodynamic diameter distribution and B) autocorrelation function of a PS-*sc*-PLA-PS micelle dispersion in CH ($c = 5.0 \text{ g L}^{-1}$) determined by DLS. C) TEM micrograph of the respective micelles. The dispersion was prepared by adding a mixture of PS-*b*-PLLA and PS-*b*-PDLA in DCM ($V = 2 \text{ mL}$, $c = 50 \text{ g L}^{-1}$) to CH ($V = 18 \text{ mL}$), subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO_4 vapor and appears dark.

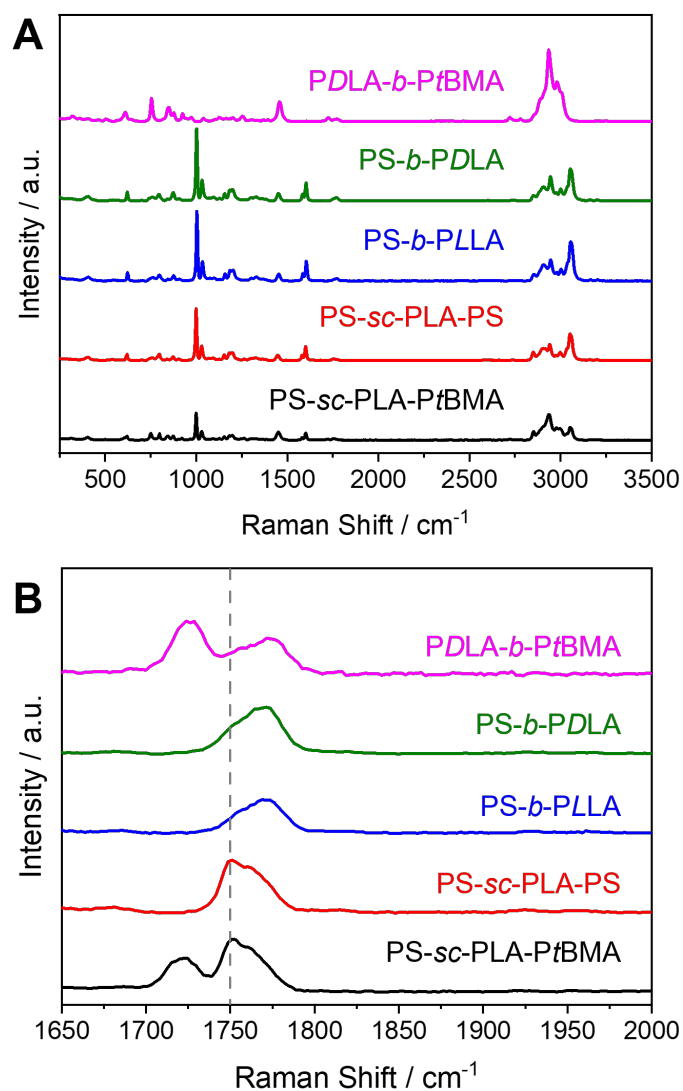


Fig. S4.7 Raman spectra of employed diblock copolymers and dried SC micelles. A) Full spectra and B) zoom-ins of the carbonyl stretching vibration regime (dashed line indicates location of SC specific band).

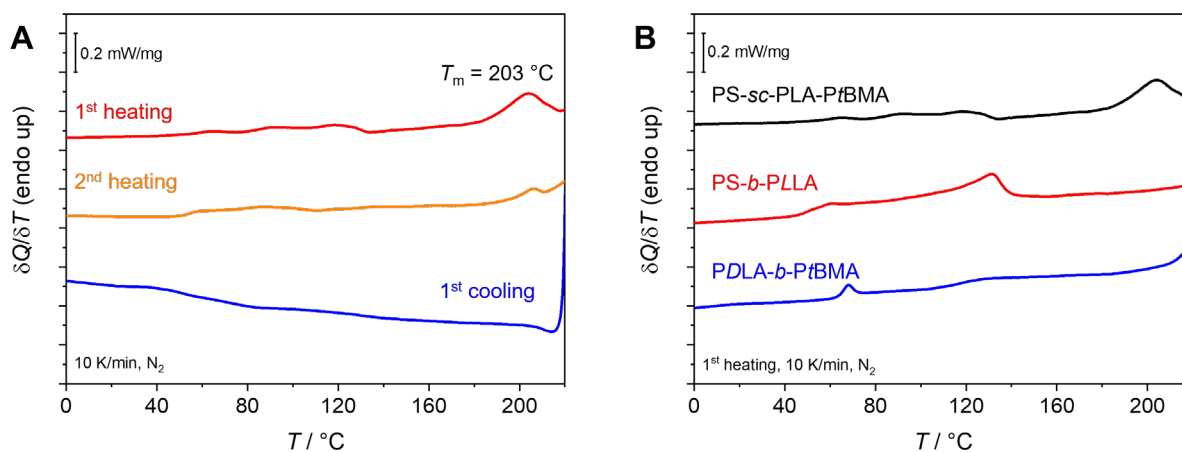


Fig. S4.8 A) DSC measurements of freeze-dried PS-*sc*-PLA-PtBMA micelles. B) 1st heating traces of freeze-dried PS-*sc*-PLA-PtBMA micelles and the respective diblock copolymers used for their preparation.

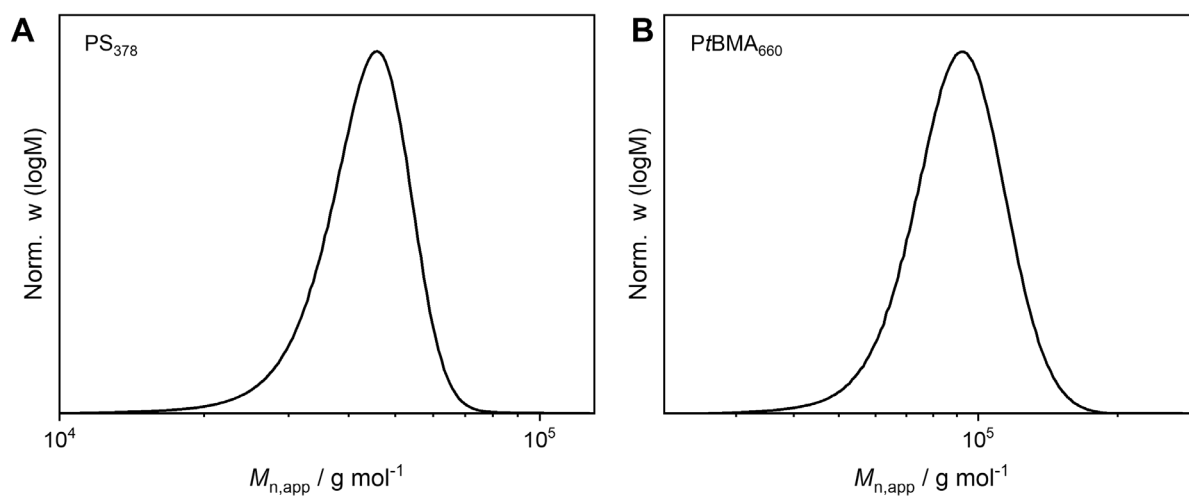


Fig S4.9 Apparent molecular weight distributions of A) PS and B) PtBMA homopolymers (CHCl_3 -SEC, PS calibration).

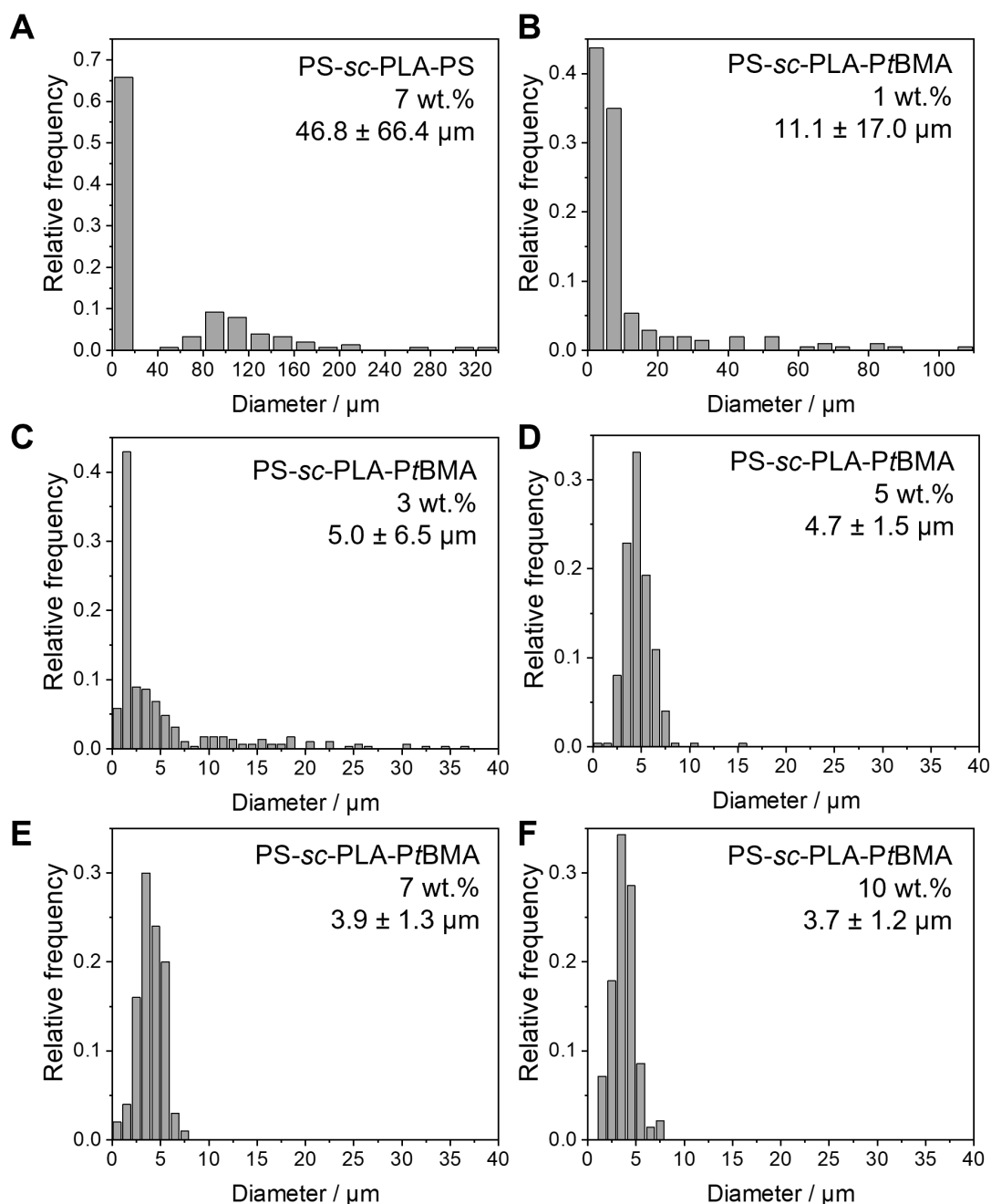


Fig. S4.10 Histograms of PS droplet diameter distributions determined by Raman imaging of PS/PtBMA (30/70 (w/w)) blends compatibilized with A) 7 wt% PS-*sc*-PLA-PS micelles or different amounts of patchy PS-*sc*-PLA-PtBMA micelles: B) 1, C) 3, D) 5, E) 7 and F) 10 wt%. For size evaluation at least 100 PS domains from different positions were counted.

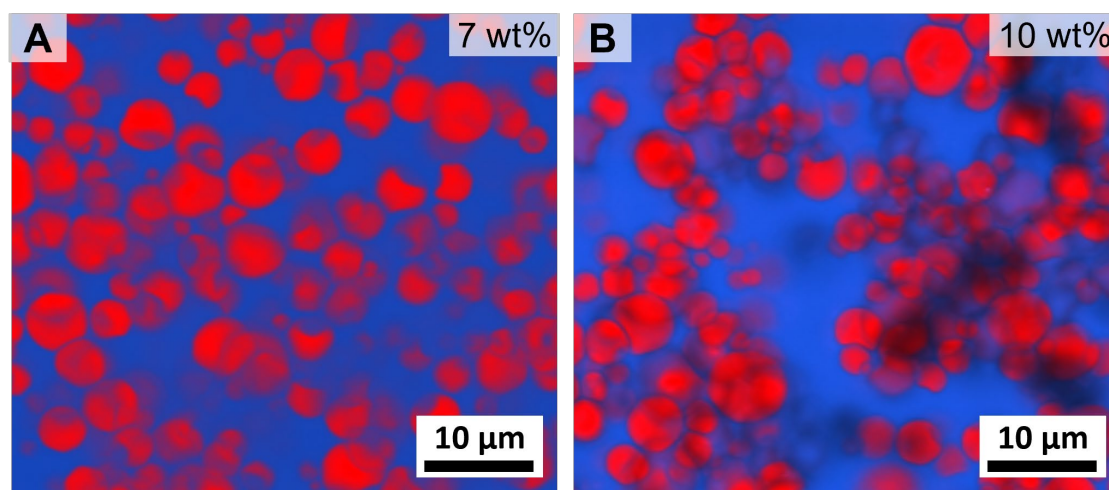


Fig. S4.11 Spatial component distribution at higher magnification extracted from Raman imaging for PS/PtBMA (30/70 (w/w)) blends compatibilized with A) 7 wt% and B) 10 wt% patchy PS-*sc*-PLA-PtBMA micelles. The domains colored in red represent PS droplets being dispersed in a continuous PtBMA matrix (depicted in blue).

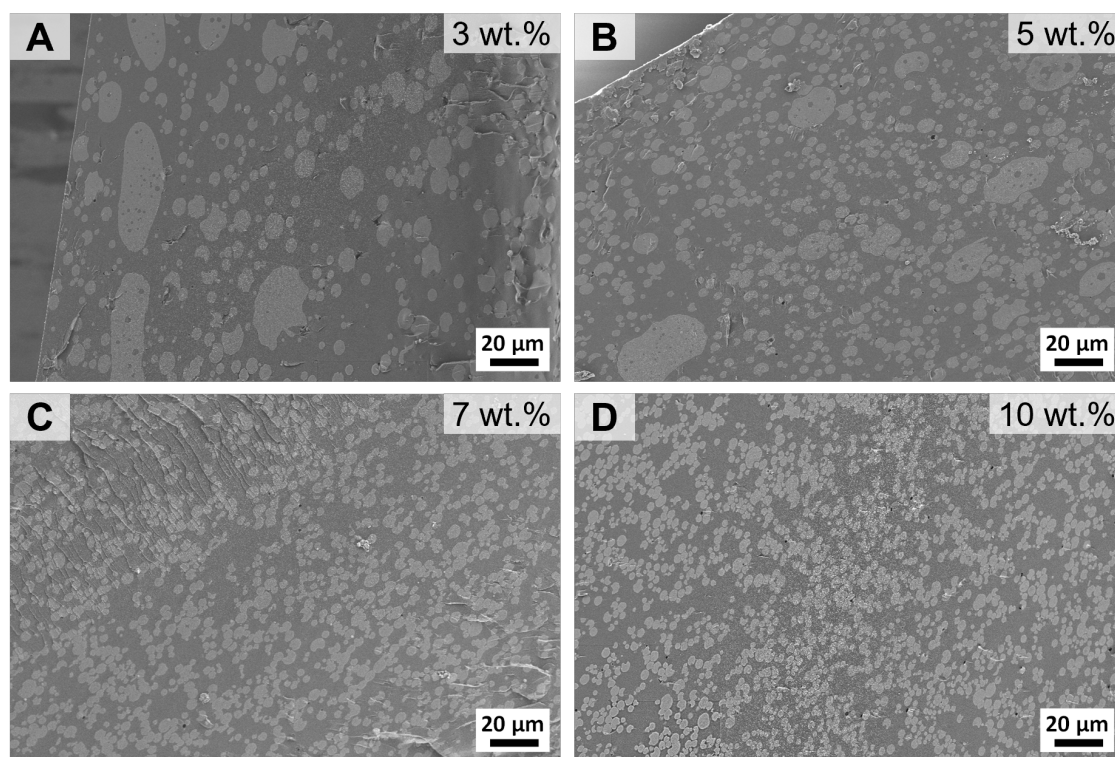
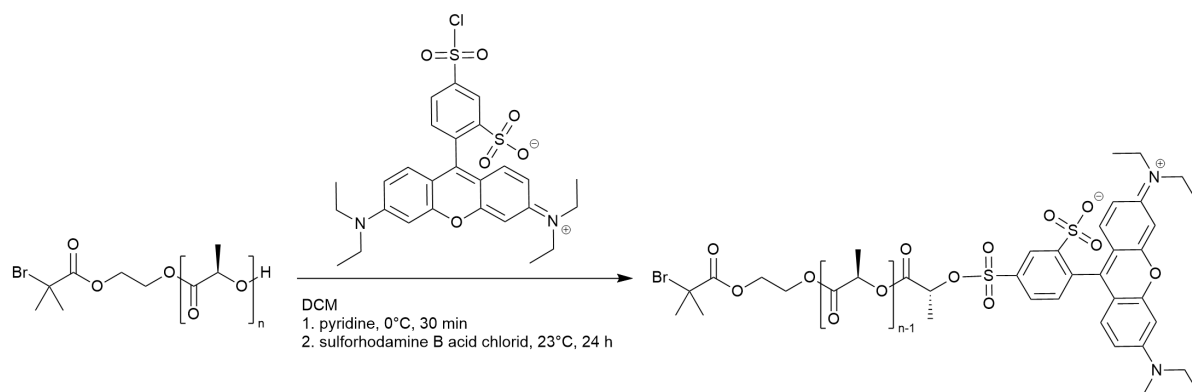


Fig. S4.12 Overview SEM images of the fracture surfaces of PS/PtBMA (30/70 (w/w)) blends compatibilized with A) 3, B) 5, C) 7 and D) 10 wt% patchy PS-*sc*-PLA-PtBMA micelles, taken at lower magnification. The PS domains were selectively stained with RuO₄ vapor to enhance contrast and appear bright.



Scheme S4.3 Synthesis of fluorescently labelled PDLA homopolymer (PDLA₆₂-RB).

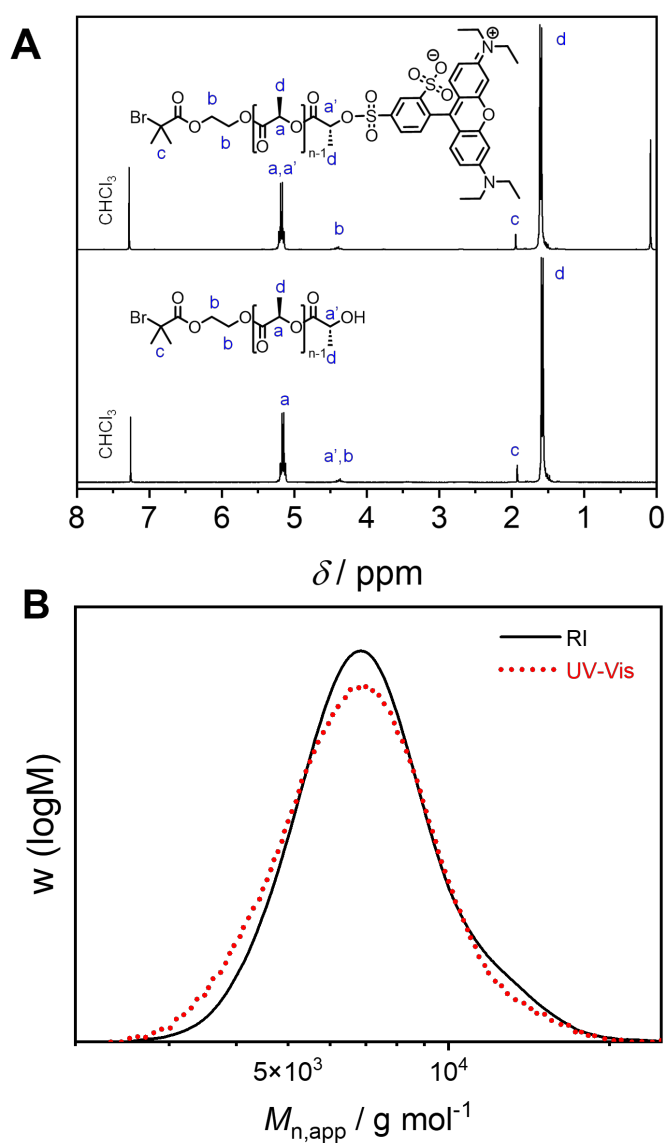


Fig. S4.13 A) ^1H NMR (CDCl_3 , 300 MHz) spectra of PDLA₆₂-Br and PDLA₆₂-RB. B) Apparent molecular weight distributions of PDLA₆₂-RB (THF-SEC, PS calibration, UV-vis detector at $\lambda = 580$ nm). The identical RI and UV-vis traces for PDLA₆₂-RB prove the successful end-functionalization of PDLA₆₂ with sulforhodamine B.

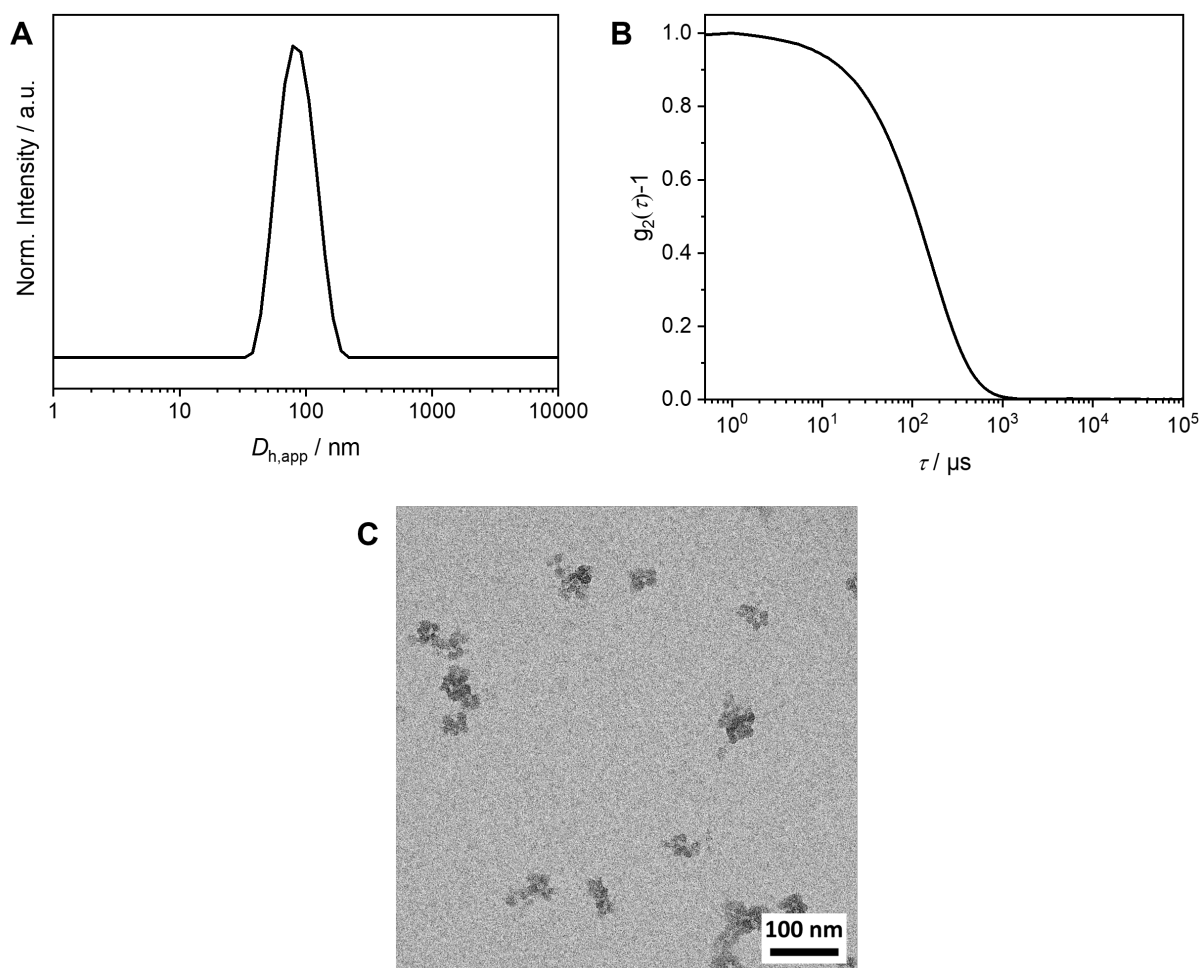


Fig. S4.14 A) Hydrodynamic diameter distribution and B) autocorrelation function of a PS-*sc*-PLA-PtBMA_RB micelle dispersion in CH ($c = 1.0 \text{ g L}^{-1}$) determined by DLS. C) TEM micrograph of the respective micelles. The dispersion was prepared by the addition of a mixture of PS-*b*-PLLA, PS-*b*-PDLA and PDLA₆₂-RB (10 wt% of total PDLA amount) in DCM ($V = 300 \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO₄ vapor and appears dark.

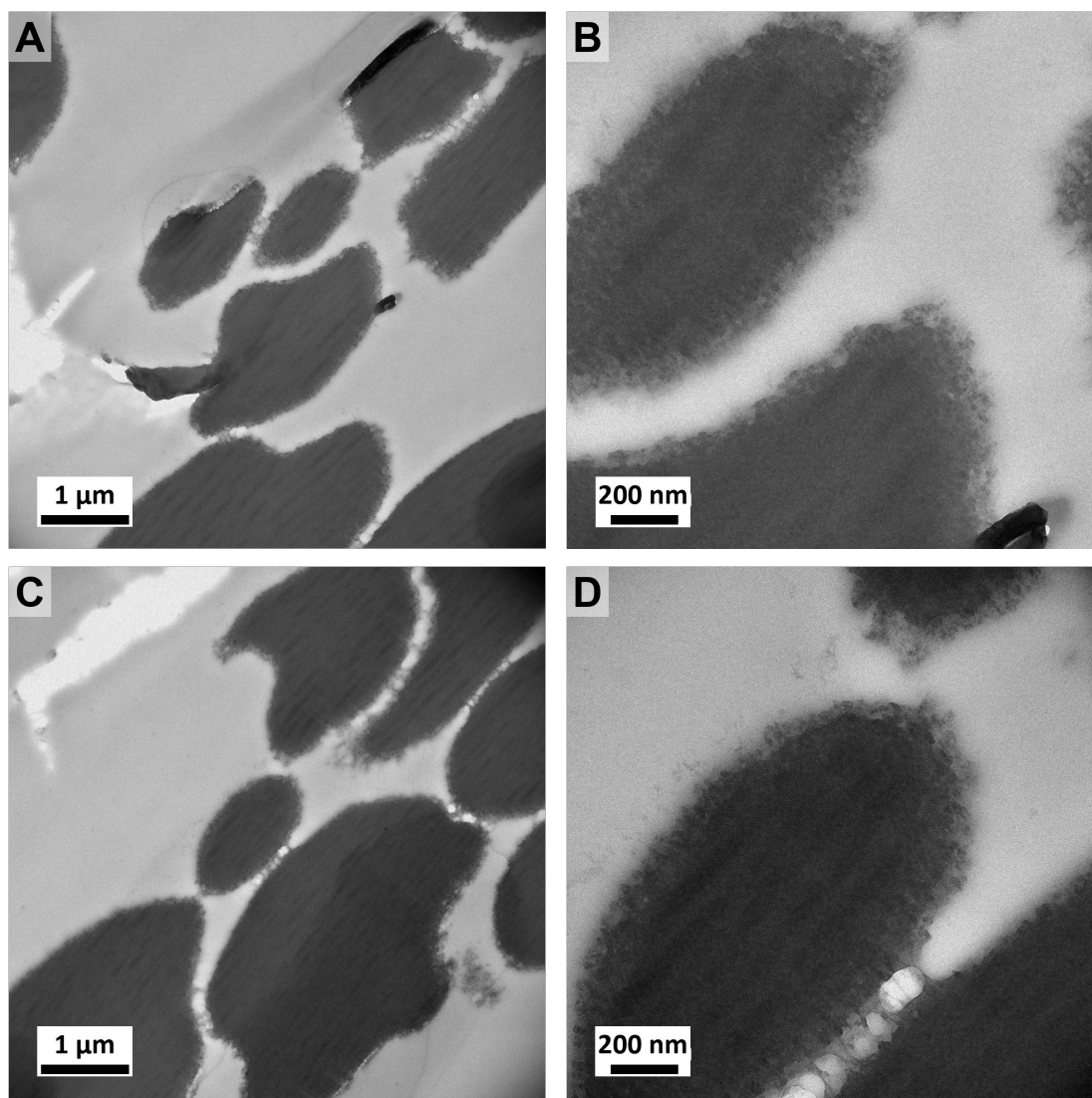
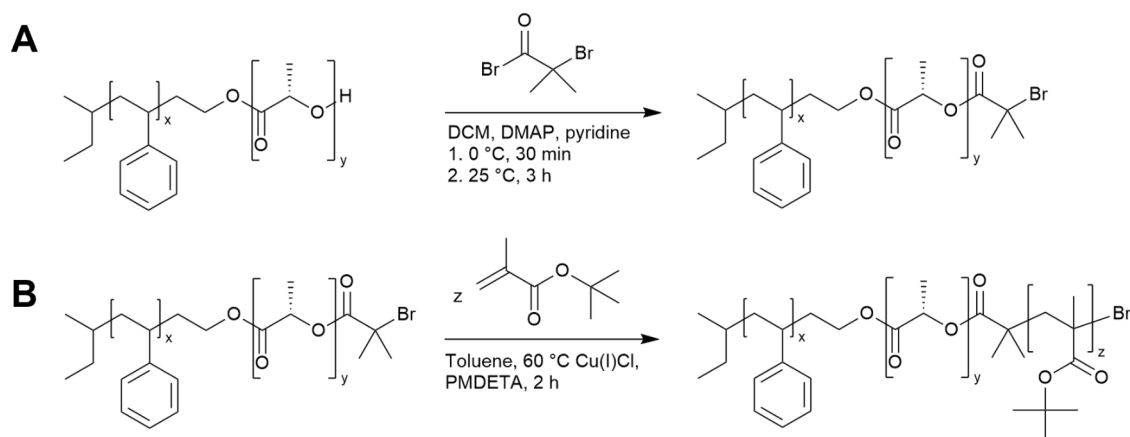


Fig. S4.15 TEM micrographs of a thin film of a PS/PtBMA (30/70 (w/w)) blend compatibilized with 7 wt% patchy PS-*sc*-PLA-PtBMA micelles. The PS domains were selectively stained with RuO₄ vapor to enhance contrast and appear dark.



Scheme S4.4 Synthesis of A) the PS-*b*-PLLA-Br diblock copolymer end-functionalized with an ATRP initiating site ($S_{169}LLA_{96}$ -Br) and B) the PS-*b*-PLLA-*b*-PtBMA triblock terpolymer ($S_{169}LLA_{96}T_{200}$).

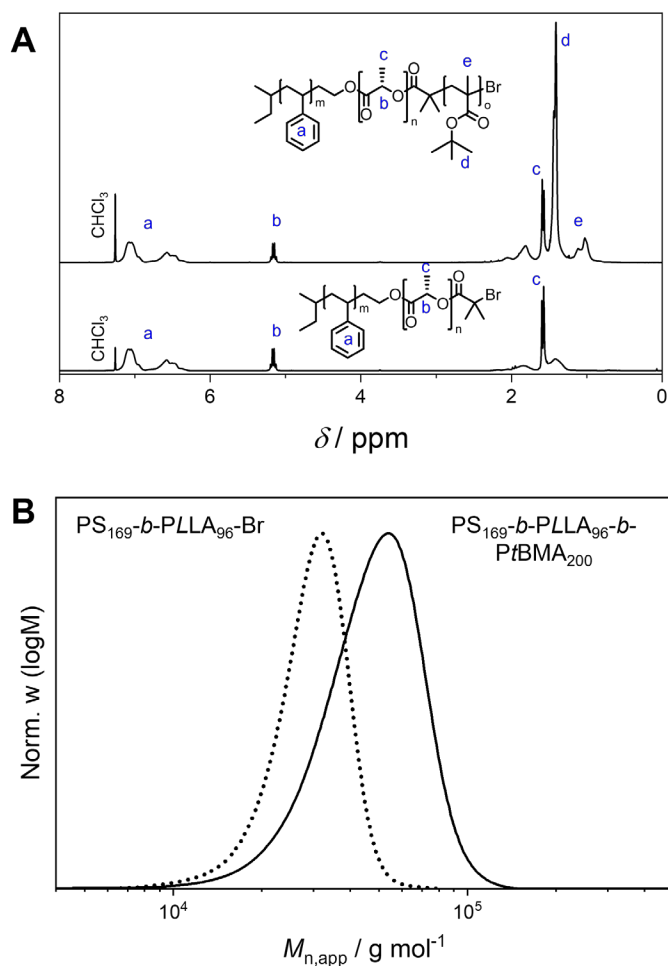


Fig. S4.16 A) ^1H NMR (CDCl_3 , 300 MHz) spectra and B) apparent molecular weight distributions (CHCl_3 -SEC, PS calibration) of PS_{169} -*b*- PLLA_{96} -Br and PS_{169} -*b*- PLLA_{96} -*b*-PtBMA $_{200}$.

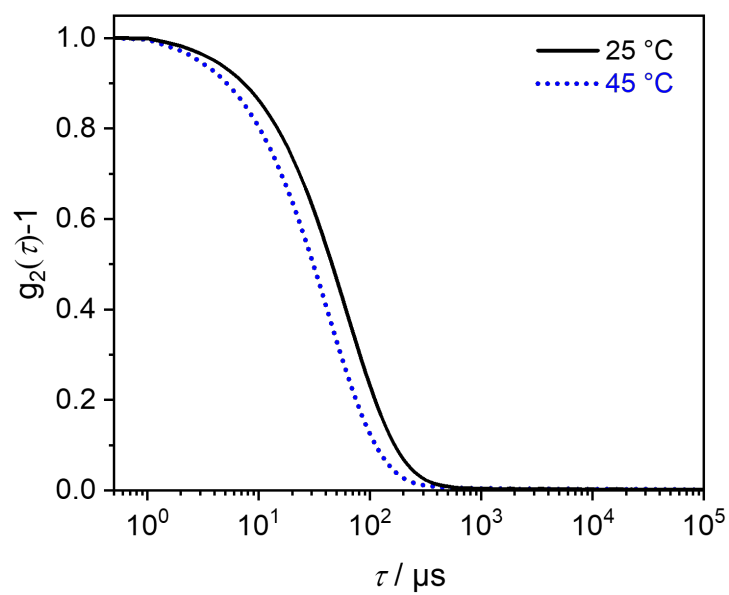


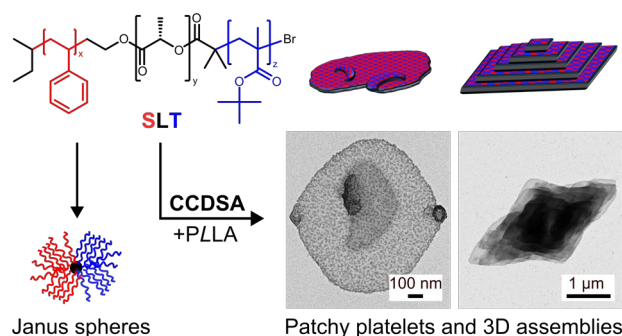
Fig. S4.17 Autocorrelation functions from DLS for PS-*b*-PLLA-*b*-PtBMA Janus micelles ($c = 5 \text{ g L}^{-1}$, CH) at 25 and 45 °C.

5 From Janus Spheres to Twisted Patchy Platelets and their 3D Assemblies by Co-Crystallization-Driven Self-Assembly

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Abstract

Surface-compartmentalized particles, such as Janus and patchy micelles, have attracted growing interest owing to their unique corona properties enabling diverse applications. Crystallization-driven self-assembly (CDSA) is a powerful tool for preparing worm-like patchy micelles with crystalline cores. However, platelet-like (2D) micelles and 3D assemblies with a non-concentric arrangement of corona patches have not yet been realized. Here, we report on the self-assembly of polystyrene-*block*-poly(*L*-lactide)-*block*-poly(*tert*-butyl methacrylate) (SLT) triblock terpolymers featuring a crystallizable PLLA middle block and two highly incompatible corona-forming blocks (PS and *Pt*BMA). Direct dissolution of neat SLT at 45 °C in cyclohexane, a selective solvent for the corona-forming blocks, yields spherical Janus micelles with an amorphous PLLA core as crystallization is strongly hindered under these conditions. Surprisingly, upon blending SLT with PLLA homopolymer, co-crystallization-driven self-assembly (CCDSA) results in twisted platelet-like micelles with a non-concentric, nanometer-sized patchy corona that further form defined 3D assemblies. The high interfacial activity of the twisted patchy platelets allows their use in emulsion stabilization, underlining their application potential. Notably, the twisted patchy platelets exhibit a higher interfacial activity with respect to the corresponding spherical patchy micelles, which is in contrast to the behavior of Janus discs and spheres.

Keywords: Janus, patchy, platelet micelles, triblock terpolymers, self-assembly, crystallization-driven self-assembly

5.1 Introduction

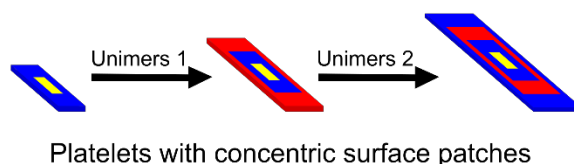
Crystallization-driven self-assembly (CDSA) of block copolymers with a crystallizable block has emerged as powerful tool for the production of a plethora of well-defined, complex micellar architectures. One of the most relevant contribution to this field was the development of living CDSA, employing seeded-growth or self-seeding concepts, which allows control over length, length distribution, and corona chemistry.^{1–6} Living CDSA also paved the way to a huge variety of well-defined micellar (super)structures that were not accessible before, for example, non-centrosymmetric cylindrical block comicelles,⁷ non-covalent supermicelles of various shapes (fish-spine-, cross-, train-track-like, or single-stranded),^{8–10} colloidosomes,¹¹ and π -conjugated one-dimensional (1D) and three-dimensional (3D) nanostructures.^{12–14} Moreover, CDSA has become the preferred strategy for generating 2D platelet micelles with defined shape and size, as crystallization usually favors structures of low curvature.^{2,3,15,16} One way to achieve core-crystalline platelet micelles is to increase the core-corona block length ratio, as shown by Manners, Winnik and co-workers.¹⁷ Another, highly efficient approach is co-crystallization-driven self-assembly (CCDSA) of crystalline-coil diblock copolymers with the respective crystallizable homopolymer, as shown first for poly(ferrocenyl dimethylsilane) (PFS) and poly(*ε*-caprolactone) (PCL) containing block copolymers.^{18–21} CCDSA is now widely used for polyester based systems to construct two-dimensional (2D) platelets of tailored size and functionality,^{22–29} whereby poly(*L*-lactide) (PLLA) containing block copolymers have proven particularly versatile, due to their biocompatibility and degradability.^{30–33} While CDSA and CCDSA have been extensively utilized for the fabrication of 1D and 2D core-crystalline micelles (CCMs), the construction of 3D structures remains comparably rare.³⁴ These structures, featuring stacked, branched, spherulitic or flower-like shapes, are driven by defects in the crystalline lamellar precursors, like screw-dislocations within the crystal growth process, the formation of additional secondary nucleation sites, or the stacking of lamellae in the self-assembly process.^{35–41}

CDSA has established as versatile method for the preparation of worm-like (or cylindrical) CCMs with a patch-like surface compartmentalized corona.^{1,42–44} In contrast to Janus micelles, which consist of two separated faces with different chemistry and/or polarity, patchy micelles feature multiple compartments in their corona.^{45–55} The unique corona structure of Janus micelles (and particles) together with their superior interfacial activity have been harnessed for various applications, like as compatibilizers for polymer blends, in emulsion stabilization, interfacial catalysis, for surface functionalization, and biomedical applications.^{50,52,56–60} In contrast, there are less reports on patchy micelles, although they show comparable interfacial

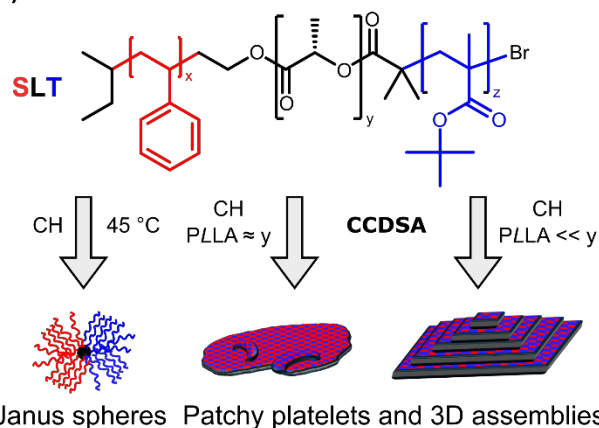
properties. So far, patchy micelles have been utilized in hierarchical self-assembly,^{55,61–66} as template for the regioselective incorporation of nanoparticles enabling applications in heterogeneous catalysis,^{67–70} or as blend compatibilizers.^{71,72} 2D surface-compartmentalized CCMs with concentric surface patterns/patches can be produced by sequential CCDSA, using different block copolymer/homopolymer blends (Scheme 1A).^{18,22,23,26,27,73–75} However, the realization of 2D micelles with a "truly" patchy corona (non-centrosymmetric, nanometer-sized soluble patches) remains an open challenge. To the best of our knowledge, there is only one report on patchy 2D CCMs. However, in this case the patchy structure was induced by selectively switching one corona block insoluble.⁷⁶

Herein, we report on the synthesis and self-assembly of polystyrene-*block*-poly(*L*-lactide)-*block*-poly(*tert*-butyl methacrylate) (PS-*b*-PLLA-*b*-PtBMA, SLT) triblock terpolymers with a crystallizable PLLA middle block. Next to the self-assembly of the neat SLT triblock terpolymers in a selective solvent for the corona-forming blocks (PS and PtBMA) also CCDSA with PLLA homopolymers is explored. We show that the micelle morphology can be switched from amorphous spherical Janus micelles, formed by the neat SLT triblock terpolymers, to twisted 3D platelet micelle assemblies with a patchy PS/PtBMA corona, driven by co-crystallization with a PLLA homopolymer (Scheme 1B). In addition, the obtained micelles are tested for their potential application as particulate surfactants.

A) Previous reports:



B) This work:



Scheme 5.1 Schematic illustration of (A) preparation of platelets with a concentric arrangement of surface patches via sequential CCDSA, as reported in literature, and (B) transition from Janus spheres to patchy twisted platelets and 3D pyramids by CCDSA of SLT and PLLA.

5.2 Results and Discussion

5.2.1 Polymer synthesis

The SLT triblock terpolymers were synthesized through a combination of living anionic, ring-opening (ROP) and atom transfer radical (ATRP) polymerization, as depicted in **Scheme S5.1**. A detailed description of the synthetic procedures and analytical data (**Figure S5.1, S5.2, Table S5.1**) is provided in the Supporting Information. In brief, hydroxy-terminated polystyrene (PS-OH), prepared by living anionic polymerization of styrene followed by end-capping with ethylene oxide, was used as macroinitiator for the organo-catalyzed ROP of *L*-lactide. The resulting PS-*b*-PLLA diblock copolymer was subsequently converted into an ATRP macroinitiator (PS-*b*-PLLA-Br) through esterification of the hydroxy end-group with α -bromoisobutyryl bromide. Successful functionalization was confirmed by proton nuclear magnetic resonance spectroscopy (^1H NMR) as evidenced by the downfield shift of the methine proton signal of the terminal repeating unit ($\delta = 4.3$ ppm) after the esterification reaction (**Figure S5.1C,D**). In the last step, the SLT triblock terpolymer was obtained by ATRP of *t*BMA using Cu(I)Cl and PMDETA as catalyst. Degrees of polymerization ($\bar{P}_n$) and composition were calculated from ^1H NMR using the absolute molecular weight of the PS-OH precursor obtained from matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-ToF MS) as internal reference. The corresponding ^1H NMR and MALDI-ToF MS spectra for S₁₅₆L₈₂T₁₁₅ (SLT-1, indices correspond to $\bar{P}_n$ of the respective block) are shown as an example in **Figure 5.1A** and **S5.1A**. According to size exclusion chromatography (SEC) all reaction steps proceeded without side reactions, resulting in a narrowly distributed SLT triblock terpolymer with a low dispersity ($\mathcal{D} = 1.12$) (**Figure 5.1B**). In the same manner, a SLT triblock terpolymer with a longer P*t*BMA block was synthesized (S₁₆₉L₉₆T₂₀₀) and is denoted as SLT-2 (**Figure S5.2, Table S5.1**).

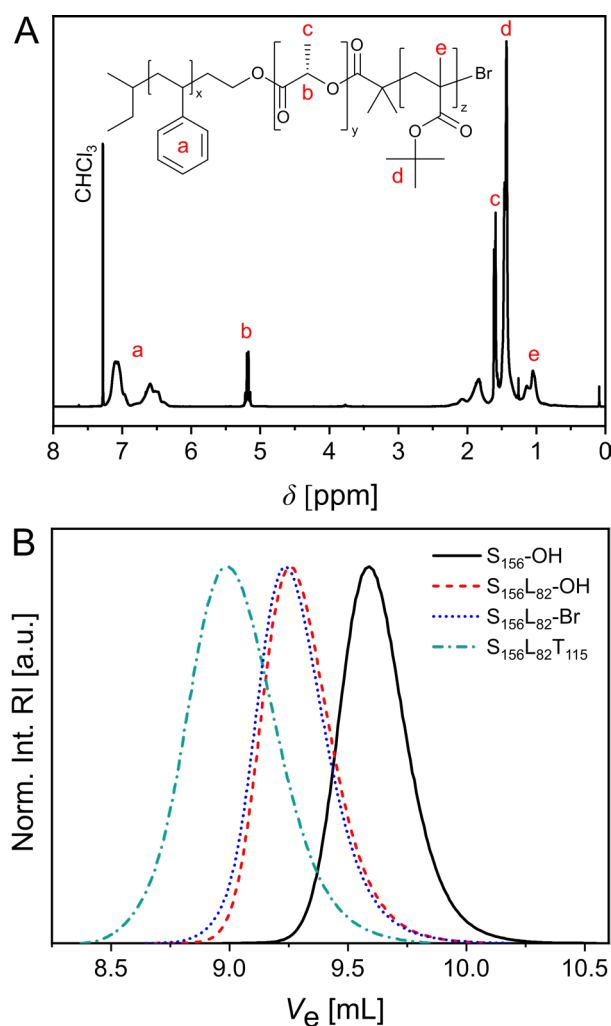


Figure 5.1 (A) ^1H NMR (CDCl_3) spectra of SLT-1 triblock terpolymer. (B) CHCl_3 -SEC (PS calibration) traces of SLT-1 and the respective precursors.

5.2.2 Janus micelles by self-assembly of neat SLT triblock terpolymers

Cyclohexane (CH) was selected as solvent for the self-assembly experiments as it selectively dissolves the corona-forming PS and PtBMA blocks, while the core-forming PLLA middle block remains insoluble. Thermal annealing of a SLT-1 ($\text{S}_{156}\text{L}_{82}\text{T}_{115}$) dispersion in CH ($c = 1 \text{ g L}^{-1}$) at 45°C for 2 h, followed by aging at 25°C for at least 24 h while gentle stirring results in the formation of narrowly distributed micelles with an apparent hydrodynamic diameter of $D_{\text{h,app}} = 37 \pm 15 \text{ nm}$ as revealed by dynamic light scattering (DLS) (**Figure 5.2A**). Transmission electron microscopy (TEM) shows the formation of spherical micelles featuring a Janus-type compartmentalized corona (**Figure 5.2B**, for means of clarity selected Janus micelles are highlighted by blue solid circles). Samples for TEM were treated with RuO_4 vapor prior to imaging, which selectively stains PS. Accordingly, PS appears dark in the micrographs, PLLA and PtBMA bright. If the Janus spheres are aligned in a proper way on the carbon-coated grid, they can be distinguished as micelles with a bright appearing PLLA core, which is surrounded

by a dark PS and a bright PtBMA hemisphere. The PtBMA hemisphere is hardly discernable due to low electron contrast on the carbon film and partial electron beam degradation.⁷⁷ A minor fraction of the micelles shows a patch-like PS/PtBMA corona segregation (highlighted by red dotted circles in **Figure 5.2B**), which might be attributed to the relatively short PtBMA block length. In comparison, for SLT-2 (S₁₆₉L₉₆T₂₀₀), featuring a longer PtBMA block, a further increased fraction of Janus micelles was observed in TEM analysis, while the micelle size slightly increased to $D_{h,app} = 50 \pm 20$ nm (**Figure S5.3**). The fraction of micelles with a Janus-type corona segregation is 87% for SLT-1 and 92% for SLT-2, respectively (**Figure S5.4**).

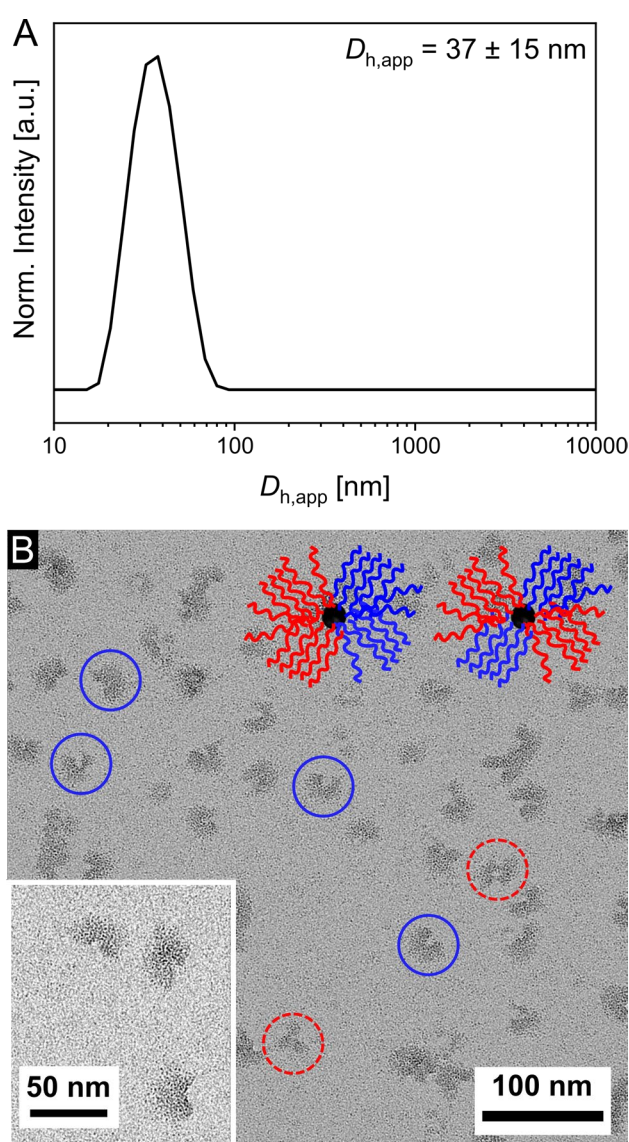


Figure 5.2 (A) Hydrodynamic diameter distribution from DLS for SLT-1 micelles prepared by thermal annealing and aging in CH ($c = 1$ g L⁻¹). (B) TEM micrograph of the corresponding micelles with a Janus-like (left sketch, blue solid circles) or patchy (right sketch, red dashed circles) PS/PtBMA corona. PS was selectively stained with RuO₄ and appears dark.

The formation of spherical micelles was surprising on a first glance as the PLLA middle block should be able to crystallize, favoring the formation of low curvature structures, like cylindrical or platelet-like micelles. To probe whether the PLLA core of the micelles is crystalline or amorphous the dispersion was freeze-dried and analyzed by differential scanning calorimetry (DSC). The absence of a melting endotherm in the first heating trace indicates that the PLLA core is amorphous under the employed self-assembly conditions (**Figure S5.5**). Accordingly, the obtained spherical Janus micelles are likely formed by direct dissolution of the bulk material without crystallization being involved. SLT-1 forms a lamella-lamella morphology in bulk as revealed by TEM and expected from composition (equal weight fraction of end blocks) and the high incompatibility of PS and PtBMA (**Figure S65.A**). A similar behavior was reported for symmetrical PS-*b*-polybutadiene-*b*-PtBMA triblock terpolymers, forming lamella-lamella morphologies irrespective of the polybutadiene content.⁷⁷ Due to the exerted confinement, the PLLA middle block is not able to crystallize within the lamellar microdomains, as again no melting transitions could be detected by DSC (**Figure S5.6B**). This underlines the assumption that the Janus micelles were formed by dissolution of the bulk structure, leading to a break-up of the initially lamellar structure into spherical Janus micelles due to corona chain repulsion. It is noted that no defined micellar assemblies were observed for SLT triblock terpolymers with shorter PLLA middle blocks.

Next, we addressed the question whether crystallization could be induced by varying the self-assembly conditions, enabling the formation of anisotropic (e. g. cylindrical) micellar structures. Hence, we used the commonly employed approach for CDSA and dissolved the SLT-1 triblock terpolymer in dichloromethane (DCM) as a non-selective solvent ($c = 10 \text{ g L}^{-1}$), followed by drop-wise addition to CH, a non-solvent for the PLLA middle block, to induce crystallization. This resulted in a dispersion of SLT-1 micelles ($c = 1 \text{ g L}^{-1}$) in a CH/DCM (9/1 (v/v)) mixture. The dispersion was aged for 48 h at 25 °C before removing DCM by evaporation. Afterwards, the dispersion was refilled with CH to restore the initial concentration of $c = 1 \text{ g L}^{-1}$. In contrast to the results obtained for the direct dissolution in pure CH, DLS exhibits a bimodal distribution of the hydrodynamic diameters. Next to the peak at around 40 nm an additional peak emerged around 500 nm (**Figure S5.7A**). It is important to note that in DLS the intensity scales with the factor R^6 , meaning that although the larger structures dominate the intensity signal, the smaller micelles are still predominant in number. In good accordance with DLS the TEM micrographs shown in **Figure S5.7B,C** depict the presence of two distinct morphologies. Next to the small spherical Janus micelles, cylindrical micelles with a continuous, bright appearing PLLA core are observable. The corona of the cylindrical micelles

appears homogeneously dark, despite the presence of the highly immiscible PS and P*t*BMA blocks that should give rise to a microphase-separated corona structure. However, P*t*BMA is prone to electron beam degradation and, thus, the size of P*t*BMA domains might be strongly underestimated or they might even be not discernable in TEM. Surprisingly, the DSC 1st heating trace of the freeze-dried SLT-1 micelle dispersion still displays no melting endotherm. This may result from the low amount of the cylindrical micelles within the dispersion in combination with a low degree of crystallization (**Figure S5.8**). For SLT-2 a similar behavior was observed, as DLS and TEM show a mixture of spherical Janus and cylindrical patchy micelles (**Figure S5.9**). However, the corona segregation is now more pronounced, which is attributed to the higher fraction of P*t*BMA. Furthermore, various self-assembly conditions were investigated, including changes in annealing temperature and aging times. However, regardless of the method, the resulting micellar dispersions consistently contained a mixture of Janus spheres and cylindrical micelles (**Figure S5.10**). Although the fraction of cylindrical micelles could be increased under certain conditions, a complete transition to cylindrical micelles could not be achieved. The observed strongly hindered crystallization of the PLLA block within SLT triblock terpolymers is attributed to its middle block position, with both ends linked to highly incompatible amorphous blocks (PS and P*t*BMA). This might lead to a significant steric shielding hampering crystallization.

5.2.3 Twisted patchy platelets and 3D assemblies by co-crystallization-driven self-assembly of SLT with PLLA

As mentioned in the Introduction, CCDSA of crystalline-coil block copolymers with the respective crystallizable homopolymer is a versatile method for the formation of 2D assemblies. As for the neat SLT triblock terpolymers only ill-defined, mixed micellar structures were obtained under CDSA conditions, we speculated that the addition of a PLLA homopolymer might promote crystallization to obtain defined core-crystalline micelles. To this end, a PLLA₆₄ homopolymer was synthesized (details on the synthesis can be found in the Supporting Information, **Scheme S5.2**, **Figure S5.11**). For the co-crystallization experiments a similar approach as described above was chosen. First, SLT-1 and PLLA₆₄ were dissolved separately in DCM ($c = 10 \text{ g L}^{-1}$) and the solutions were mixed in a 1:1 volumetric ratio, that is, the content of the PLLA homopolymer in the mixture is 50 wt%. This will be denoted as SLT-1 + PLLA₆₄ (50 wt%) in the following, giving the PLLA₆₄ weight fraction in brackets. After a mixing time of 15 min the DCM solution ($V = 300 \text{ }\mu\text{L}$) was added drop-wise to CH ($V = 2.7 \text{ mL}$) under moderate stirring (400 rpm), resulting in a micelle dispersion in CH/DCM (9/1 (v/v)) and a concentration of $c = 1 \text{ g L}^{-1}$. After stirring for 1 min the dispersion was aged at $T = 25 \text{ }^{\circ}\text{C}$ for

5 d without stirring. Subsequently, DCM was removed by evaporation over 4 h followed by refilling with CH to restore the initial concentration ($c = 1 \text{ g L}^{-1}$). Directly upon addition of the blend solution to CH the dispersion turned turbid, indicating the formation of larger sized micellar assemblies which tend to settle to the bottom of the vial. However, they can be redispersed easily by gentle shaking by hand. DLS displays a narrow size distribution and an apparent hydrodynamic diameter of $D_{h,app} = 1300 \pm 200 \text{ nm}$, confirming the formation of larger assemblies (**Figure 5.3A**). TEM and scanning electron microscopy (SEM) reveal the formation of round-shaped, platelet-like micelles, most of them featuring twists and multilayered step-like structures (**Figure 5.3B, S5.12**). Notably, platelets with an overall smaller size show fewer or no additional layers, indicating that the defects occur statistically. For size evaluation the area of 130 platelets was measured and converted to the equivalent diameter assuming a perfect spherical cross-section, resulting in an average size of $1.60 \pm 0.84 \mu\text{m}$. The respective histogram indicates a bimodal size distribution, which is attributed to the presence of the smaller single-layered platelets (**Figure S5.13**).

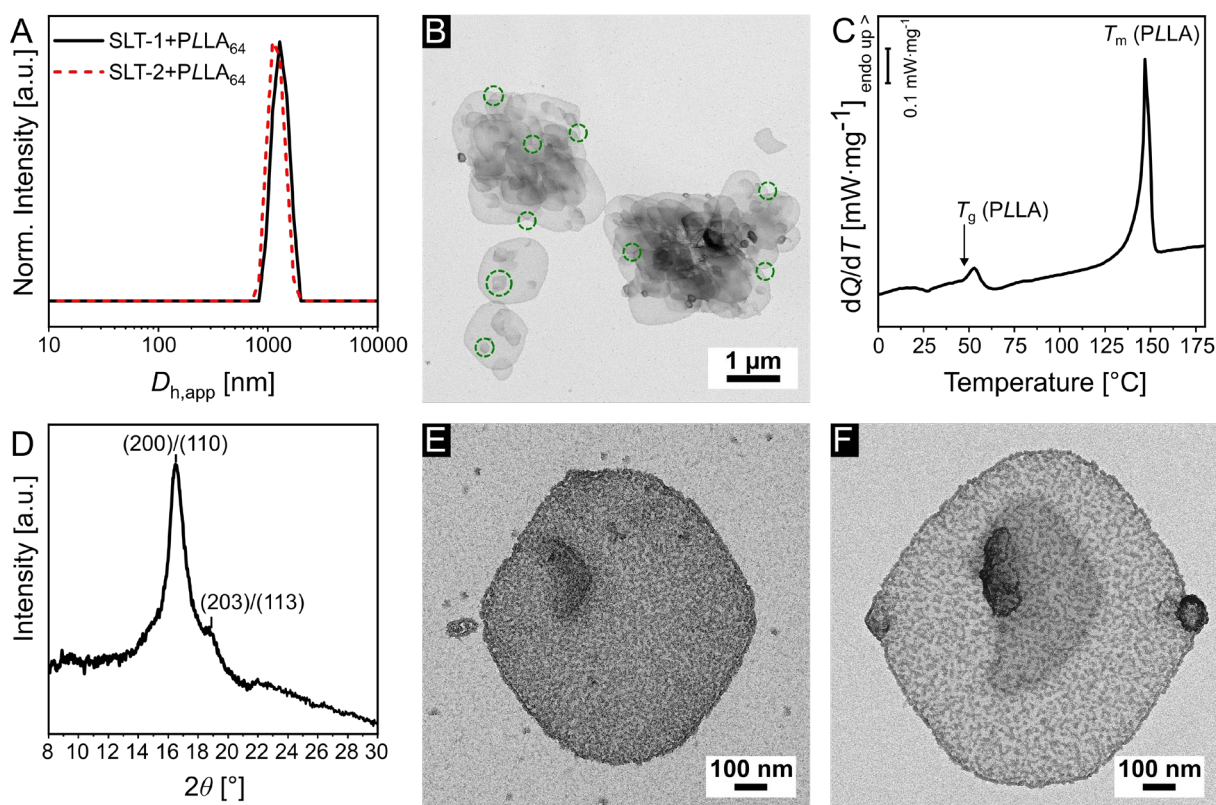


Figure 5.3 (A) Hydrodynamic diameter distributions from DLS for SLT-1 + PLLA₆₄ (50 wt%) and SLT-2 + PLLA₆₄ (50 wt%) micelles in CH ($c = 1 \text{ g L}^{-1}$). (B) TEM micrograph of the corresponding platelet micelles. The green circles indicate selected twisted and multilayered areas. (C) DSC 1st heating trace and (D) WAXS profile of the freeze-dried micelle dispersion. High magnification TEM micrographs of single platelets: (E) SLT-1 + PLLA₆₄ (50 wt%) and (F) SLT-2 + PLLA₆₄ (50 wt%) micelles with a patchy PS/PtBMA corona. PS was selectively stained with RuO₄ and appears dark.

The formation of 3D twisted platelet micelles is attributed to the co-crystallization of the PLLA₆₄ homopolymer and the SLT triblock terpolymer. This assumption is supported by DSC of the freeze-dried dispersion, showing a pronounced melting endotherm in the first heating trace with a peak melting temperature of $T_m = 147\text{ }^{\circ}\text{C}$ (**Figure 5.3C**). The degree of crystallinity was determined to $\alpha = 41\%$. Wide-angle X-ray scattering (WAXS) was used to probe the crystal structure of the PLLA core. The WAXS profile shows broad Bragg peaks at $2\theta = 16.5^{\circ}$ and 19° , corresponding to the crystal planes with Miller indices of (200)/(110) and (203/113), respectively (**Figure 5.3D**).⁷⁸ The position of the most intense Bragg peak at $2\theta = 16.5^{\circ}$ indicates that the PLLA *a*-phase (typically $2\theta = 16.7^{\circ}$) was preferentially formed under the employed CCDSA conditions. This is reasonable, as for low molecular weight PLLA the *a*-form is favored ($\bar{P}_n < 6000\text{ g mol}^{-1}$ for employed SLT-1 and PLLA₆₄).⁷⁸ However, as the Bragg peaks are rather broad an unambiguous distinction from the PLLA *d*-phase (typically $2\theta = 16.3^{\circ}$) is not possible.

Notably, the high-magnification TEM micrograph depicted in **Figure 5.3E** shows that the surface of the twisted platelet micelles is characterized by a heterogenous distribution of nanometer sized PS (dark, selectively stained with RuO₄) and PtBMA (bright) patches. The patchy structure of the micelle corona is attributed to the strong incompatibility of the corona forming PS and PtBMA blocks (Flory-Huggins interaction parameter: $\chi = 0.08\text{--}0.10$).⁷⁹ Interestingly, the patchy structure is similar to the surface patterns found for ultrathin triblock terpolymer films, where the middle block selectively adsorbs on the substrate surface.⁸⁰ The patchy surface structure of the platelets can be tailored by the SLT triblock terpolymer composition, as exemplified for SLT-2 (S₁₆₉L₉₆T₂₀₀). CCDSA of SLT-2 + PLLA₆₄ (50 wt%) was conducted under identical conditions as described above. The overall shape and size of the twisted platelet micelles is comparable as deduced from the TEM micrographs in **Figures 5.3F**, **S5.14** and DLS ($D_{h,app} = 1200 \pm 200\text{ nm}$, **Figure 5.3A**), respectively. However, the appearance of the patchy surface is altered, appearing brighter with an increased distance between the dark PS patches. This can be attributed to the PtBMA corona block being significantly longer compared to the PS block. Accordingly, the PtBMA weight fraction in the soluble corona is with 62 wt% significantly higher compared to that of the patchy platelet micelles prepared with SLT-1 (51 wt% PtBMA in corona). The nature of these 3D twisted assemblies will be addressed later on at the end of this section.

The morphology of the twisted patchy platelet assemblies formed by CCDSA of SLT-1 + PLLA₆₄ (50 wt%) was also confirmed by atomic force microscopy (AFM). The corres-

ponding topography images shown in **Figure 5.4A,B** (additional AFM data are provided in **Figure S5.15**) resemble the structures found in the TEM studies (**Figure 5.3B, S5.12**).

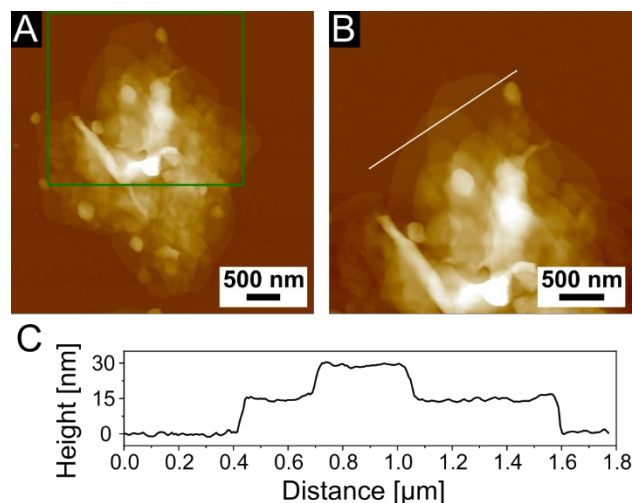


Figure 5.4 (A, B) AFM topography images of a twisted patchy SLT-1 + PLLA₆₄ platelet micelle assembly and (C) the corresponding height profile taken at the position indicated by a line in (B). The green box in (A) marks the position, where the higher magnification image in (B) has been acquired; for (A) $\Delta z = 600$ nm and for (B) $\Delta z = 500$ nm.

We have estimated the thickness of the crystalline PLLA platelet cores using the height profile extracted from the AFM topography image (**Figure 5.4C**). The height profile features distinct steps of 14 - 15 nm on average that correspond to the thickness of the stacked platelet micelles in the assemblies. Typically, the fold length for PLLA bulk crystallization is ≈ 32 repeating units, corresponding to a crystallite thickness of about 10 nm.^{81–83} Hence, taking the contribution of the amorphous PS and *Pt*BMA corona blocks at the fold surface into account, it can be assumed that the PLLA block in SLT-1 (S₁₅₆L₈₂T₁₁₅) has to fold once or twice and the PLLA₆₄ chains have to fold once upon CCDSA to adapt an overall thickness of about 14 - 15 nm. It is noted that the patchy structure of the corona is not discernable in the respective phase contrast images (**Figure S5.15A,C**), probably due to the similar glass transitions temperatures of PS and *Pt*BMA resulting in an insufficient contrast in stiffness.

Next, we studied the influence of aging time and stirring speed on the micelle morphology. To this end, the combination of SLT-1 with 50 wt% PLLA₆₄ was used as a standard system. The aging time between the addition of the mixed polymer solution in DCM to CH and the final removal of DCM was varied between 1, 3 and 5 days. The immediate occurrence of turbidity after the addition of the DCM mixture to CH suggests that the micelle formation is a rapid process. However, the amount of remaining dissolved SLT unimers (or small, non-crystalline micellar assemblies) might be influenced by the aging time. DLS reveals narrow size

distributions with comparable hydrodynamic diameters ($D_{h,app} \approx 1200$ nm) irrespective of the employed aging time (**Figure S5.16A**). This is underlined by TEM, showing twisted platelet micelles of comparable size and morphology (**Figure S5.16B-D**). However, in TEM micrographs taken at higher magnification ill-defined small micellar assemblies can be noticed for 1 and 3 days aging time, which most probably arise from non-crystallized SLT triblock terpolymer present in solution. These small structures were not detected in DLS due to the radii dependence of scattering intensity (proportional to R^6). For an aging time of 5 days smaller assemblies are hardly visible and, thus, the aging time was fixed to 5 days for the following experiments. Notably, twisted platelets are already present when the sample for TEM was prepared directly from the CH/DCM mixture, indicating that the formation of the twisted superstructures does not arise from the removal of DCM (**Figure S5.17**).

One major parameter influencing the micelle size is the number of nuclei formed during the initial stages of the co-crystallization process. This number is mainly affected by the stirring speed during the addition of the DCM mixture to CH. A higher stirring speed should result in more nuclei and, thus, smaller micelle sizes and vice versa. An increase of the stirring speed to 1000 rpm had no effect, as DLS and TEM analyses showed no difference compared to the moderate speed of 400 rpm employed before (**Figure S5.18A,B**). However, using a significantly lower stirring speed of 100 rpm resulted in a distinct change in micelle size and shape. The autocorrelation function obtained by DLS shows a two-step decay with longer decay times, indicating the presence of larger assemblies (**Figure S5.18C**). As the complex decay behavior hinders reliable size distribution analysis using the standard DLS software only the autocorrelation function is presented. TEM analysis reveals that particles of significantly larger sizes (over 5 μ m) were formed (**Figure S5.18D**). The larger particles exhibit a rather complex multi-layer structure being less defined compared to the twisted platelet micelles obtained at 400 rpm, likely caused by insufficient mixing at lower stirring speeds. Based on these results it was decided to keep the stirring speed unchanged at 400 rpm for the following experiments.

Our results show that crystallization is strongly hindered for the neat SLT triblock terpolymers and only CCDSA with a PLLA homopolymer leads to the formation of defined core-crystalline micelles. Hence, we assume that the PLLA homopolymer first forms active nuclei that can further induce co-crystallization of the SLT triblock terpolymer. In addition, co-crystallization with PLLA homopolymer reduces the grafting density of PS and PtBMA corona chains at the fold surface of the growing patchy core-crystalline platelets. This reduces steric shielding at the crystal growth front, favoring the attachment of SLT triblock terpolymer unimers. Hence, the fraction of PLLA employed in CCDSA should play a decisive role. We have systematically

varied the fraction of PLLA₆₄ homopolymer between 1 and 60 wt%. The size distributions from DLS are bimodal for PLLA₆₄ fractions below 30 wt%, showing significantly smaller structures with $D_{h,app} \approx 35$ nm next to larger assemblies being several 100 nm in size (**Figure S5.19**). The exact ratio of smaller to larger structures cannot be extracted from DLS due to the radii dependence of scattering intensity, but the peak at $D_{h,app} \approx 35$ nm decreases with increasing PLLA content and vanishes completely for PLLA₆₄ fractions ≥ 30 wt%. This indicates that the smaller structures diminish or even disappear at sufficiently high PLLA₆₄ fractions. Notably, the size of the smaller structures is very close to the size of the Janus micelles formed upon self-assembly of the neat SLT-1 triblock terpolymer in CH ($D_{h,app} = 37 \pm 10$ nm, **Figure 5.2A**). This might hint to the formation of Janus micelles as side product in CCDSA at low PLLA₆₄ fractions. This is confirmed by TEM, revealing the presence of small, spherical micelles with a Janus-type corona structure (**Figure 5.5**). From the TEM micrographs it appears that the fraction of Janus micelles decreases with increasing PLLA₆₄ content and are hardly detectable at 50 and 60 wt% (**Figure 5.3B, S5.20**). The morphology of the larger sized structures also changes with the PLLA₆₄ fraction, giving some insights in the self-assembly mechanism. Small platelet-like micelles are formed at 1 wt% PLLA₆₄, from which cylindrical micelles protrude at the edges. The length and number of these cylindrical micelles, being attached to the central platelet, decrease with increasing PLLA₆₄ fraction and vanish at 30 wt% PLLA₆₄. At the same time, the size of the central patchy platelets increases, and twisted platelet-like structures emerge. A similar effect was described for CCDSA of PCL based block copolymers with PCL homopolymer.²⁰ A possible explanation for the observed structures at low PLLA fractions (< 10 wt% PLLA) is that in the initial stage platelet-like micelles are formed by co-crystallization of SLT-1 and PLLA₆₄. These can act as seeds for the epitaxial crystallization of the remaining SLT-1 unimers, forming the protruding cylindrical micelles. Co-crystallization is evidenced by the patchy corona structure of the formed platelets and the observation that neat PLLA₆₄ does not form defined platelet-like structures employing the same assembly conditions (**Figure S5.21**).

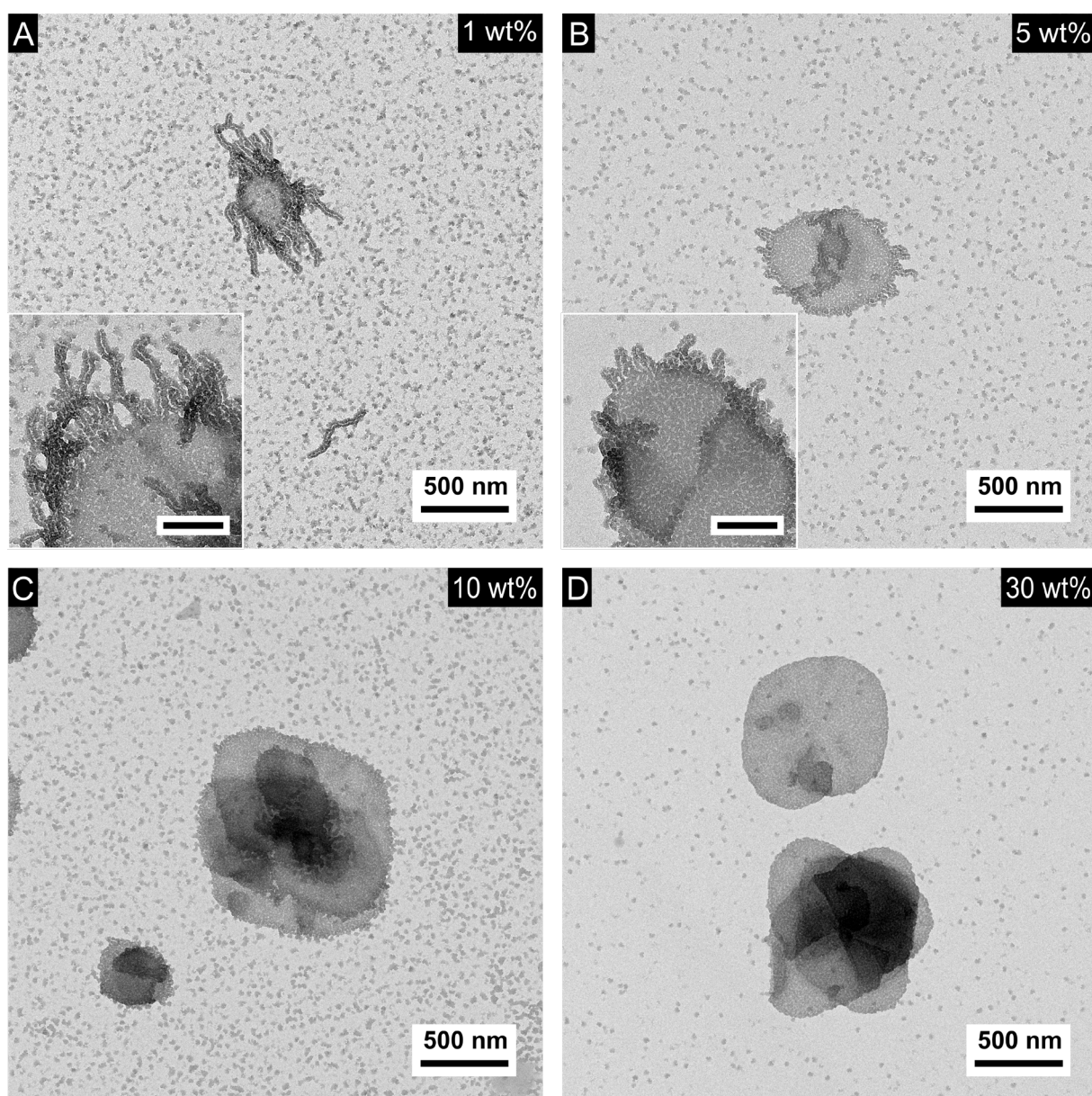


Figure 5.5 TEM micrographs of a SLT-1 + PLLA₆₄ micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$) with different fractions of PLLA₆₄ in the mixture. (A) 1 wt%, (B) 5 wt%, (C) 10 wt% and (D) 30 wt% (Scale bar insets = 200 nm). PS was selectively stained with RuO₄ and appears dark.

As under the employed conditions crystallization for neat SLT-1 is strongly hindered due to steric shielding of the PLLA middle block by the soluble PS and *Pt*BMA corona blocks, only a certain fraction can be incorporated in the protruding cylindrical micelles. Simultaneously, the remaining SLT-1 forms amorphous Janus micelles, where the confinement within the micellar core prevents further crystallization. This is consistent with the observation that for neat SLT-1 only a certain fraction of cylindrical micelles is formed under identical self-assembly conditions, whereby amorphous Janus micelles represent the main fraction (**Figure S5.7**). Accordingly, with increasing PLLA₆₄ fraction a larger amount of SLT-1 will be incorporated in the platelet-like micelles by co-crystallization in the early stage. Concomitantly, the number

and length of the cylindrical “grafts” decrease and finally disappear at 30 wt% PLLA₆₄. DLS (**Figure S5.19**) shows a rather broad monomodal size distribution ($D_{h,app} = 900 \pm 200$ nm) for the sample with 30 wt% PLLA₆₄ and the structure of the twisted platelet micelles observed by TEM (**Figure 5.5D**) is nearly identical to that observed for 50 wt% PLLA₆₄ (**Figure 5.3B,E**). However, amorphous Janus micelles can still be recognized, showing that SLT-1 was not completely incorporated during co-crystallization. Complete incorporation can be achieved by further increasing the PLLA₆₄ fraction to 50 and 60 wt%. Here, only 3D twisted platelet micelles, being similar in size and shape, were formed (**Figure 5.3B, S5.20**).

An important parameter that has not been considered thus far is the crystallization rate. Since the PLLA homopolymer drives the crystallization process, this rate might be modulated by varying its degree of polymerization. With decreasing degree of polymerization the solubility increases, slowing down the crystallization kinetics. O'Reilly, Dove and coworkers have shown in CDSA studies on PLLA based block copolymers that 2D platelet-like micelles are favored over cylinders when the soluble corona block is significantly larger than the crystallizable PLLA block (low solvophobic block fraction), or for shorter PLLA blocks at fixed corona/core ratio. This was attributed to a better solubility, which lead to a slower crystallization and formation of well-defined diamond-shaped platelets.^{84–86} Hence, we speculated whether a shorter PLLA₃₄ homopolymer might alter the structure of the micellar assemblies formed by CCDSA with SLT-1. To ensure comparable preparation conditions, again a PLLA₃₄ fraction of 50 wt% and an aging time of 5 days were used. In contrast to the experiment with PLLA₆₄, the dispersion showed a much stronger turbidity directly after the addition of the DCM mixture to CH, indicating the formation of larger assemblies. Time-dependent light scattering experiments were conducted to evaluate the crystallization kinetics, comparing the evolution of the scattering intensity in the first 2 h after the addition (**Figure S5.22**). For the dispersion prepared with PLLA₆₄ the scattering intensity reached a constant high value right at the beginning, suggesting a rapid formation of the twisted platelet-like assemblies. In contrast, for PLLA₃₄ a further increase in scattering intensity was observed over the tracked 2 h, indicating a slower growth. SEM and TEM analyses reveal the formation of patchy platelets that stack together in *z*-direction to form defined 3D pyramidal structures (**Figure 5.6A,B, S5.23**). Interestingly, the edges of the platelets are much sharper and the platelets show a more symmetric lozenge-shape compared to the platelets formed when the longer PLLA₆₄ was used (**Figure 5.3, S5.12**), which might be attributed to the slower assembly kinetics. The patchy surface structure of the platelets becomes obvious in the higher magnification image shown in **Figure 5.6C**.

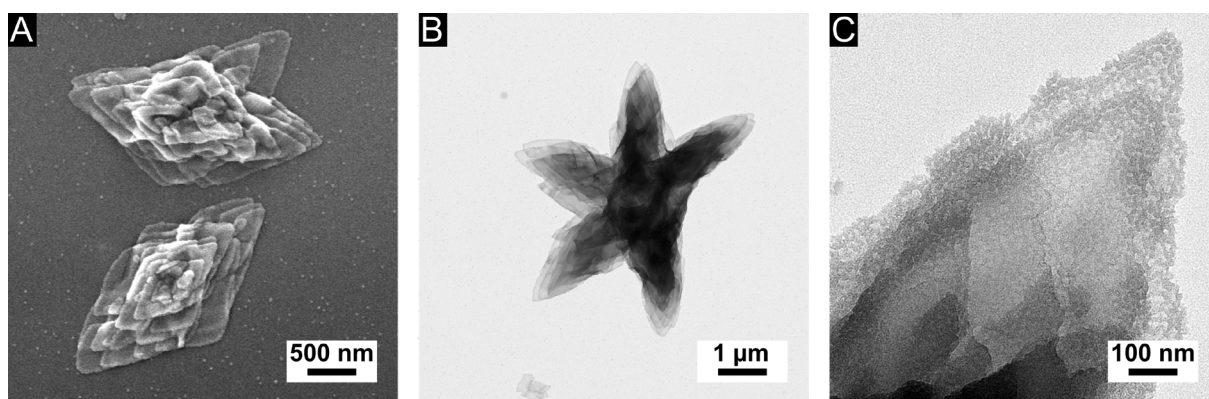


Figure 5.6 (A) SEM image and (B, C) TEM micrographs of 3D pyramidal structures composed of stacked patchy platelets, which were prepared by CCDSA of SLT-1 + PLLA₃₄ (50 wt%) in CH. PS appears bright in SEM and dark in TEM due to selective staining with RuO₄ vapor.

The pyramidal structure of the SLT-1 + PLLA₃₄ assemblies was confirmed by AFM (**Figure S5.24A,B**) and from the respective height profiles (**Figure S5.24C,D**) a platelet thickness of about 14 nm on average can be extracted, which is very close to the value (14 – 15 nm) observed for SLT-1 + PLLA₆₄ (**Figure 5.4C**). Accordingly, it can be assumed that the PLLA block of SLT-1 (S₁₅₆L₈₂T₁₁₅) has to fold once or twice upon CCDSA, whereby the PLLA₃₄ chains do not fold and are incorporated in the stretched conformation (fold length of 32 units corresponds to ≈ 10 nm, cf. discussion on **Figure 5.4C**). In addition, the WAXS profile of the freeze-dried SLT-1 + PLLA₃₄ (50 wt%) dispersion also shows Bragg peaks at $2\theta = 16.5^\circ$ and 19° (**Figure S5.24E**), revealing that the crystal structure was not altered when a shorter PLLA₃₄ homopolymer was used.

Similar stacked, pyramidal superstructures were also found in CCDSA of PCL or PFS based block copolymers with the respective homopolymers, conjugated block copolymers, polymerization-induced CDSA of rod-coil block copolymers, diblock copolymers with an asymmetric PLA stereoblock, or crystalline inclusion complexes of block copolymers.^{20,40,41,87–89} Such structures are also frequently formed in the crystallization of homopolymers,^{90,91} whereby screw dislocations or unbalanced stresses at the fold surfaces are the main driving forces for their formation. Concerning the 3D assemblies of twisted or stacked patchy platelets in this study, most of the single patchy platelets exhibit randomly located defects, where the platelet is twisted (**Figure S5.12**). From these defects, new platelets emerge, growing in a different orientation. This indicates that twisting induced by screw dislocations or anisotropic stresses at the fold surface of the platelets is also the driving force for the formation of 3D platelet micelle assemblies in CCDSA of SLT with PLLA.

5.2.4 Interfacial activity of twisted patchy platelet micelles

To evaluate the potential of the twisted patchy platelet micelles as particulate surfactants, their interfacial activity at the CH/water interface was investigated employing the pendant-drop method. A SLT-1 + PLLA₆₄ (50 wt%) dispersion in CH was diluted to a concentration of $c = 0.1 \text{ g L}^{-1}$ and the interfacial tension was measured in dependence of time. For comparison, the interfacial activity of SLT-1 Janus micelles prepared by direct dissolution in CH was also examined at identical concentration. **Figure 5.7A** reveals a significant decrease of the quasi-equilibrium interfacial tension, determined as average over the last 30 min of the measurement, to $\gamma = 24.8 \pm 0.1 \text{ mN m}^{-1}$ for the twisted patchy platelet micelles ($\gamma = 43.3 \pm 0.1 \text{ mN m}^{-1}$ for pristine CH/water interface). Hence, the patchy platelet micelles show an excellent interfacial activity, which is attributed to the synergistic combination of an amphiphilic corona (PS/PtBMA patches) with the Pickering effect of (nano)particles. In comparison, SLT-1 Janus micelles show a slightly better performance and γ is further reduced to $23.7 \pm 0.1 \text{ mN m}^{-1}$. This might arise from the fact that at identical mass concentration ($c = 0.1 \text{ g L}^{-1}$) the number of patchy platelets in the dispersion is significantly smaller due to their larger size.

In addition, the patchy platelets were compared to spherical micelles with a patchy PS/PtBMA corona, prepared by stereocomplex-driven self-assembly (SCDSA), as reported in our previous work.⁷¹ These spherical patchy micelles feature comparable lengths of the soluble corona blocks, ruling out any effects of corona width on the interfacial properties. Notably, compared to patchy platelets their interfacial activity is lower as they reduce the interfacial tension to only $\gamma = 28.0 \pm 0.1 \text{ mN m}^{-1}$. This is contrary to the behavior found for Janus particles, as spherical Janus micelles exhibit a significantly higher interfacial activity than Janus discs.^{92,93} This was attributed to the fact that some of the Janus discs adsorb in an unfavorable orientation at the CH/water interface, that is, with the PS side facing the water phase. This further on leads to desorption/readsorption processes or stacking of the discs, both decreasing the interfacial activity. In contrast, for the patchy platelets both sides are identical and the amphiphilic Janus structure is formed “in situ” at the liquid-liquid interface by selective collapse/swelling of the respective insoluble/soluble corona patches. This results in the observed improved interfacial activity of the patchy platelets with respect to that of patchy spherical micelles.

As a representative example, the emulsification performance of the twisted patchy platelet micelles was tested in a CH/water mixture (50/50 (v/v)), using a dispersion at $c = 1 \text{ g L}^{-1}$ (**Figure 5.7B**). Hereby, the emulsion phase settled at the bottom, with excess CH forming the upper layer, indicative of a water-in-oil (w/o) emulsion driven by the density difference between

water ($\rho = 1.00 \text{ g cm}^{-3}$) and CH ($\rho = 0.78 \text{ g cm}^{-3}$). This result is consistent with previous findings on emulsions stabilized by Janus particles.⁹⁴ The emulsion stabilized with the patchy platelet micelles was stable for several weeks, whereas the neat CH/water mixture demixed instantaneously after shaking. This underlines the excellent interfacial activity of the twisted patchy platelets. In addition, we have prepared fluorescently labelled patchy platelets to prove their preferential accumulation at the water-droplet/CH interface by fluorescence microscopy, following a similar procedure as reported previously.⁷¹ To this end, 10 wt% of the PLLA₆₄ homopolymer was replaced by a rhodamine B labelled PLLA₆₄-RB homopolymer in the preparation of SLT-1 + PLLA₆₄ (50 wt%) twisted patchy platelets (denoted as SLT-1 + PLLA₆₄/PLLA₆₄-RB (50 wt%)). Details on synthesis and characterization of PLLA₆₄-RB can be found in the Supporting Information (**Scheme S5.3, Figure S5.25**). The overall shape of the twisted platelets (and their assemblies) as well as the patchy structure of the platelet corona is comparable to the non-labelled SLT-1 + PLLA₆₄ (50 wt%) patchy platelets, pointing to a homogeneous incorporation of PLLA₆₄-RB in the micelles (**Figure S5.26**). **Figure 5.7C** shows the respective fluorescence microscopy image of the water/CH mixture emulsified with the fluorescently labelled SLT-1 + PLLA₆₄/ PLLA₆₄-RB (50 wt%) platelet micelles. The bright rim surrounding the dispersed water droplets clearly shows the expected preferential accumulation of the patchy platelets at the water droplet/CH interface.

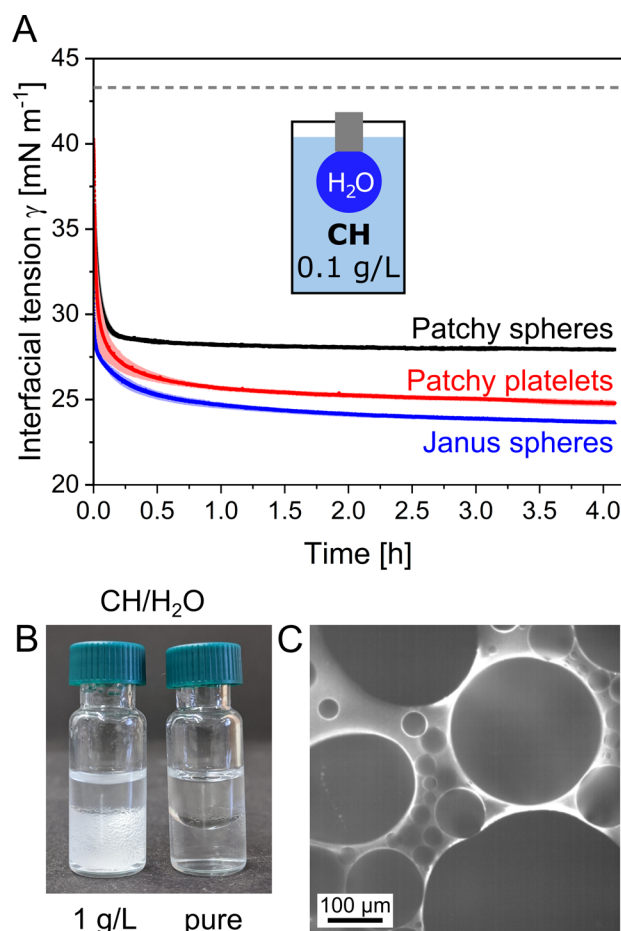


Figure 5.7 (A) Interfacial tension isotherms of spherical patchy micelles formed by SCDSA of PS₁₆₉-*b*-P_{LLA}₁₀₆ and PDLA₁₀₀-*b*-P_{tBMA}₁₃₂ diblock copolymers, twisted patchy platelet micelles formed by CCDSA of SLT-1 + P_{LLA}₆₄ (50 wt%) and spherical SLT-1 Janus micelles at the CH/water interface ($c = 0.1 \text{ g L}^{-1}$ in CH). The shown isotherms correspond to the average of three consecutive measurements and the respective standard deviations are displayed as transparent areas (discernable at short measurement times). The dashed grey line is the interfacial tension at the pristine CH/water interface measured as reference. (B) CH/water mixture emulsified with patchy SLT-1 + P_{LLA}₆₄ (50 wt%) platelet micelles ($c = 1 \text{ g L}^{-1}$ in CH). The photograph on the right corresponds to the respective pure solvent mixture that separated immediately after shaking. (C) Fluorescence microscopy image of a CH/water mixture emulsified with fluorescently labelled SLT-1 + P_{LLA}₆₄/ P_{LLA}₆₄-RB (50 wt%) patchy platelet micelles ($c = 1 \text{ g L}^{-1}$ in CH). 10 wt% of the added P_{LLA}₆₄ was replaced by fluorescently labelled P_{LLA}₆₄-RB.

5.3 Conclusion

This work demonstrates the straightforward preparation of twisted platelet micelles with a non-concentric nanometer-sized patchy surface pattern by CCDSA of PS-*b*-P_{LLA}-*b*-P_{tBMA} (SLT) triblock terpolymers with P_{LLA} homopolymers. The patchy platelet micelles further assemble to twisted 3D platelet structures or stacked pyramidal structures, depending on the chain length of the employed P_{LLA} homopolymer. Thermal annealing of the neat SLT triblock terpolymers in cyclohexane, a selective solvent for the PS and P_{tBMA} corona blocks, yields spherical

micelles with an amorphous PLLA core and a Janus-type PS/PtBMA corona. The formation of Janus micelles with an amorphous core is attributed to the strongly hindered crystallization of the PLLA middle block in the SLT triblock terpolymers. In contrast, blending of SLT with PLLA homopolymer induces co-crystallization, resulting in twisted 2D platelet micelles with a non-concentric patch-like corona segregation. The formation of 3D multilayer structures, consisting of twisted patchy platelets, is most likely driven by screw-dislocations or unbalanced stresses at the fold interface during crystal growth. Interestingly, the twisted patchy platelet micelles show a high interfacial activity and were successfully tested as stabilizers for emulsions. The interfacial activity of the patchy platelets was found to be significantly higher with respect to that of spherical patchy micelles, which is in contrast to the behavior of Janus particles. For the latter, Janus discs feature a lower interfacial activity compared to spherical Janus micelles. This highlights the potential of patchy platelets micelles as particulate surfactants for emulsion stabilization or blend compatibilization.

Our work shows that core-crystalline patchy platelet micelles are accessible by CCDSA of triblock terpolymers with the respective crystallizable homopolymer, even when crystallization of the middle block is strongly hindered for the neat triblock terpolymer. This opens a broad platform for the construction of patchy platelets by CCDSA, which can be easily transferred to other triblock terpolymers with “potentially” crystallizable middle blocks. The unique structure of the patchy corona and the excellent interfacial activity opens future applications not only as particulate surfactants or compatibilizers but also as template for the immobilization of nanoparticles in heterogeneous catalysis.

Associated Content

Supporting Information. The Supporting Information is available free of charge at <http://pubs.acs.org>.

Materials, methods, experimental procedures, ^1H NMR spectra and SEC traces of polymers, DSC thermograms, DLS measurements, additional WAXS data and SEM, TEM and AFM micrographs.

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Supporting Information

Experimental Procedures and Methods

Materials. All chemicals were used as received unless otherwise noted. Ethylene oxide (Linde, 3.0) was stirred over calcium hydride (CaH_2) at 0 °C for 3 h before being transferred into a storage ampoule. Prior to use, ethylene oxide was additionally purified over *n*-butyllithium (*n*-BuLi) at 0 °C. Tetrahydrofuran (THF, 99.9%, extra pure, Thermo Scientific) for anionic polymerization was purified by successive distillation over CaH_2 and potassium and stored under nitrogen until use. Dichloromethane (DCM, $\geq 99.8\%$ stabilized with amylene, analytical reagent grade, Thermo Scientific) used for lactide polymerization was dried by distillation over CaH_2 . Styrene ($>99\%$, Sigma-Aldrich) was stirred over di-*n*-butylmagnesium (Bu_2Mg) under nitrogen and condensed into a storage ampoule. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, $>98\%$, TCI) was dried by distillation over CaH_2 . *D*- and *L*-lactide ($\geq 99.8\%$, PURASORB® D and L, Corbion, Amsterdam, The Netherlands) were recrystallized from toluene and stored under argon until use. Pyridine ($>99\%$, Carl Roth) was dried successively over potassium hydroxide (KOH, $>85\%$, Carl Roth) and CaH_2 and distilled prior to use. *tert*-Butyl methacrylate (*t*BMA, 98%, TCI) was passed through a column with basic aluminum oxide. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich) was distilled prior to use. *n*-Pentane (technical grade) was purified by distillation. Copper(I) chloride (Cu(I)Cl , 99%, Sigma-Aldrich) was stirred in glacial acetic acid for 6 h, washed with glacial acetic acid and ethanol and dried *in vacuo* for 24 h. Sulforhodamine B acid chloride (pure, Thermo Scientific), Bu_2Mg (1.0 M in heptane, Sigma-Aldrich), *sec*-butyllithium (*sec*-BuLi, 1.3 M in cyclohexane/hexane, Thermo Scientific), benzoic acid (p.a., AlppiChem), 2-hydroxyethyl 2-bromo*isobutyrate* (HEBiB, 95%, Sigma-Aldrich), α -bromo*isobutyryl bromide* (98%, Sigma-Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Sigma-Aldrich), CaH_2 (Merck), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, HPLC grade, Sigma-Aldrich), silver trifluoroacetate (AgTFA , $>99.9\%$, Sigma-Aldrich), deuterated chloroform (CDCl_3 , 99.8%, Deutero), ruthenium(III) chloride hydrate (ReagentPlus®, Sigma-Aldrich), sodium hypochlorite solution (NaOCl , 10 – 15 wt% in water, Thermo Scientific), acetic acid ($\geq 99.7\%$, analytical reagent grade, Thermo Scientific), cyclohexane (CH , $\geq 99.8\%$, analytical reagent grade, Thermo Scientific), and methanol (MeOH , $\geq 99.9\%$, analytical reagent grade, Thermo Scientific).

Synthesis of PS-*b*-PLLA. PS-*b*-PLLA diblock copolymers were prepared by a combination of living anionic polymerization and organo-catalyzed ring-opening polymerization as published elsewhere.¹ Briefly, hydroxy terminated polystyrene (PS-OH) was synthesized by living anionic polymerization of styrene in THF at $-70\text{ }^{\circ}\text{C}$ using *sec*-BuLi as initiator, followed by end-capping with ethylene oxide (Scheme S1A). PS-OH was then used as macroinitiator for the ring-opening polymerization of *L*-lactide in DCM employing the organobase DBU as a catalyst (Scheme S1B).

Representative NMR data: ^1H -NMR (300 MHz, CDCl_3): $\delta = 7.24\text{--}6.29$ (m, CH_{arom}), 5.15 (q, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$), 4.33 (q, $J = 7.1$ Hz, $-\text{COCH}(\text{CH}_3)\text{OH}$), 1.57 (d, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$) ppm.

Synthesis of PS-*b*-PLLA based ATRP macroinitiator. PS-*b*-PLLA-Br was synthesized as described in previous work by esterification of the hydroxy end-group of PS-*b*-PLLA with α -bromoisobutyryl bromide using pyridine and DMAP as catalyst (Scheme S1C).²

Representative NMR data: ^1H -NMR (300 MHz, CDCl_3): $\delta = 7.24\text{--}6.29$ (m, CH_{arom}), 5.15 (q, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$), 1.57 (d, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$) ppm.

Synthesis of PS-*b*-PLLA-*b*-PtBMA. PS-*b*-PLLA-*b*-PtBMA triblock terpolymers were synthesized by ATRP of *t*BMA in toluene at $60\text{ }^{\circ}\text{C}$ using PS-*b*-PLLA-Br as macroinitiator and $\text{Cu(I)Cl}/\text{PMDETA}$ as catalyst as described in more detail in a previous publication (Scheme S1D).²

Representative NMR data: ^1H -NMR (300 MHz, CDCl_3): $\delta = 7.24\text{--}6.29$ (m, CH_{arom}), 5.16 (q, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$), 1.57 (d, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$), 1.54 – 1.31 (m, $\text{C}(\text{CH}_3)_3$), 1.20 – 0.97 (m, CH_2CCH_3) ppm.

Synthesis of hydroxy terminated and fluorescently labelled PLLA homopolymers. PLLA homopolymers and PLLA₆₄-RB were synthesized as previously published.² Briefly, PLLA₃₂ and PLLA₆₄ were synthesized by organo-catalyzed ring-opening polymerization of *L*-lactide employing HEB*t*B as initiator and DBU as catalyst (Scheme S2). PLLA₆₄-RB was obtained by esterification of the hydroxy end-group with sulforhodamine B acid chloride (Scheme S3).

Representative NMR data: ^1H -NMR (300 MHz, CDCl_3): $\delta = 5.16$ (q, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$), 4.45 – 4.33 (m, $\text{OCH}_2\text{CH}_2\text{O}$, $\text{COCH}(\text{CH}_3)\text{OH}$), 1.92 (s, $\text{C}(\text{CH}_3)_2$), 1.57 (d, $J = 7.1$ Hz, $\text{COCH}(\text{CH}_3)\text{O}$) ppm.

Table S5.1 Molecular characteristics of the employed polymers.

Sample ^a	Integral a/b/e (Fig 1A) ^b	Composition [wt.%]	M_n^b [g mol ⁻¹]	$\bar{D}^c$
PLLA₃₄		LLA ₁₀₀	2 500	1.13
PLLA₆₄		LLA ₁₀₀	4 700	1.06
S₁₅₆-OH	-	S ₁₀₀	16 000	1.06
S₁₅₆L₈₂-OH	780/81/-	S ₇₃ L ₂₇	22 300	1.07
S₁₅₆L₈₂-Br	780/82/-	S ₇₃ L ₂₇	22 450	1.08
S₁₅₆L₈₂T₁₁₅ (SLT-1)	780/82/346	S ₄₂ L ₁₅ T ₄₃	38 700	1.12
S₁₆₉-OH	-	S ₁₀₀	17 600	1.06
S₁₆₉L₉₆-OH	845/95/-	S ₇₂ L ₂₈	24 500	1.06
S₁₆₉L₉₆-Br	845/96/-	S ₇₂ L ₂₈	24 600	1.10
S₁₆₉L₉₆T₂₀₀ (SLT-2)	845/96/601	S ₃₃ L ₁₃ T ₅₄	51 600	1.15

a) Indices denote the number averaged degree of polymerization. For PLLA the number corresponds to lactic acid repeating units.

b) Determined by ¹H NMR using $M_n(\text{PS}_{156}) = 16\,300$ g/mol and $M_n(\text{PS}_{169}) = 17\,550$ g/mol (from MALDI-ToF mass spectrometry) for internal signal calibration.

c) Determined by CHCl₃-SEC employing a PS calibration.

Preparation of spherical Janus-type micelles. The SLT triblock terpolymer was dispersed in cyclohexane (CH) at a concentration of $c = 1$ g L⁻¹. After gentle shaking (200 rpm, thermo shaker HLC MKR-13, Ditabis) at $T = 45$ °C for 2 h the dispersion was cooled to $T = 25$ °C (cooling rate: 1 K min⁻¹) and shaken for 16 h (200 rpm).

CDSA of neat SLT triblock terpolymers. In a 5 mL snap lid vial, equipped with a small magnetic stirring bar, a solution of the SLT triblock terpolymer in DCM (300 μL, $c = 10$ g L⁻¹) was added dropwise to CH (2.7 mL) while stirring (approximately 400 rpm), resulting in a micelle dispersion with a concentration of $c = 1$ g L⁻¹ and a final solvent ratio of CH/DCM = 9/1 (v/v). After subsequent stirring for 1 min, the dispersion was aged at room temperature without stirring for at least one day. The dispersion was opened to air to evaporate the DCM over 4 h. To restore the initial concentration CH was added to the remaining dispersion.

Preparation of patchy platelet micelles by crystallization-driven co-assembly (standard conditions). Separate solutions of the SLT triblock terpolymer and PLLA₆₄ homopolymer in DCM ($c = 10 \text{ g L}^{-1}$) were mixed together in the desired volumetric ratio. Exemplary, for a 1:1 ratio the content of PLLA homopolymer in the mixture is 50 wt%, which is denoted as SLT + PLLA₆₄ (50 wt%), giving the weight fraction of PLLA homopolymer in brackets. In a 5 mL snap lid vial, equipped with a small magnetic stirring bar, the obtained mixture (300 μL) was added dropwise to CH (2.7 mL) while stirring (approximately 400 rpm), resulting in a micelle dispersion with a concentration of $c = 1 \text{ g L}^{-1}$ and a final solvent ratio of CH/DCM = 9/1 (v/v). After subsequent stirring for 1 min, the dispersion was aged at $T = 25 \text{ }^{\circ}\text{C}$ without stirring for 5 days. The dispersion was opened to air to evaporate the DCM over 4 h. To restore the initial concentration CH was added to the remaining dispersion.

Fluorescently labelled patchy platelet micelles. Solutions of SLT-1, PLLA₆₄ and PLLA₆₄-RB in DCM ($c = 10 \text{ g L}^{-1}$) were mixed together in a 10:9:1 volumetric ratio (10 wt% of the PLLA₆₄ homopolymer was replaced by a rhodamine B labelled PLLA₆₄-RB homopolymer). The dispersion of fluorescently labelled micelles was prepared the same way as described above and is denoted as SLT + PLLA₆₄/PLLA₆₄-RB (50 wt%) micelles.

Preparation of SLT bulk films. Prior to bulk film preparation, the glass vial was hydrophobized by reacting with trimethylsilyl chloride. First, 50 mg of the SLT triblock terpolymer were dissolved in 1 mL of chloroform and stirred for 1 hour. The solution was then poured in the hydrophobized glass vial and the solvent was allowed to evaporate slowly over a period of 5 days. The bulk film was removed by breaking the vial after freezing in liquid nitrogen, followed by drying *in vacuo* for 24 h (20 mbar).

Proton Nuclear Magnetic Resonance (¹H NMR) Spectroscopy. The polymers were characterized by ¹H NMR spectroscopy (Bruker Ultrashield 300 spectrometer) using CDCl₃ ($\delta(\text{CHCl}_3) = 7.26 \text{ ppm}$) as solvent.

Size-Exclusion Chromatography (SEC). SEC measurements were performed with an Agilent 1200 Infinity system (Agilent Technologies, Santa Clara, CA, USA) equipped with a SDV gel precolumn (particle size = 5 μm , PSS, Mainz, Germany). CHCl₃-SEC was carried out with a SDV linear XL gel column (particle size = 5 μm) with porosity range from 10^2 to $10^5 \text{ \AA}$ (PSS,

Mainz, Germany) using CHCl_3 (HPLC grade) as eluent. The samples were measured at a flow rate of 0.5 mL min^{-1} at 23°C and a refractive index (RI) detector (1260 Infinity, Agilent Technologies, Santa Clara, CA, USA) was used. THF-SEC was performed with four SDV gel columns (particle size = $5 \mu\text{m}$) with porosity range from 10^2 to $10^5 \text{ \AA}$ (PSS, Mainz, Germany). THF (HPLC grade) was used as eluent and the samples were measured at a flow rate of 1.0 mL min^{-1} at 40°C . For detection a RI detector (Agilent Technologies, Santa Clara, CA, USA) or a variable wave-length detector (VWD, Agilent Technologies, Santa Clara, CA, USA) were used. Prior to analyses all samples were dissolved and filtered through a $0.2 \mu\text{m}$ PTFE filter. The SEC systems were calibrated with narrowly distributed PS standards (PSS calibration kit) and toluene (HPLC grade) was used as internal standard in all cases.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-ToF MS). MALDI-ToF MS was performed with a Bruker Daltonics autoflex maX (Bruker, Germany) equipped with a smartbeam-II solid state laser and operating in linear mode. The samples were prepared by the dried droplet method using DCTB as matrix and AgTFA as ionization agent. All components were dissolved in THF (HPLC grade) at a concentration of $c = 10 \text{ g L}^{-1}$ and mixed together in a volumetric ratio of matrix/sample/ionization agent = 20/5/1.

Differential Scanning Calorimetry (DSC). DSC measurements of the bulk samples and the freeze-dried micelles dispersions were performed on a Phoenix 204 F1 (Netzsch, Selb, Germany) using aluminum crucibles with pierced lids. Measurements were done under a nitrogen atmosphere within a temperature range of -20 to 200°C at a scanning rate of 10 K min^{-1} .

The degree of crystallinity α was determined with the following equation:

$$\alpha = \frac{\Delta H_m}{f_{\text{PLA}} \cdot \Delta H_m^0} \cdot 100\% = \frac{22 \text{ J g}^{-1}}{0.575 \cdot 93 \text{ J g}^{-1}} \cdot 100\% = 41\% \quad (1)$$

where ΔH_m is the measured enthalpy of fusion, ΔH_m^0 is the theoretical enthalpy of fusion of a 100% crystalline PLLA (93 J g^{-1})³ and f_{PLA} is the weight fraction of PLLA.

Dynamic Light Scattering (DLS). DLS measurements were performed using a Zetasizer Nano S (Malvern Panalytical, UK) instrument equipped with a He-Ne laser ($\lambda = 632.8 \text{ nm}$) and a detector placed at $\theta = 173^\circ$. Unless otherwise noted, the micelle dispersions were measured at a concentration of $c = 1.0 \text{ g L}^{-1}$ at 25°C in quartz glass cuvettes (10.0 mm path length), which were sealed with Teflon caps to prevent solvent evaporation. The data were evaluated using the

Malvern Zetasizer software (version 7.13) and the implemented distribution analysis fit option. The results are displayed as normalized intensity weighted size distributions, and the micelle sizes are reported as apparent hydrodynamic diameter ($D_{h,app}$) determined from the average of three replicate measurements. For the kinetic measurements, the derived count rate was reported as the theoretical value corresponding to 100% laser power with zero attenuation, expressed in kilocounts per second (kcps).

Transmission Electron Microscopy (TEM). The TEM measurements were carried out with a JEOL JEM-2200FS field emission TEM. The energy filtering transmission electron microscope (EFTEM) was operated at an acceleration voltage of 200 kV. Zero-loss filtered micrographs ($\Delta E \approx 0$ eV) were taken with a bottom mounted CMOS camera system (OneView, Gatan) and the images were processed with a digital image processing software (Digital Micrograph 3.11, Gatan). The diluted micelle dispersions ($c = 0.1 \text{ g L}^{-1}$, $V = 10 \text{ }\mu\text{L}$) were dropped on a carbon-coated copper grid and residual solvent was removed directly by blotting with a filter paper followed by drying of the coated copper grid in vacuo (24 h, $1 \cdot 10^{-5}$ mbar). The samples were stained for 7 min with RuO_4 vapor, which was formed in situ from RuCl_3 hydrate and an aqueous NaOCl solution. Afterwards, the samples were kept in a fume hood for at least 1 h to ensure the complete removal of any unreacted RuO_4 . The sizes of the twisted platelet micelles were determined with the software Fiji using the freehand selection tool or the implemented “Segment anything model” (SAMJ, Meta AI).⁴ To this end, the area of 130 platelet micelles from multiple positions were measured and converted to the respective equivalent diameter assuming a perfect spherical cross-section. For TEM investigation of the bulk morphologies, the sample was cut into ultrathin sections (cut thickness: 50–60 nm) at room temperature using a Leica UC7 ultramicrotome (Leica, Wetzlar, Germany).

Scanning Electron Microscopy (SEM). SEM measurements were done with a Zeiss Ultra Plus at an acceleration voltage of 1–3 kV and with a SE2 detector. Samples of the micelle dispersions were measured on the carbon-coated copper grids used in TEM measurements, which were attached to electrically conductive carbon adhesive discs. The samples were sputtered with a thin layer of platinum of around 2 nm with a Cressington sputter coater 208HR.

Atomic Force Microscopy (AFM). AFM measurements were carried out with a Dimension Icon (Bruker, Billerica, MA, USA) equipped with a Nanoscope V controller under ambient conditions. For the acquisition of the TappingMode AFM images OMCL-AC160TS-R3

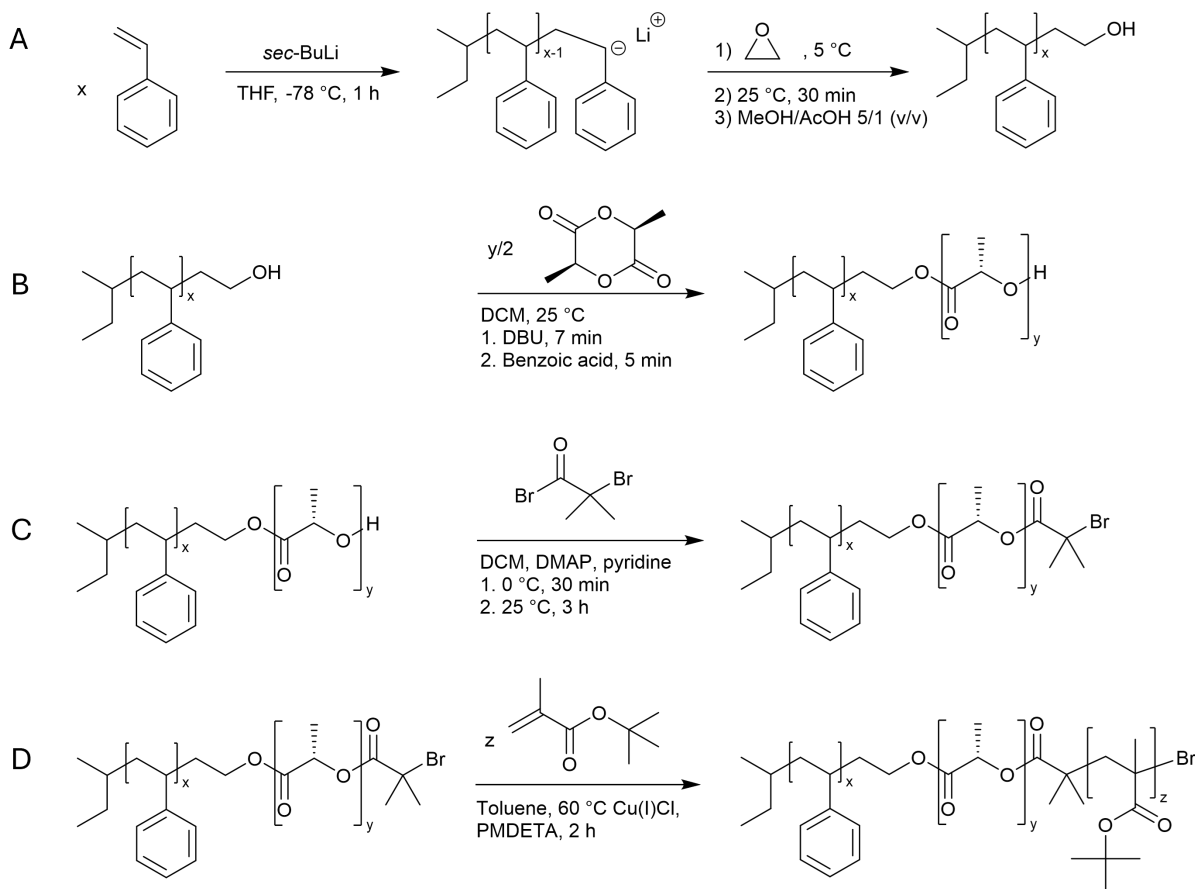
cantilevers (Olympus Corporation, Shinjuku, Tokyo, Japan) with a typical resonance frequency of 300 kHz and a nominal spring constant of 26 N/m were used. A target amplitude of 500 mV was applied, which resulted in a drive amplitude of approximate 150 mV. Images of different scan sizes were acquired with 512 x 512 pixels. AFM height and phase images were processed and evaluated using the NanoScope Analysis software (version 1.8, Bruker, Billerica, MA, USA).

Interfacial Tension measurements were conducted employing a DS25 from Krüss. For the measurements, a dispersion of the micelles in CH ($c = 0.1 \text{ g L}^{-1}$) was placed in a cuvette (10 mm, QS) and the interfacial tension was determined with the software “Advanced Drop Shape Analysis” (version 1.6.2.0) and the method “Pendant Drop” using a droplet volume of $V = 16 \text{ }\mu\text{L}$ (deionized water, canula diameter = 0.8 mm). The interfacial tension isotherms are displayed as the average of three measurements with standard deviations displayed as transparent areas. The quasi-equilibrium interfacial tensions were determined as average over the last 30 min of the respective measurement, where the interfacial tension levels off. The interfacial tension of the pristine water/cyclohexane interface was determined to $\gamma = 43.3 \pm 0.1 \text{ mN m}^{-1}$.

Fluorescence Microscopy. Fluorescence imaging was performed on a MT200 imaging system (PicoQuant) built around an Olympus IX73 inverted microscope. Samples were illuminated with an Excelitas X-Cite 120 metal-halide lamp (dichroic beamsplitter HC-BS484 and excitation filter HC440/SP, both AHF). The emitted light was collected through a plan achromat 20x objective (NA = 0.40; Olympus), passed through an emission filter HC458LP (AHF) and recorded with an wave-length insensitive iDS CMOS camera. Image acquisition and instrument control were performed using the SymphoTime64 software (PicoQuant).

Wide-Angle X-Ray Scattering (WAXS). WAXS measurements were conducted with an Incoatec (Geesthacht, Germany) I μ S equipped with a microfocus source and a monochromator for CuK α radiation ($\lambda = 1.5406 \text{ }\text{\AA}$). 2D scattering patterns were recorded with a Vantec 500 2D detector (Bruker AXS, Karlsruhe). The freeze-dried samples were placed in a 1 mm thick plate, covered on both sides with a Kapton film. The data were collected in transmission mode in air. The respective 1D intensity profiles were generated by radial integration of the 2D scattering patterns and the background was subtracted afterwards, which allows a better fine tuning of background intensity.

Supporting Figures



Scheme S5.1 Synthesis of (A) PS-OH, (B) PS-*b*-PLLA, (C) PS-*b*-PLLA-Br and (D) PS-*b*-PLLA-*b*-PtBMA.

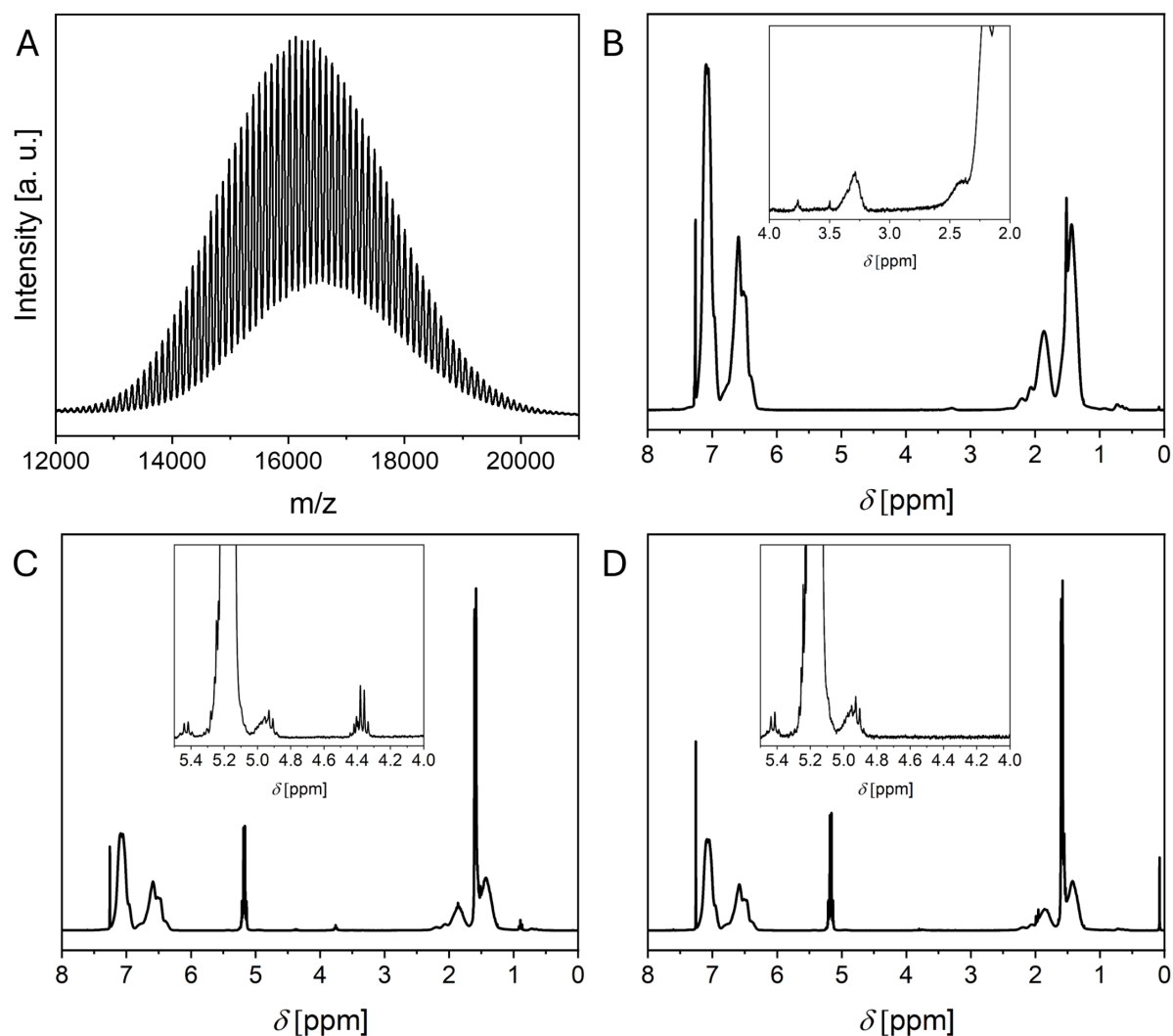


Figure S5.1 Characterization of SLT-1 ($S_{156}L_{82}T_{115}$) precursors. (A) MALDI-ToF mass spectrum of the PS_{156} -OH precursor (matrix: DCTB, salt: AgTFA). 1H NMR ($CDCl_3$, 300 MHz) spectra of (B) PS_{156} -OH, (C) PS_{156} -*b*- $PLLA_{82}$ and (D) PS_{156} -*b*- $PLLA_{82}$ -Br. Successful end-group functionalization was confirmed by the downfield shift of the methine proton signal of the terminal repeating unit ($\delta = 4.3$ ppm) after the esterification reaction.

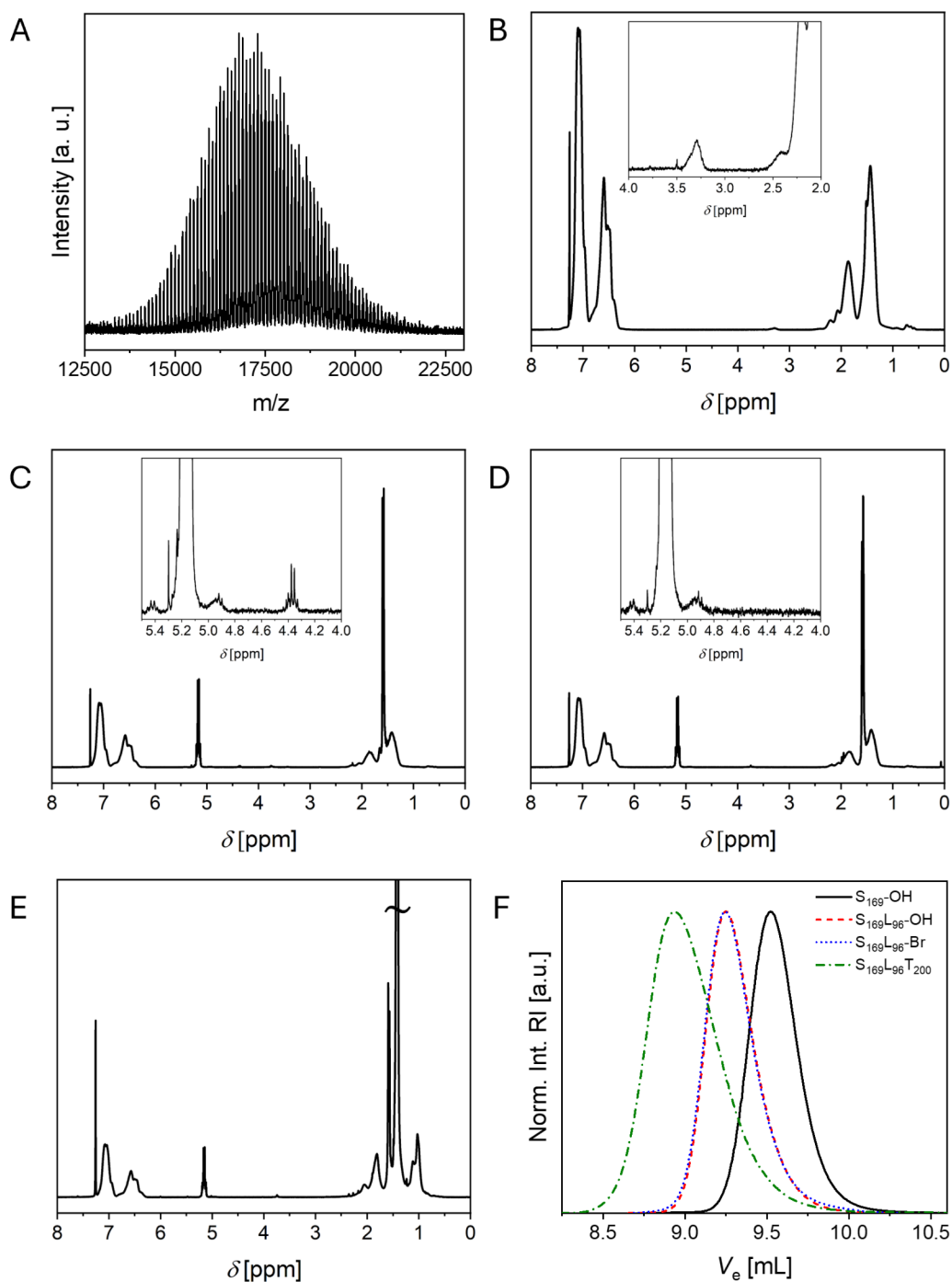


Figure S5.2 Characterization of SLT-2 ($S_{169}L_{96}T_{200}$) and the respective precursors. (A) MALDI-ToF mass spectrum of the PS_{169} -OH precursor (matrix: DCTB, salt: AgTFA). 1H -NMR ($CDCl_3$, 300 MHz) spectra of (B) PS_{169} -OH, (C) PS_{169} -*b*- $PLLA_{96}$, (D) PS_{169} -*b*- $PLLA_{96}$ -Br and (E) PS_{169} -*b*- $PLLA_{96}$ - $PtBMA_{200}$. Successful end-group functionalization was confirmed by the downfield shift of the methine proton signal of the terminal repeating unit ($\delta = 4.3$ ppm) after the esterification reaction. (F) $CHCl_3$ -SEC (PS calibration) traces of SLT-2 and the respective precursors.

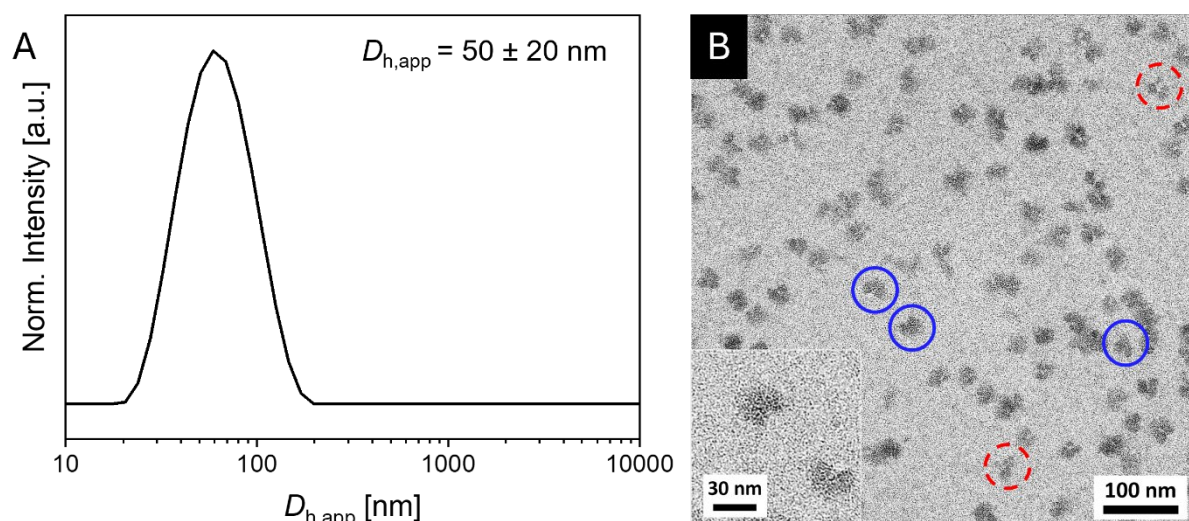


Figure S5.3 (A) Hydrodynamic diameter distribution from DLS for a SLT-2 micelle dispersion ($c = 1 \text{ g L}^{-1}$) prepared by thermal annealing (2 h at $T = 45^\circ \text{C}$) and aging (16 h at $T = 25^\circ \text{C}$) in CH. (B) TEM micrograph of the corresponding micelles with a Janus-like PS/*Pt*BMA corona (blue solid circles). A minor fraction of micelles exhibit a patch-like compartmentalized corona (red dotted circles). PS was selectively stained with RuO_4 and appears dark.

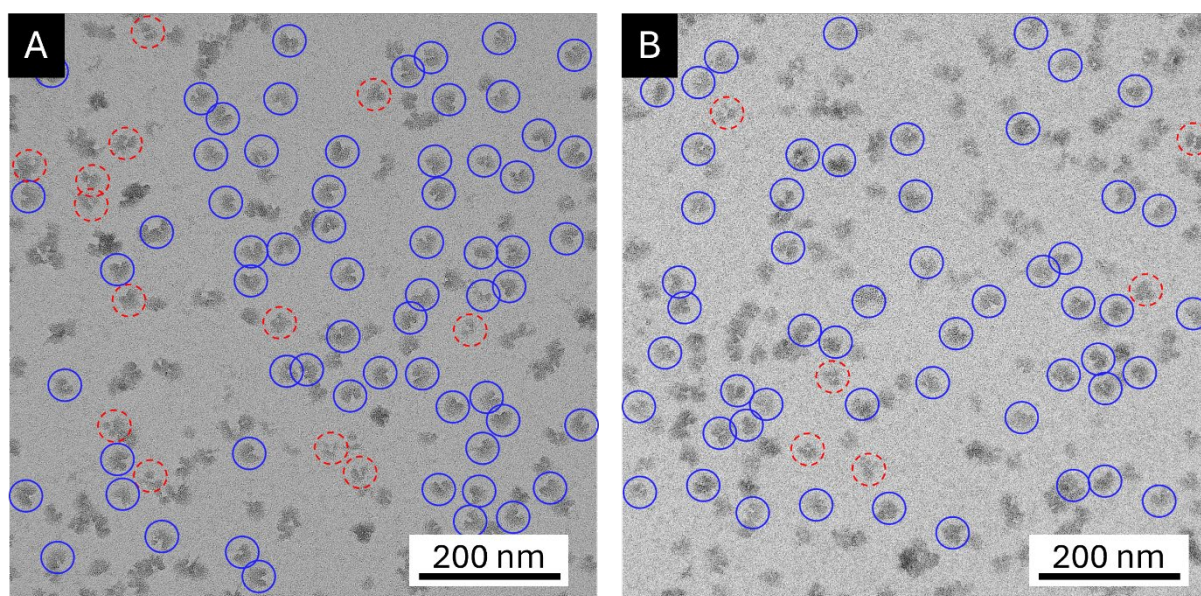


Figure S5.4 TEM micrographs of (A) SLT-1 and (B) SLT-2 micelles prepared by thermal annealing (2 h at $T = 45^\circ \text{C}$) and subsequent aging (16 h at $T = 25^\circ \text{C}$) in CH. The micelles show a Janus-like (blue solid circles) or patchy (red dashed circles) corona segregation. For the determination of the respective fraction only micelles where the core was unambiguously visible were counted, as otherwise a clear differentiation of the corona structure is difficult. At least 70 micelles were evaluated for each sample.

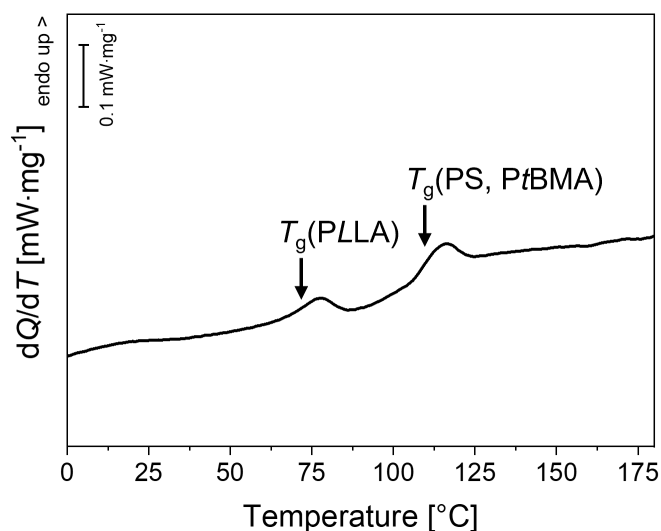


Figure S5.5 DSC 1st heating trace of freeze-dried SLT-1 Janus micelles prepared by thermal annealing and aging in CH.

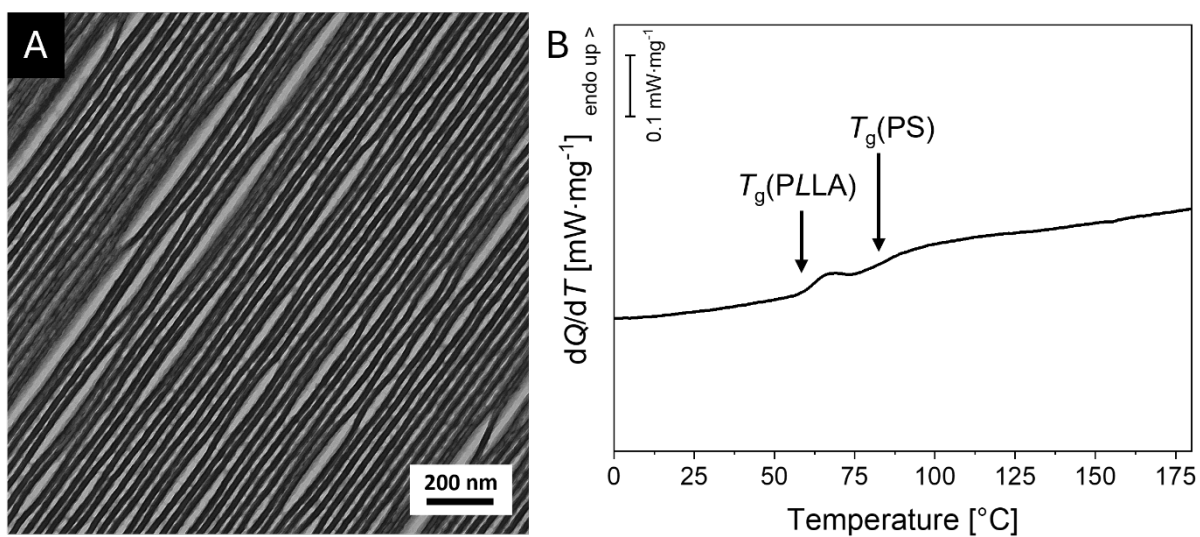


Figure S5.6 (A) TEM micrograph of a SLT-1 bulk film cast from CHCl_3 solution. PS was selectively stained with RuO_4 and appears dark, PLLA and PtBMA appear bright. (B) DSC 1st heating trace of the respective bulk film.

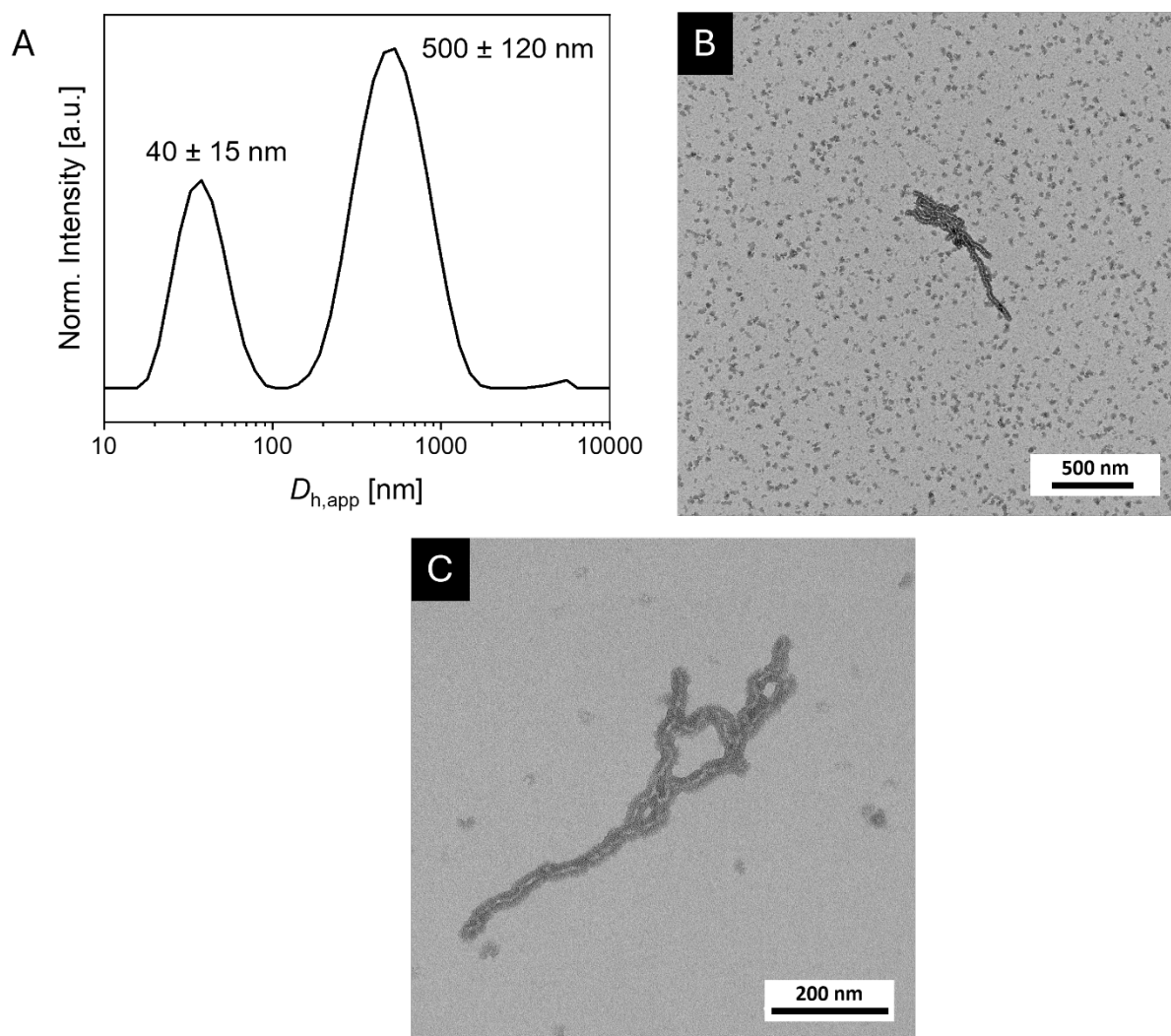


Figure S5.7 (A) Hydrodynamic diameter distribution from DLS for a SLT-1 micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a SLT-1 solution in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 2 d, subsequent evaporation of DCM and refilling with CH. (B,C) TEM micrographs of the SLT-1 micelle dispersion showing the presence of a mixture of Janus-type and patchy spherical micelles as well as cylindrical micelles. PS was selectively stained with RuO_4 and appears dark.

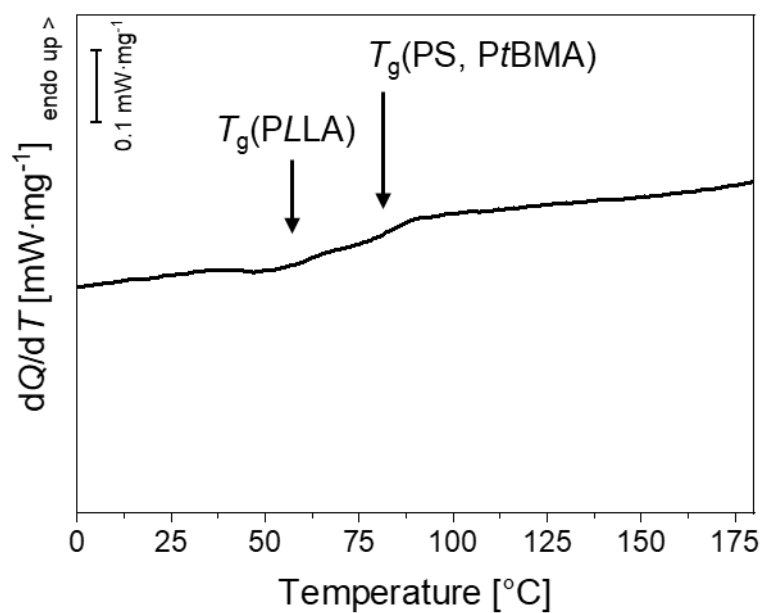


Figure S5.8 DSC 1st heating trace of a freeze-dried SLT-1 micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a SLT-1 solution in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 2 d, subsequent evaporation of DCM and refilling with CH.

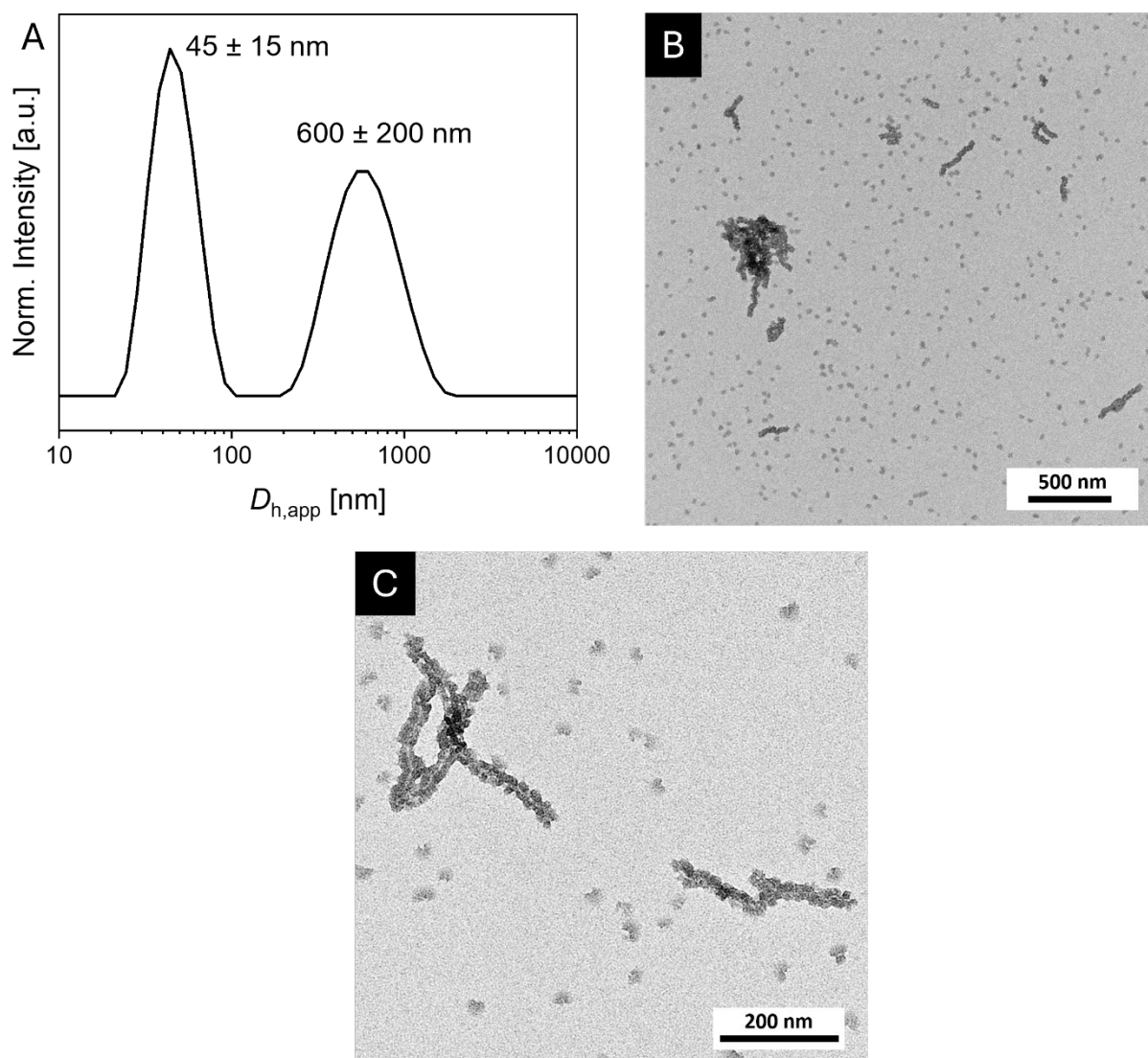


Figure S5.9 (A) Hydrodynamic diameter distribution from DLS for a SLT-2 micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a SLT-2 solution in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 1 d, subsequent evaporation of DCM and refilling with CH. (B,C) TEM micrograph of the SLT-2 micelle dispersion showing the presence of a mixture of Janus-type and patchy spherical micelles as well as cylindrical micelles. PS was selectively stained with RuO_4 and appears dark.

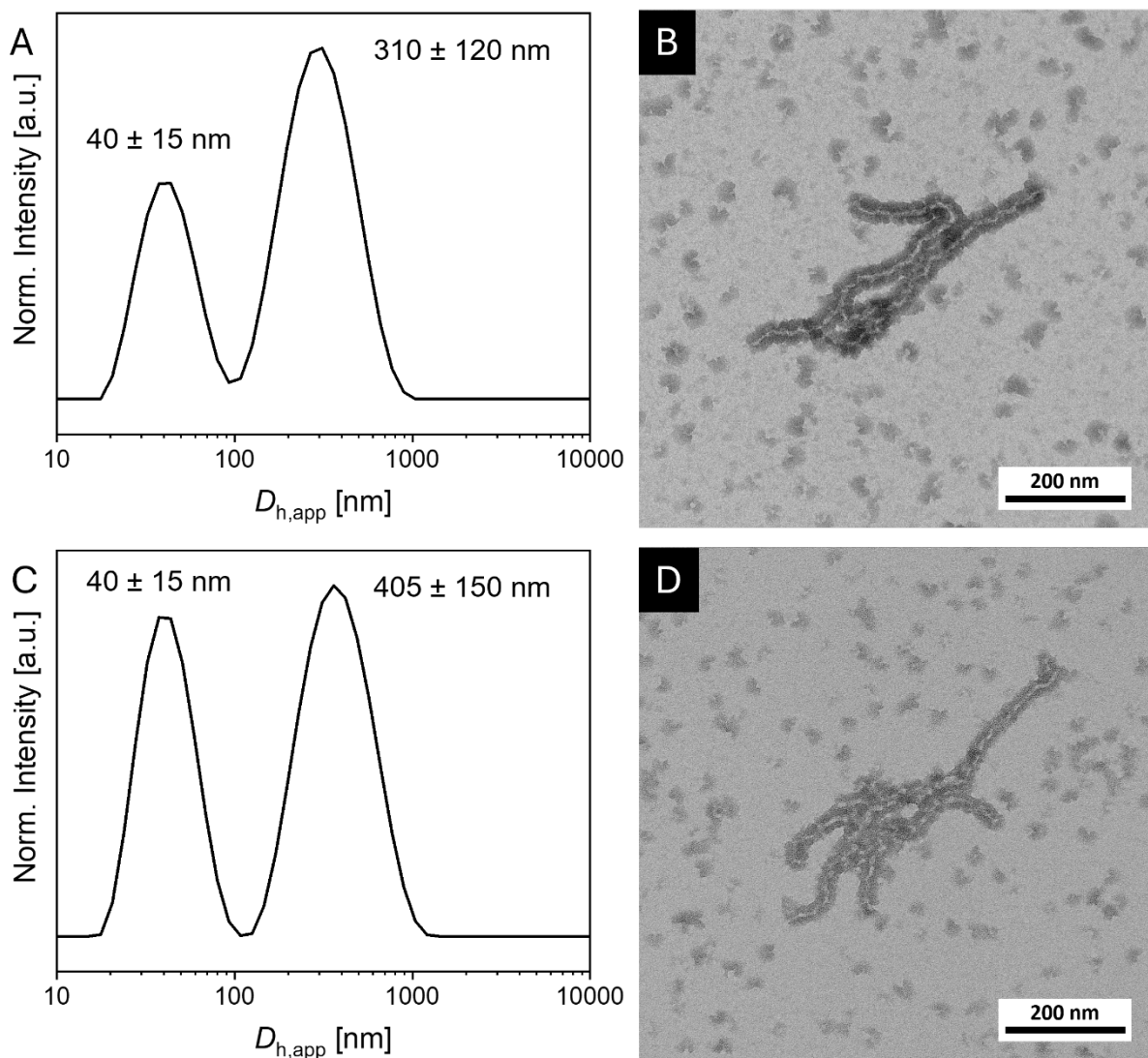
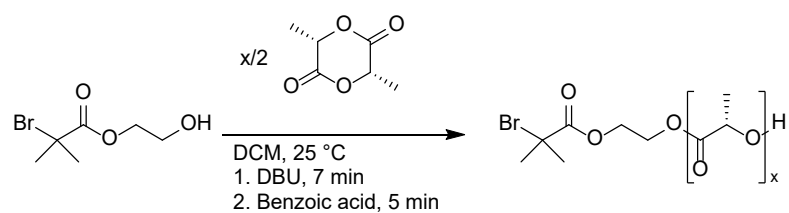


Figure S5.10 (A) Hydrodynamic diameter distribution from DLS for a SLT-1 micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a SLT-1 solution in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$) at $10 \text{ }^\circ\text{C}$, aging for 7 d at this temperature, heating to room temperature (1 K min^{-1}), subsequent evaporation of DCM and refilling with CH. (B) TEM micrograph of the SLT-1 micelle dispersion showing the presence of a mixture of Janus-type and patchy spherical micelles as well as cylindrical micelles. (C) Hydrodynamic diameter distribution from DLS for a SLT-1 micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a SLT-1 solution in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$) at $45 \text{ }^\circ\text{C}$, aging for 1 d at this temperature, cooling to room temperature (1 K min^{-1}), subsequent evaporation of DCM and refilling with CH. (D) TEM micrograph of the SLT-1 micelle dispersion showing the presence of a mixture of Janus-type and patchy spherical micelles as well as cylindrical micelles. PS was selectively stained with RuO_4 and appears dark.



Scheme S5.2 Synthesis of PLLA homopolymers.

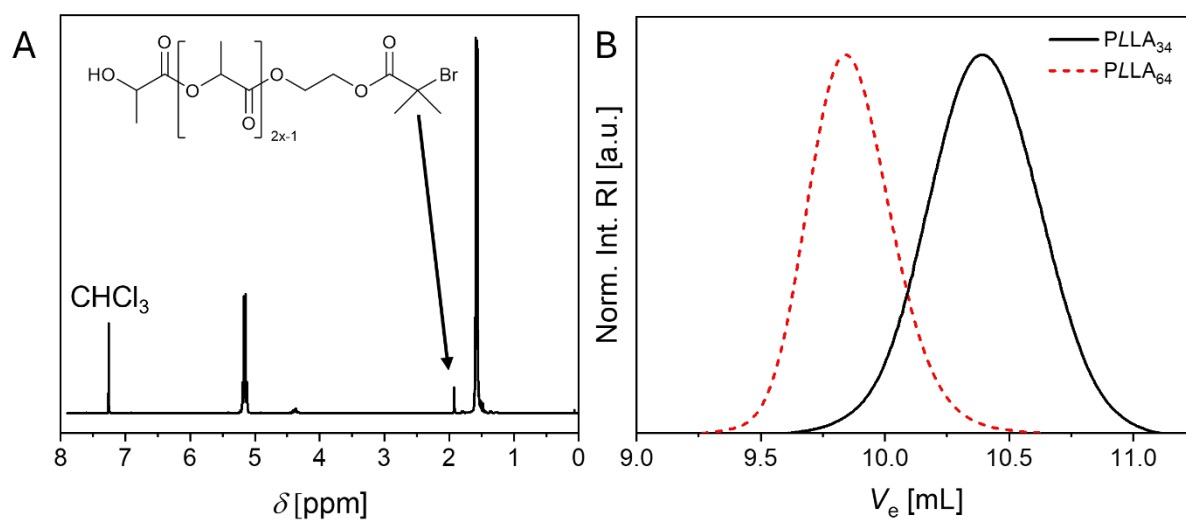


Figure S5.11 (A) ¹H-NMR (CDCl₃, 300 MHz) spectrum of PLLA₆₄. (B) CHCl₃-SEC (PS calibration) traces of PLLA₃₄ and PLLA₆₄.

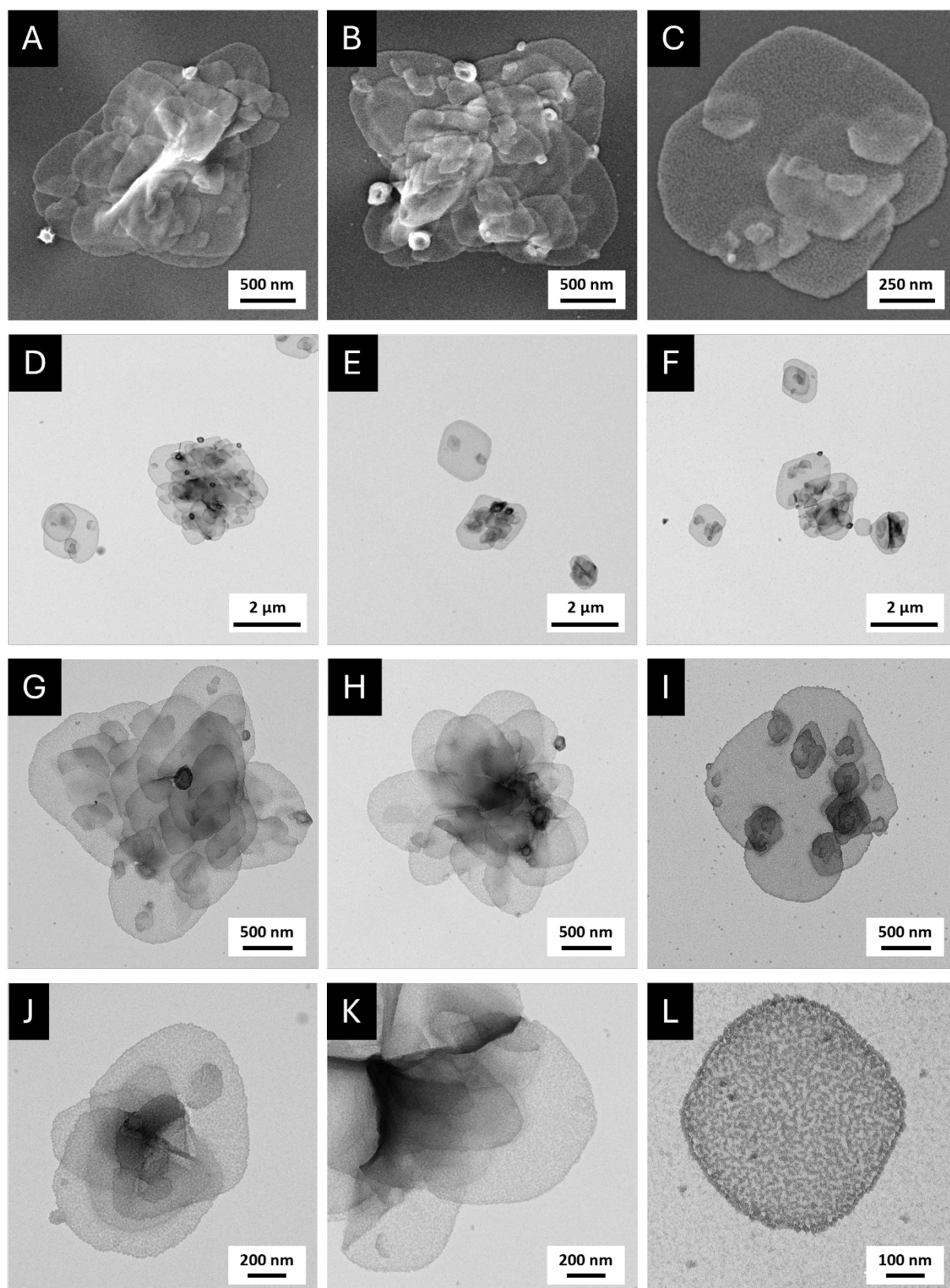


Figure S5.12 (A-C) SEM images and (D-L) TEM micrographs of a SLT-1 + PLLA₆₄ (50 wt%) micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \text{ μL}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 days, subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO₄ and appears bright in SEM and dark in TEM.

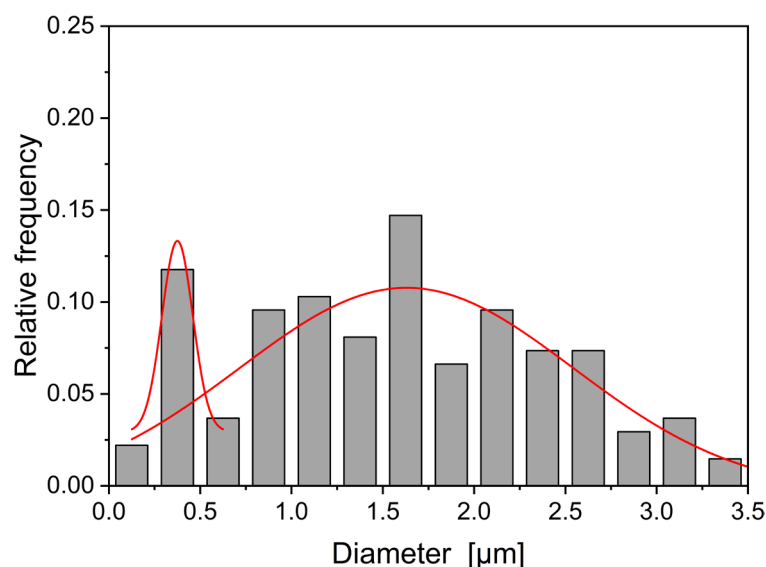


Figure S5.13 Histogram of the size distribution of SLT-1 + PLLA₆₄ (50 wt%) platelet micelles determined by TEM. The dispersion was prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 days, subsequent evaporation of DCM and refilling with CH. For size evaluation the area of 130 platelets was measured and converted to the equivalent diameter assuming a perfect spherical cross-section. The Gaussian fit curves corresponding to the bimodal distribution are displayed in red.

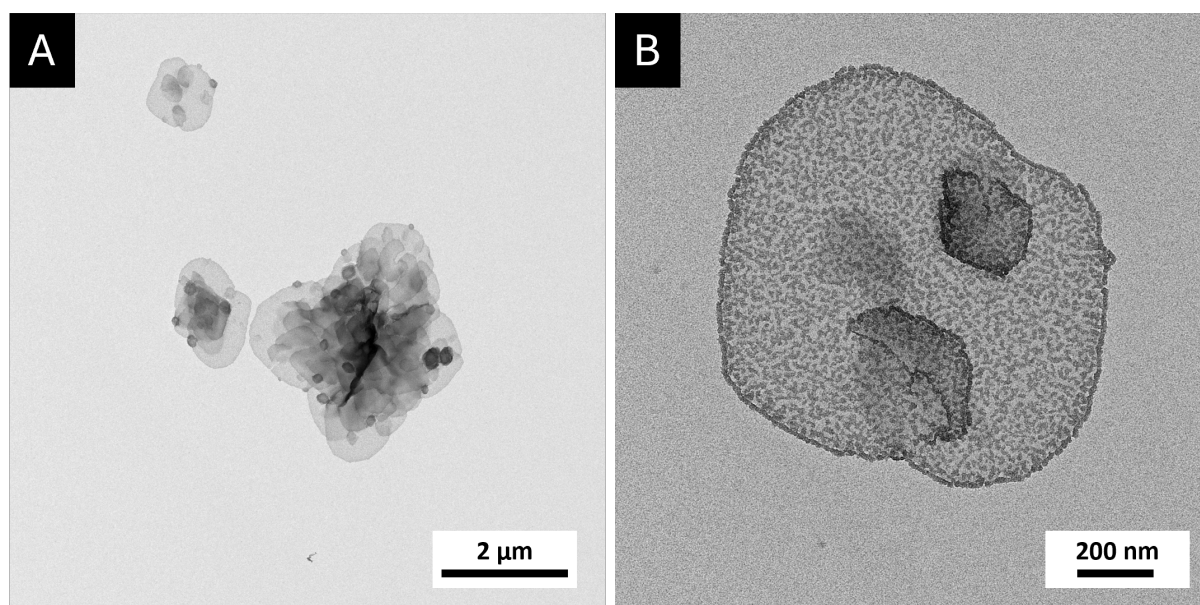


Figure S5.14 (A,B) TEM micrographs of SLT-2 + PLLA₆₄ (50 wt%) platelet micelles and assemblies. The dispersion in CH was prepared by the addition of a mixture of SLT-2 and PLLA₆₄ in DCM ($V = 300 \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 d, subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO₄ and appears dark.

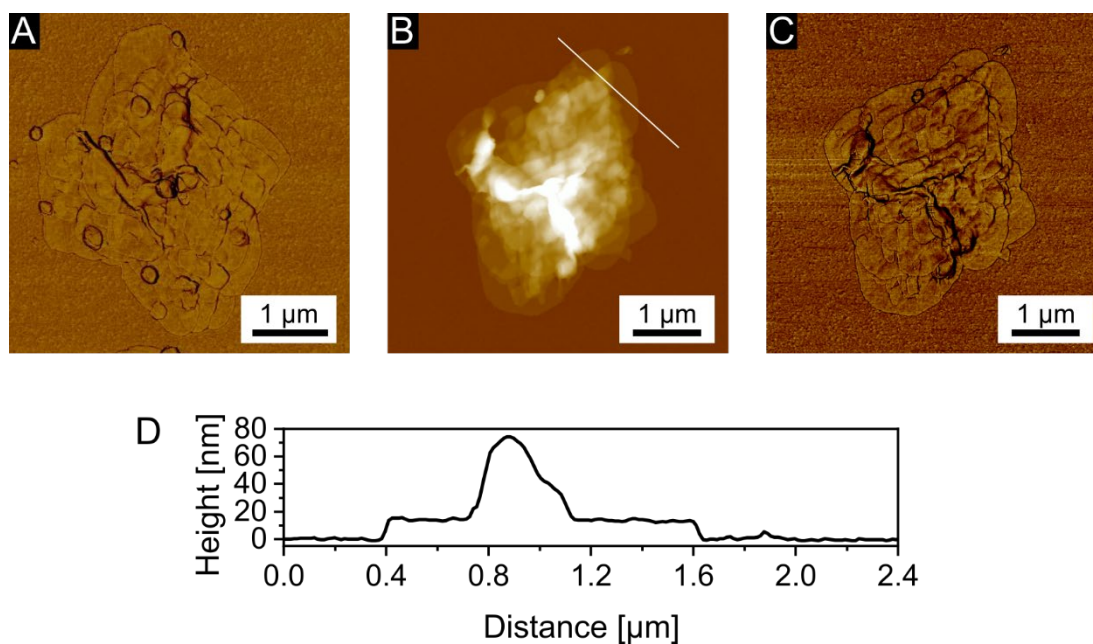


Figure S5.15 (A) AFM phase contrast image of the twisted patchy SLT-1 + PLLA₆₄ platelet micelle corresponding to the topography image shown in **Figure 4A** in the main text. Additional (B) topography and (C) phase contrast images of a twisted patchy SLT-1 + PLLA₆₄ platelet micelle and (D) the corresponding height profile taken at the position indicated by a line in (B). Z-ranges: (A) $\Delta z = 35^\circ$, (B) $\Delta z = 400$ nm, (C) $\Delta z = 10^\circ$.

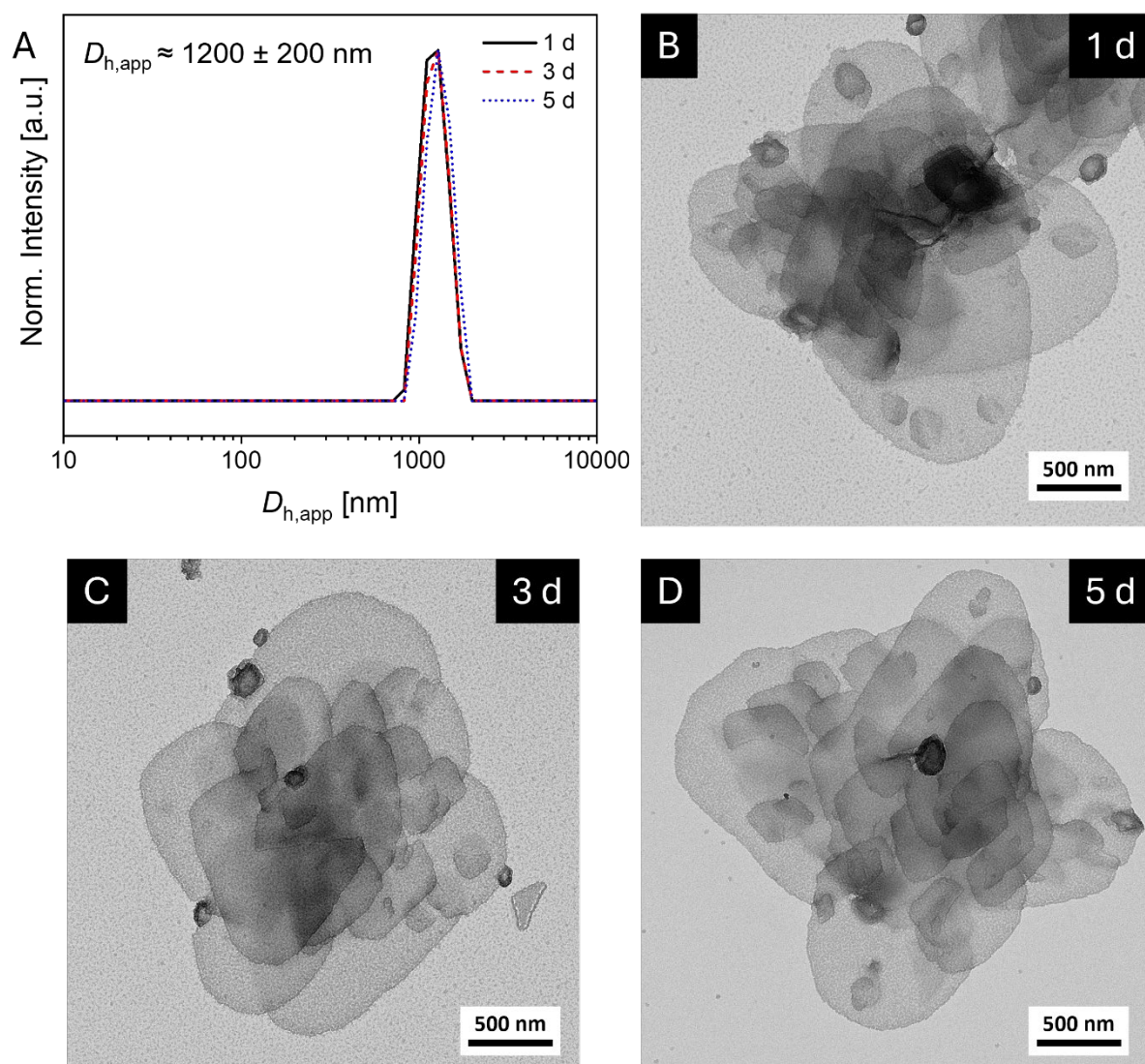


Figure S5.16 (A) Hydrodynamic diameter distributions from DLS for SLT-1 + PLLA₆₄ (50 wt%) micelle dispersions in CH ($c = 1 \text{ g L}^{-1}$). The dispersions were prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for different times as indicated, subsequent evaporation of DCM and refilling with CH. TEM micrographs of the corresponding patchy platelet micelles after an aging time of (B) 1, (C) 3 and (D) 5 d before removal of DCM. PS was selectively stained with RuO₄ and appears dark.

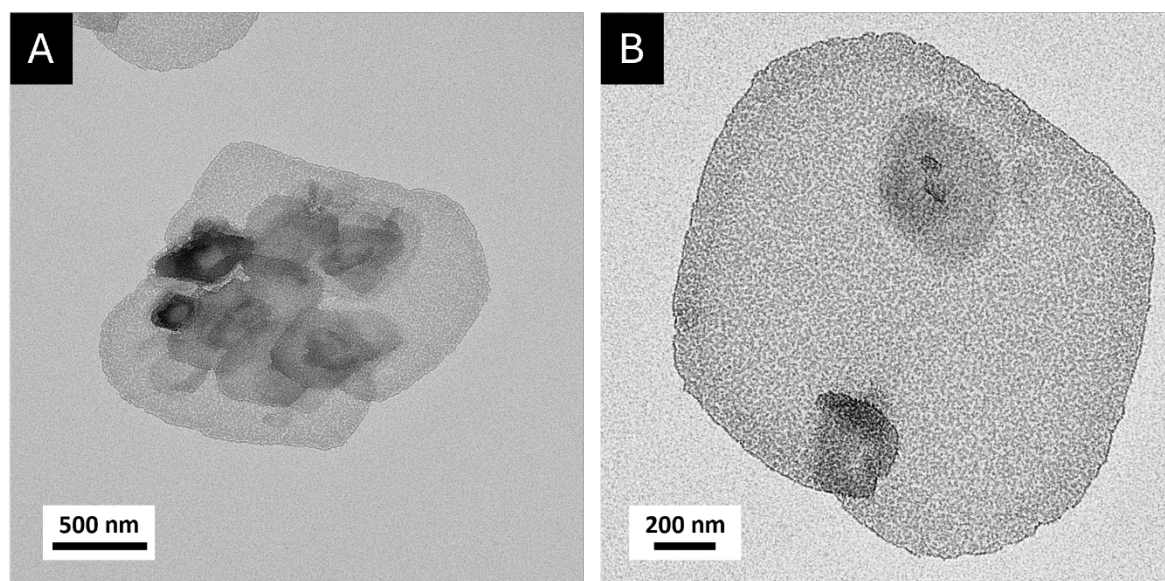


Figure S5.17 (A, B) TEM micrographs of SLT-1 + PLLA₆₄ (50 wt%) patchy platelet micelles prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$). TEM sample was prepared after aging for 5 d and before the removal of DCM. PS was selectively stained with RuO₄ and appears dark.

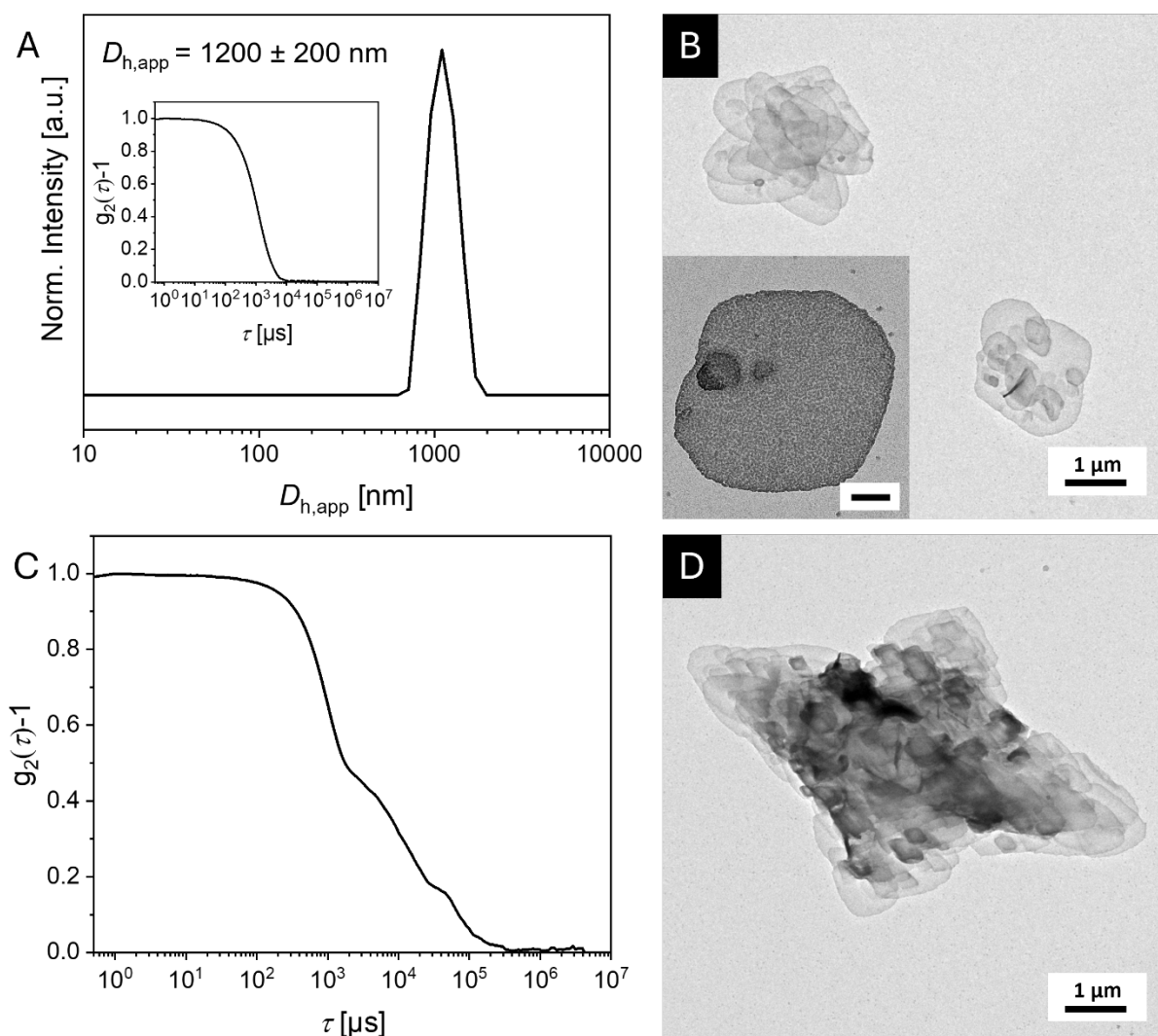


Figure S5.18 (A) Hydrodynamic diameter distribution from DLS for a SLT-1 + PLLA₆₄ (50 wt%) micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$) at a stirring speed of 1000 rpm, aging for 5 d, subsequent evaporation of DCM and refilling with CH. The inset shows the corresponding autocorrelation function with a single-step decay. (B) TEM micrographs of the corresponding patchy platelet micelles (scale bar inset: 200 nm). (C) Autocorrelation function from DLS for a SLT-1 + PLLA₆₄ (50 wt%) micelle dispersion in CH prepared analogously to (A) but at a slower stirring speed of 100 rpm. (D) TEM micrograph of a corresponding micelle assembly. PS was selectively stained with RuO₄ and appears dark.

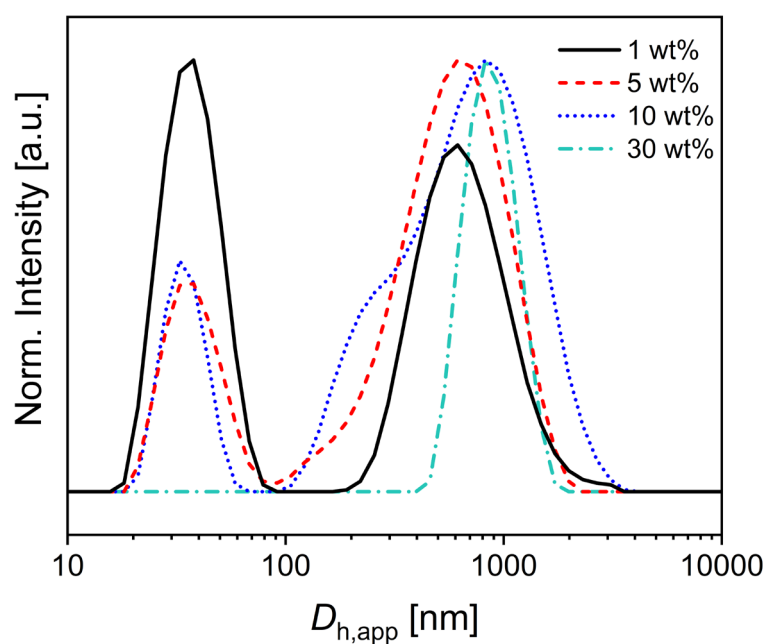


Figure S5.19 Hydrodynamic diameter distributions from DLS for SLT-1 + PLLA₆₄ micelle dispersions in CH ($c = 1 \text{ g L}^{-1}$). The dispersions were prepared by the addition of a mixture of SLT-1 and PLLA₆₄ with different PLLA₆₄ fractions in DCM ($V = 300 \text{ } \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 d, subsequent evaporation of DCM and refilling with CH.

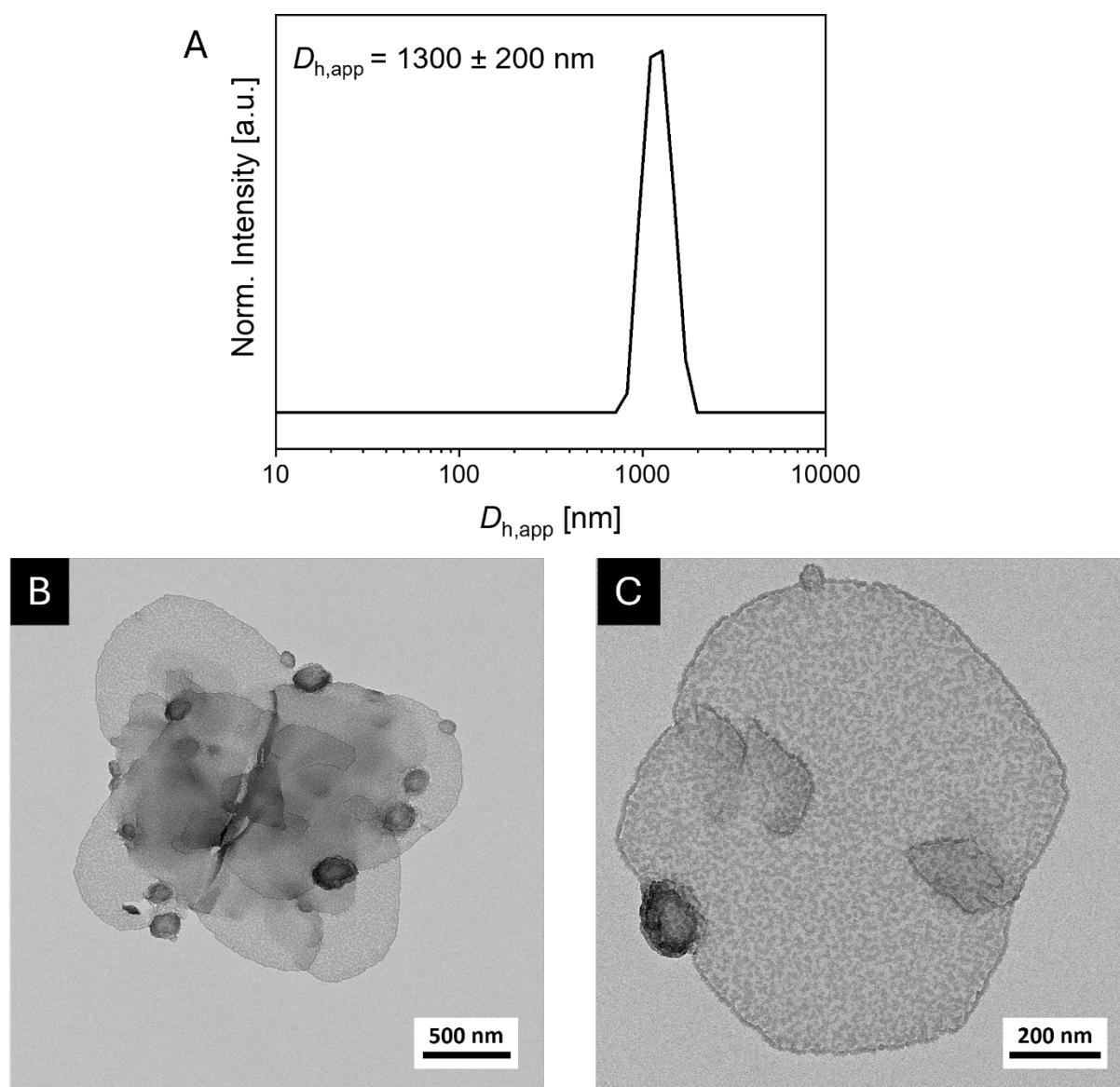


Figure S5.20 (A) Hydrodynamic diameter distributions from DLS for SLT-1 + PLLA₆₄ (60 wt%) micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$) prepared by the addition of a mixture of SLT-1 and PLLA₆₄ in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 d, subsequent evaporation of DCM and refilling with CH. (B, C) TEM micrographs of the corresponding patchy platelet micelles. PS was selectively stained with RuO₄ and appears dark.

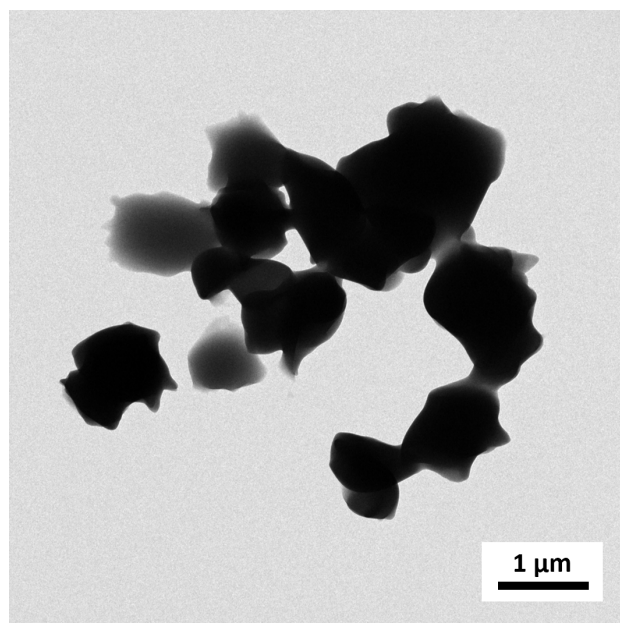


Figure S5.21 TEM micrograph of the structures formed in a $PLLA_{64}$ homopolymer dispersion in CH ($c = 1 \text{ g L}^{-1}$). The sample was prepared by the addition of a DCM solution of $PLLA_{64}$ ($V = 300 \text{ μL}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 d, subsequent evaporation of DCM and refilling with CH.

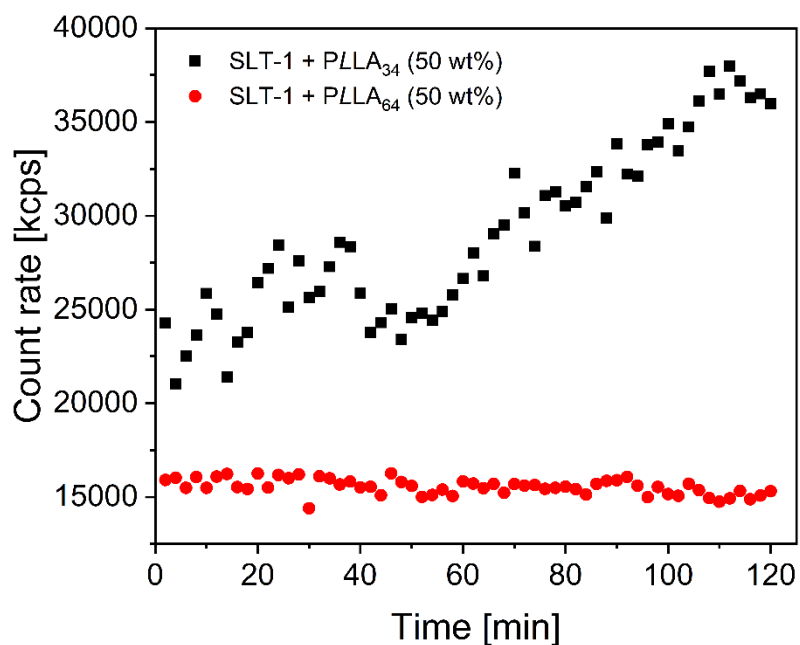


Figure S5.22 Evolution of scattering intensity with time for SLT-1 + $PLLA_{34}$ (50 wt%) and SLT-1 + $PLLA_{64}$ (50 wt%) dispersions in the early state directly after the addition of the respective DCM mixture to CH.

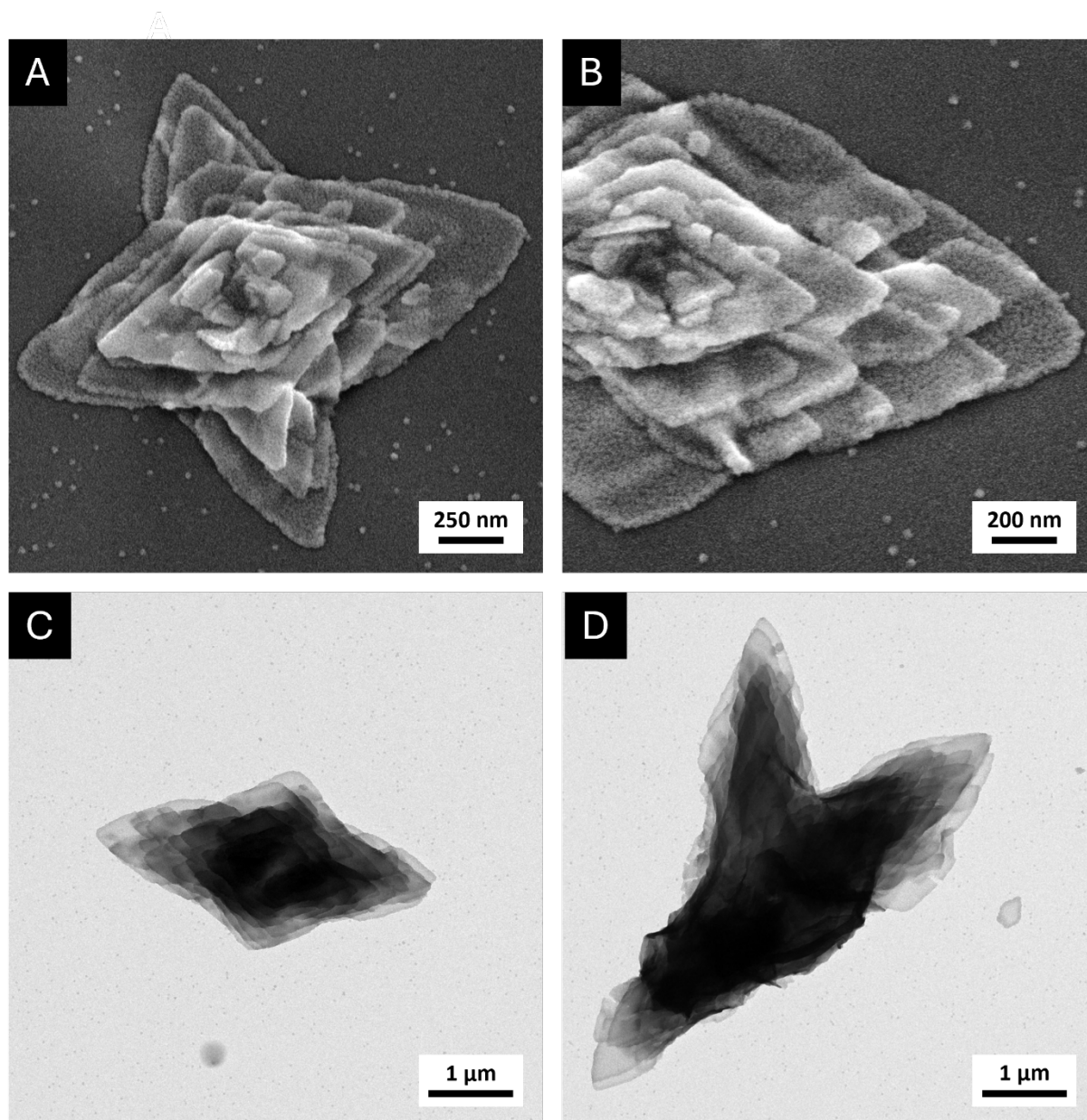


Figure S5.23 (A,B) SEM images and (C,D) TEM micrographs of a SLT-1 + PLLA₃₄ (50 wt%) micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a mixture of SLT-1 and PLLA₃₄ in DCM ($V = 300 \text{ } \mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 days, subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO₄ and appears bright in SEM and dark in TEM.

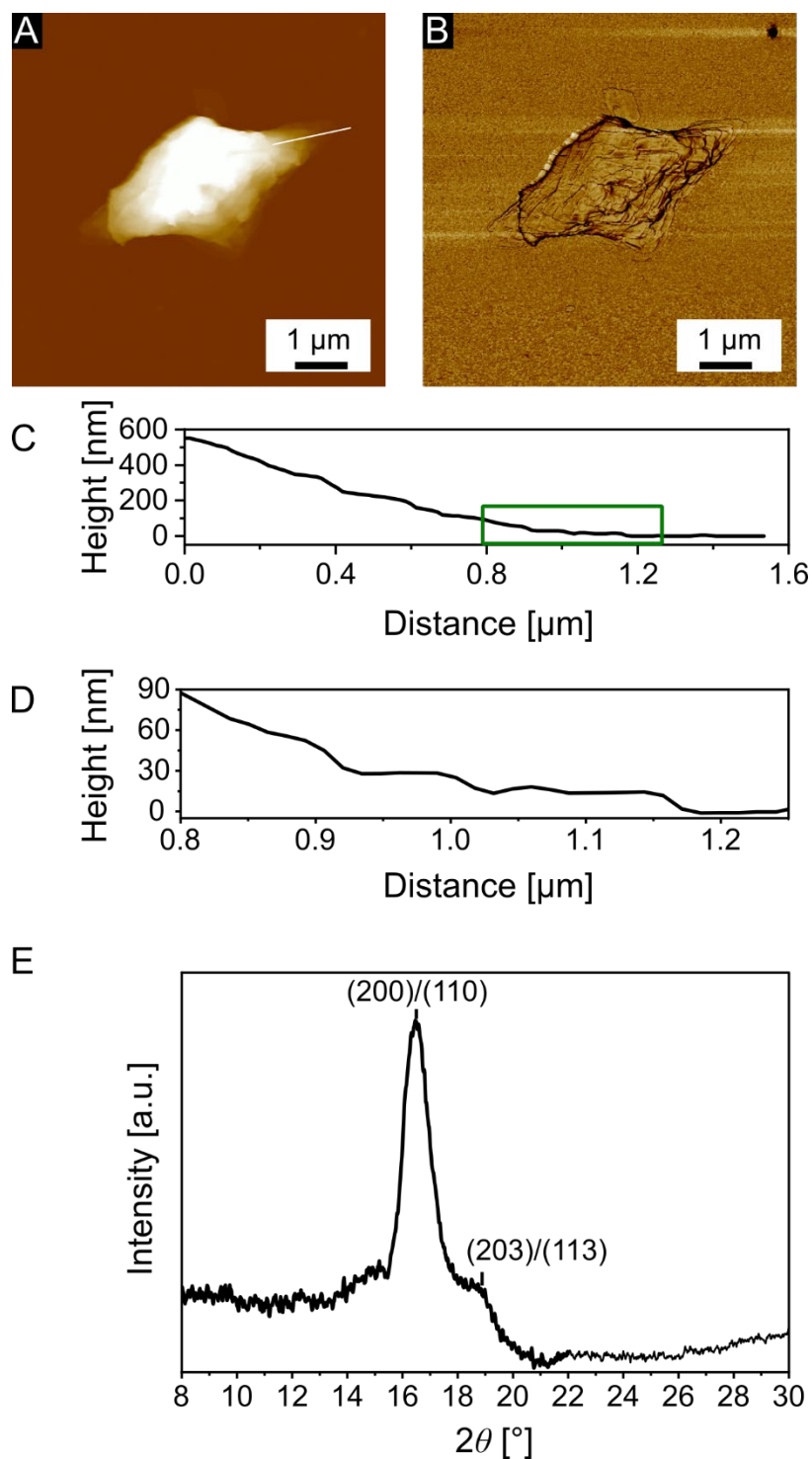
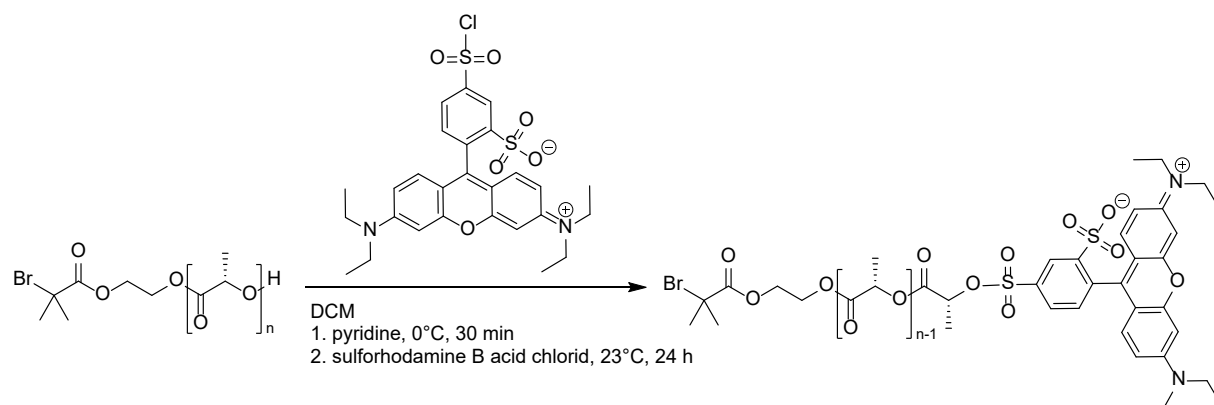


Figure S5.24 AFM (A) topography and (B) phase contrast images of a pyramidal assembly consisting of stacked SLT-1 + PLLA₃₄ patchy platelets formed by CCDSA in CH; for (A) $\Delta z = 1.6 \mu\text{m}$ and for (B) $\Delta z = 25^\circ$. (C) Height profile taken at the position indicated by a line in (A) and (D) zoom-in of the height profile in the range marked with a green box in (C). (E) WAXS profile of the freeze-dried dispersion.



Scheme S5.3 Synthesis of fluorescently labelled PLLA₆₄-RB.

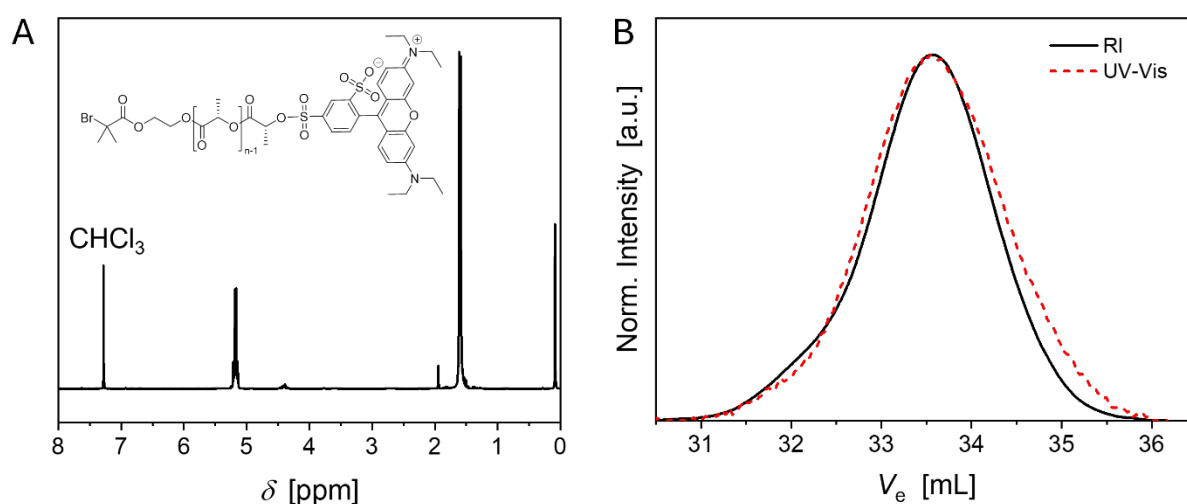


Figure S5.25 (A) ¹H NMR (CDCl₃, 300 MHz) spectra of PLLA₆₄-RB. (B) THF-SEC traces of PLLA₆₄-RB (PS calibration, UV-vis detector at $\lambda = 580$ nm). The identical RI and UV-vis traces for PLLA₆₄-RB prove the successful end-functionalization of PLLA₆₄ with sulforhodamine B.

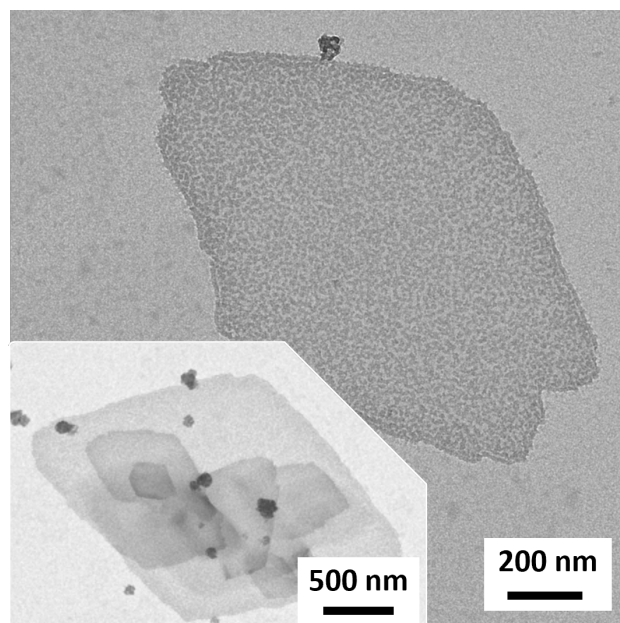


Figure S5.26 TEM micrographs of a fluorescently labelled SLT-1 + PLLA₆₄/PLLA₆₄-RB (50 wt%) micelle dispersion in CH ($c = 1 \text{ g L}^{-1}$). The dispersion was prepared by the addition of a mixture of SLT-1, PLLA₆₄ and PLLA₆₄-RB in a 10:9:1 volumetric ratio (concentration of individual solutions: $c = 10 \text{ g L}^{-1}$, 10 wt% of the PLLA₆₄ homopolymer was replaced by a rhodamine B labelled PLLA₆₄-RB homopolymer) in DCM ($V = 300 \text{ }\mu\text{L}$, $c = 10 \text{ g L}^{-1}$) to CH ($V = 2.7 \text{ mL}$), aging for 5 days, subsequent evaporation of DCM and refilling with CH. PS was selectively stained with RuO₄ and appears dark.

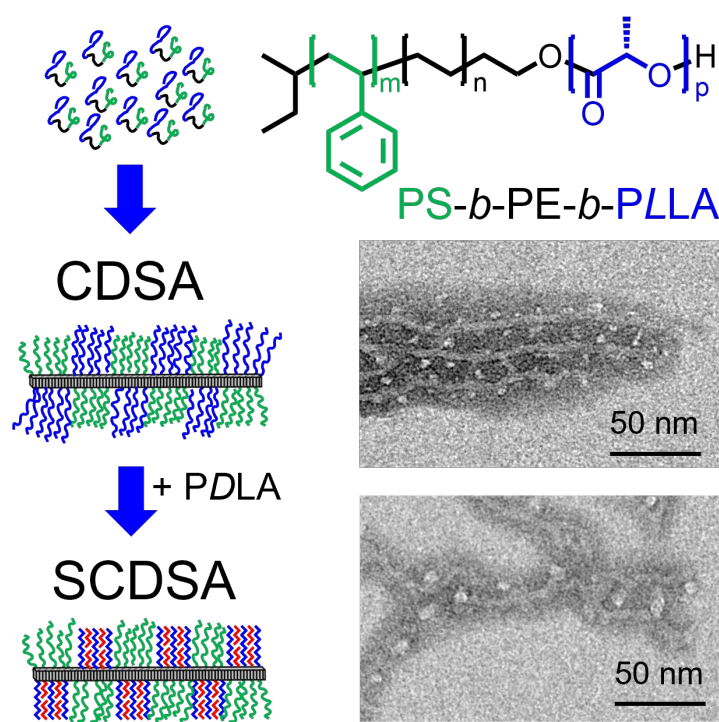
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6 Combining Crystallization- and Stereocomplex-Driven Self-Assembly for the Selective Loading of Patchy Worm-Like Core-Crystalline Micelles

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Abstract

Micelles with a patch-like microphase-separated (patchy) corona are of increasing interest as their unique corona structure opens various applications, for example, as emulsion stabilizers, blend compatibilizers, nanoparticle templates for catalysis, or hierarchical self-assembly. Crystallization-driven self-assembly (CDSA) is an efficient method for the preparation of patchy core-crystalline micelles (CCMs). However, so far studies mainly focus on CCMs with amorphous corona blocks. In this work, a combination of CDSA with stereocomplex-driven self-assembly (SCDSA) is employed to selectively load stereoregular poly(*L*-lactide) patches in the corona of worm-like CCMs (wCCMs) formed by a double-crystalline polystyrene-*block*-polyethylene-*block*-poly(*L*-lactide) (PS-*b*-PE-*b*-PLLA) triblock terpolymer. Well-defined wCCMs with an amorphous patchy PS/PLLA corona are formed by CDSA in a good solvent for the PS and PLLA blocks, that is, PLLA crystallization is hindered within the patches. However, decreasing the solvent quality for the PLLA block can induce crystallization within the partially collapsed PLLA patches, although the degree of crystallinity is comparably low (<5%). SCDSA of the patchy wCCMs with an enantiomeric poly(*D*-lactide) homopolymer is utilized to selectively form polylactide stereocomplexes within the patchy corona and, furthermore, to introduce a fluorescence dye, allowing the use of fluorescence correlation spectroscopy to study stereocomplex formation directly in dispersion.

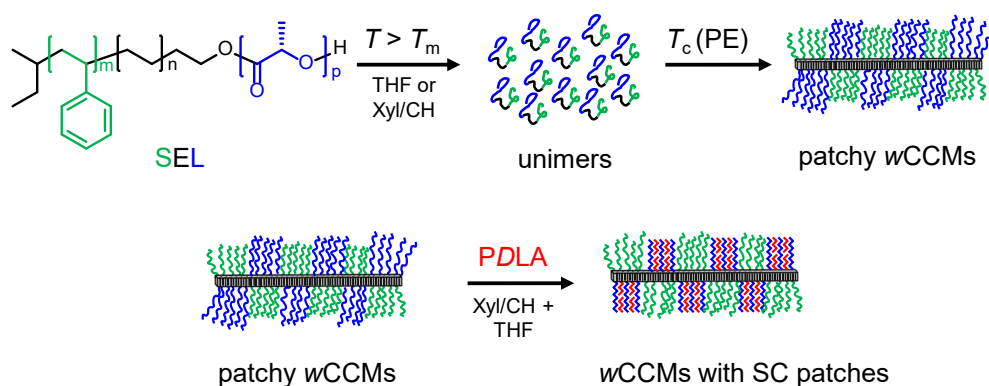
Keywords: anionic polymerization, block copolymers, crystallization-driven self-assembly, fluorescence correlation spectroscopy fluorescence labeling, patchy micelles, stereocomplex-driven self-assembly

6.1 Introduction

Surface-compartmentalized polymer micelles have attracted considerable interest due to their unique corona structure, which can be harnessed for a wide range of relevant applications [1-11]. Generally, they can be divided into Janus micelles featuring two opposing faces with different chemistry and/or polarity [12-18], and patchy micelles that are characterized by a patch-like microphase-separated corona consisting of several compartments with distinct properties [1, 7, 8, 19, 20]. Janus micelles have been utilized in numerous applications, for example, as biosensors and optical nanoprobe [21, 22], as efficient stabilizers for emulsions [23-25], for the compatibilization of polymer blends [26-29], in interfacial catalysis [30, 31], and many more. For patchy micelles, however, the main research focus so far was laid on their preparation and hierarchical self-assembly [32-38], and reports on the application of patchy micelles/particles are scarce. The patchy corona can serve as a template for the regioselective incorporation of nanoparticles, enabling applications in heterogeneous catalysis [39-42], or for constructing hierarchical superstructures when combined with supramolecular self-assembly [43, 44]. Crystallization-driven self-assembly (CDSA) has proven a powerful tool to produce well-defined one-dimensional (cylindrical/worm-like) surface-compartmentalized micelles and can also be performed in a living manner, which allows control over length, length distribution, and corona chemistry [45-49]. While, up to now, mostly triblock terpolymers with a crystallizable middle block based on polyethylene or polyferrocenyldimethylsilane linked to two amorphous and incompatible corona-forming blocks were used [50-52], there are considerably fewer studies on CDSA of triblock copolymers featuring two crystallizable blocks [53, 54]. In recent years, CDSA of conjugated polymers became more and more popular; however, reports on double-crystalline diblock co- and triblock terpolymers remain scarce [55-58]. If next to the core-forming block, also one of the corona-forming blocks is able to crystallize, two important questions arise: Does crystallization of the corona block influence CDSA, resulting in different micellar morphologies? And is crystallization within a microphase-separated corona (Janus-type or patchy) still possible, or impeded by the exerted confinement? Recent work on the self-assembly of double-crystalline poly(ϵ -caprolactone)-*block*-poly(*p*-dioxanone)-*block*-poly(*N,N*-dimethyl acrylamide) (PCL-*b*-PPDO-*b*-PDMA) triblock terpolymers might give possible answers to these questions. In this study, seeded growth experiments with PPDO-*b*-PDMA seeds led only to the crystallization of the PPDO block, while PCL stayed amorphous due to the confinement exerted when PPDO crystals were formed first (overcrowding of PCL chains tethered on the PPDO platelet surface) [59].

Besides, stereocomplex-driven self-assembly (SCDSA) between enantiomeric block copolymers based on poly(*L*-lactide) (PLLA) and poly(*D*-lactide) (PDLA) has emerged as another efficient route for the preparation of core-crystalline micelles with insoluble PLLA/PDLA stereocomplex (SC) cores [60, 61]. Most studies are based on water-soluble SC micelles employing linear block copolymers (AB-, ABA-, and ABC-type), star-shaped block copolymers, and graft copolymers with poly(ethylene oxide) (PEO) or poly(oligo(ethylene glycol) methacrylate) [62-67]. Alternatively, block copolymers with poly(acrylic acid) [68, 69], poly(*N,N*-dimethylaminoethyl methacrylate) [70, 71], poly(*N-isopropyl* acrylamide) [72], or poly(*isoglycerol* methacrylate) [73] blocks were used. Interestingly, mixing of cylindrical micelle dispersions with enantiomeric PLLA or PDLA cores induced a stereocomplex-driven morphological transition to spherical micelles, whereby the solubility of the employed diblock or triblock copolymers played an important role [69, 74]. On the contrary, there are only a limited number of reports on SCDSA in organic solvents [75-77]. Nonetheless, SCDSA in organic solvents can be a highly versatile strategy, as recently shown by the preparation of patchy SC micelles showing superior interfacial activity and performance as blend compatibilizers [78, 79].

Herein, we report the preparation of patchy worm-like core-crystalline micelles (wCCMs) with SC compartments by combining CDSA and SCDSA of a double-crystalline polystyrene-*block*-polyethylene-*block*-poly(*L*-lactide) (SEL) triblock terpolymer (Scheme 6.1). Next to the synthesis and characterization of the triblock terpolymers, the influence of solvent on CDSA to patchy wCCMs as well as on crystallization within the PLLA patches is addressed. Moreover, SCDSA of the patchy SEL wCCMs with an enantiomeric PDLA homopolymer is employed to selectively load the PLLA patches of the micelles. This is utilized to functionalize the SC patches in the wCCM corona with a fluorescence dye, enabling the verification of SC formation directly in dispersion by fluorescence correlation spectroscopy.

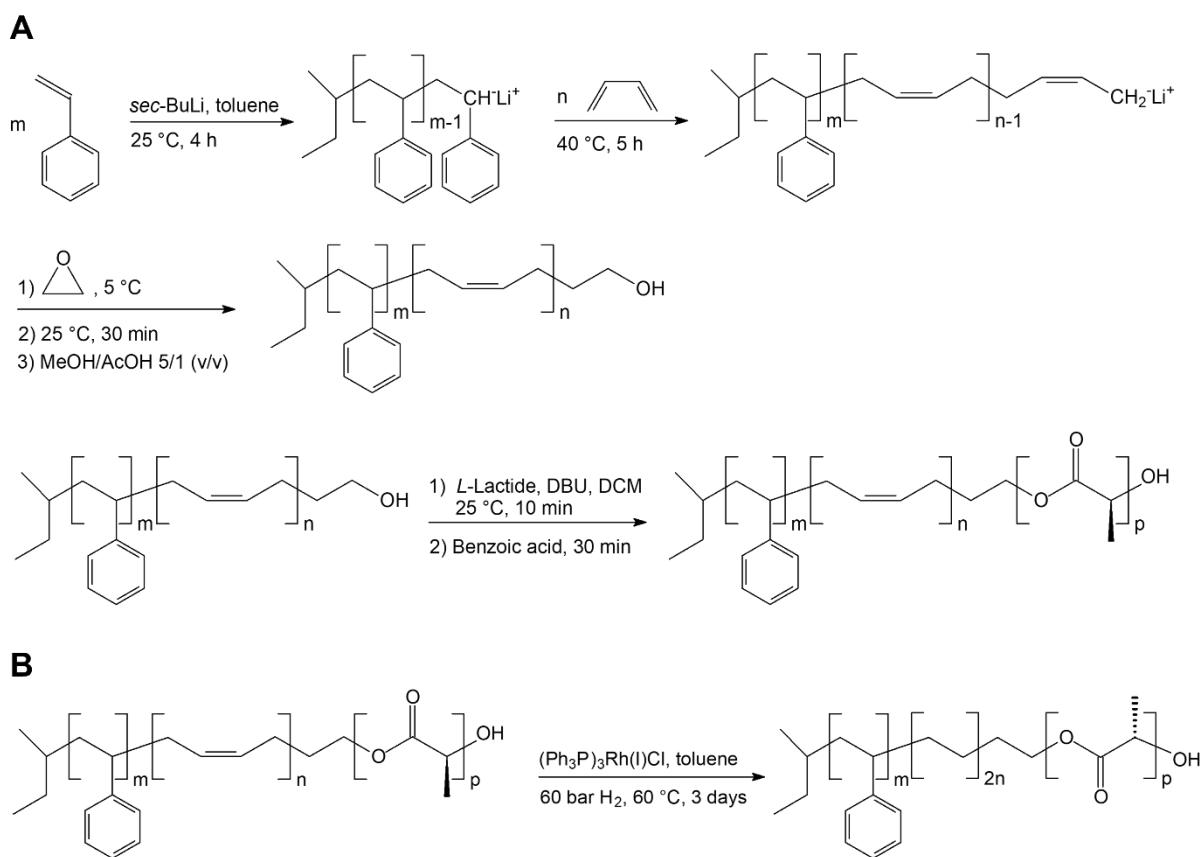


Scheme 6.1 Schematic illustration of the preparation of patchy wCCMs by CDSA of SEL triblock terpolymers (top). SCDSA with PDLA homopolymer results in the formation of PLLA/PDLA SC patches within the corona (bottom).

6.2 Results and Discussion

6.2.1 Synthesis of SEL Triblock Terpolymers

The SEL triblock terpolymers were synthesized by a combination of living anionic polymerization, organo-catalyzed ring-opening polymerization (ROP), and catalytic hydrogenation, as shown in Scheme 6.2. First, a hydroxy end-functionalized polystyrene-*block*-poly(1,4-butadiene) (SB-OH) diblock copolymer was prepared by sequential living anionic polymerization of styrene and 1,3-butadiene in toluene, using *sec*-butyllithium as the initiator, followed by end-capping with ethylene oxide (Scheme 6.2A) [80]. The combination of an organolithium initiator with toluene as a nonpolar solvent yields a polybutadiene (PB) block with a high fraction of 1,4-PB units (ca. 90 mol-%, Table 6.1), which is essential to get a pseudo polyethylene (PE) block after hydrogenation. The SB-OH diblock copolymer was then used as a macroinitiator for the organo-catalyzed ROP of *L*-lactide, employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst, which yielded the respective polystyrene-*block*-poly(1,4-butadiene)-*block*-poly(*L*-lactide) (SBL) triblock terpolymers. A detailed description of the syntheses and the employed materials is provided in the Section 4.



Scheme 6.2 (A) Synthesis of SBL triblock terpolymers by combination of living anionic polymerization and organo-catalyzed ROP of *L*-lactide, followed by (B) catalytic hydrogenation to yield the respective SEL triblock terpolymers.

The molecular characteristics of the synthesized SBL triblock terpolymers and the respective SB-OH precursors are summarized in Table 6.1. In the used nomenclature, for example, S₂₉₆B₃₁₂L₃₆₈ (SBL-1), the indices correspond to the number-average degrees of polymerization of the respective blocks. Figure 6.1 shows as an example the apparent molecular weight distributions of SBL-2 together with the corresponding PS and SB-OH precursors as determined by size exclusion chromatography (SEC, results for SBL-1 are given in Figure S6.1B). The SEC results indicate that the synthesis has proceeded without significant side reactions, yielding a narrowly distributed SBL triblock terpolymer with a dispersity of $\bar{D} = 1.10$. Only upon addition of 1,3-butadiene to the living PS a very minor fraction of the PS chains has coupled, resulting in a weak shoulder in the distributions of SB-OH and SBL-2 at lower molecular weights.

Table 6.1 Molecular characteristics of the employed triblock terpolymers and the SB-OH diblock copolymer precursor.

sample ^{a,b}	code	$\bar{M}_n(\text{PB})^c / \bar{M}_n(\text{PE})$ [g mol ⁻¹]	$\bar{M}_n(\text{PLLA})^c$ [g mol ⁻¹]	$\bar{M}_{n, \text{total}}$ [g mol ⁻¹]	$\bar{D}^d$	1,4-PB/Ethyl ^e [mol-%]
S ₂₉₆ B ₃₁₂ -OH	SB-OH	16 900	-	47 700	1.06	89/-
S ₂₉₆ B ₃₁₂ L ₃₆₈	SBL-1	16 900	26 500	74 200	1.24	89/-
S ₂₉₆ B ₃₁₂ L ₇₈₁	SBL-2	16 900	56 300	104 000	1.10	89/-
S ₂₉₆ E ₅₉₀ L ₃₆₈	SEL-1	17 500	26 500	74 800	-	-/5.8
S ₂₉₆ E ₅₉₀ L ₇₈₁	SEL-2	17 500	56 300	104 600	-	-/5.8

^a indices give the number-average degree of polymerization of the respective block; for PLLA the number corresponds to lactic acid repeating units

^b $\bar{M}_n(\text{PS}) = 30800 \text{ g mol}^{-1}$, as determined by matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry (Figure S1A)

^c determined by ¹H NMR using $\bar{M}_n(\text{PS})$ (from MALDI-ToF) for internal signal calibration

^d determined by CHCl₃-SEC employing a PS calibration

^e 1,4-PB: Average mole fraction of 1,4-PB units determined by ¹H NMR; Ethyl: Average mole fraction of ethyl branches in the PE block calculated from the mole fraction of 1,4-PB units in the respective SBL triblock terpolymer precursor

In the next step, the PB middle block of the SBL triblock terpolymers was hydrogenated employing Wilkinson's catalyst to yield SEL triblock terpolymers with a crystallizable PE middle block (Scheme 6.2B) [81]. Complete hydrogenation of the PB middle blocks to PE was proven by proton nuclear magnetic resonance (¹H NMR) spectroscopy by the absence of PB specific signals after hydrogenation (Figure 6.1B, Figure 6.S1C). In addition, differential scanning calorimetry (DSC) on bulk samples revealed melting transitions specific for PE and PLLA, showing that both blocks are able to crystallize (Figure S6.2).

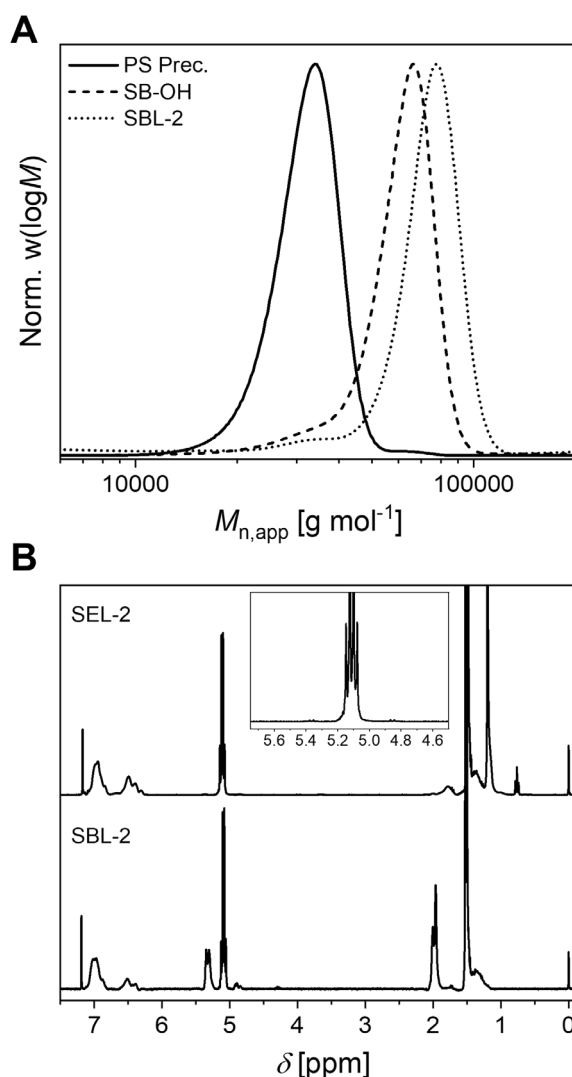


Figure 6.1 (A) Apparent molecular weight distributions of SBL-2 and the respective PS and SB-OH precursors (CHCl_3 -SEC, PS calibration). (B) ^1H NMR spectra (in CDCl_3) of SBL-2 and SEL-2 (measured at 60°C) proving complete hydrogenation by lack of PB specific signals ($\delta = 5.4\text{--}5.2$, $4.9\text{--}4.8$, and $2.1\text{--}1.9$ ppm) in SEL-2.

6.2.2 CDSA in a Good Solvent for the PS and PLLA Corona Blocks

CDSA was first studied in THF, a good solvent for both corona blocks (PS and PLLA). The optimum crystallization conditions for the PE middle block were probed by micro-DSC (μ -DSC) measurements for SEL-1 and SEL-2 at a concentration of $c = 10 \text{ g L}^{-1}$ in THF (Figure 6.2A,B). The employed temperature profile is depicted in Figure S6.3.

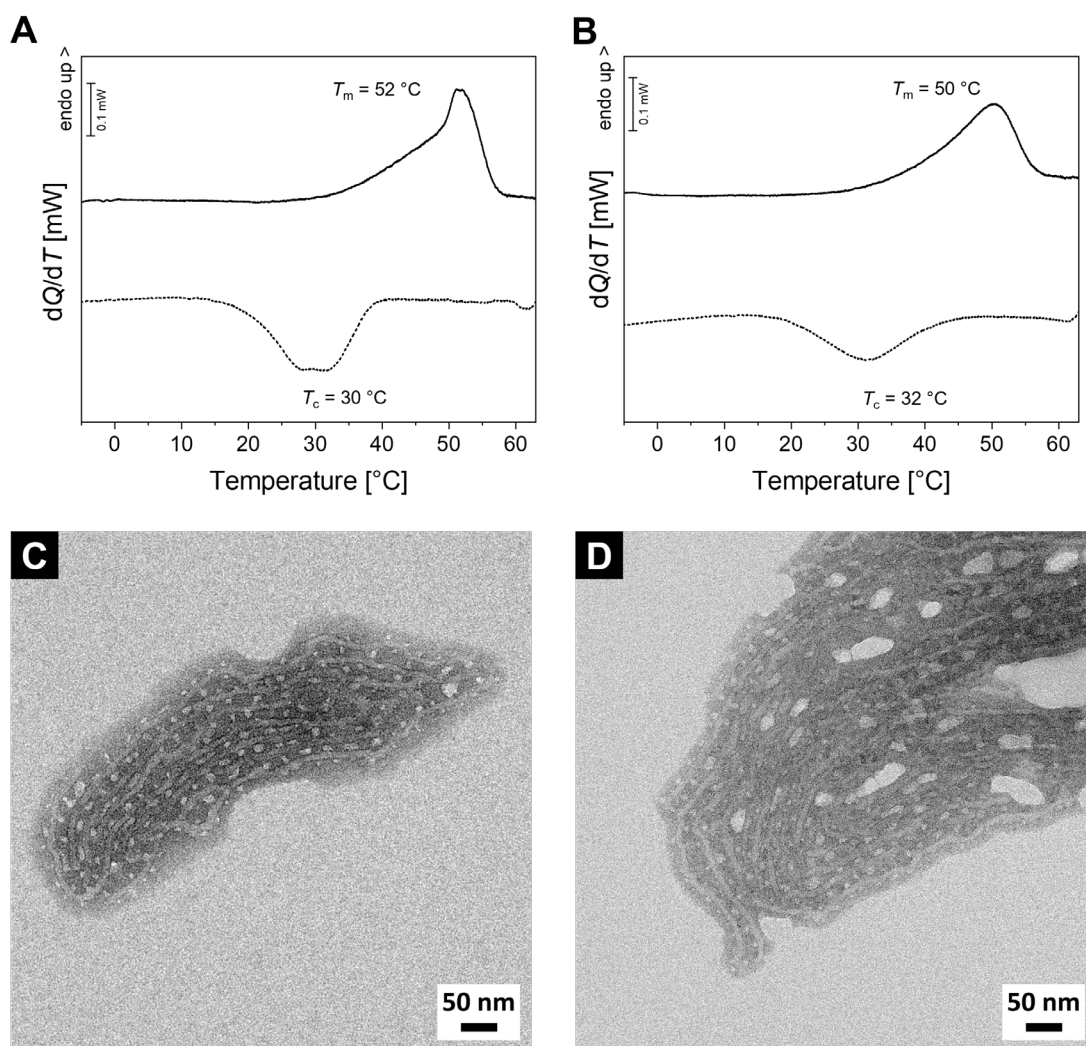


Figure 6.2 μ -DSC heating and cooling traces for (A) SEL-1 and (B) SEL-2 in THF at $c = 10 \text{ g L}^{-1}$ (scanning rate: 0.5 K min^{-1}). TEM micrographs of wCCMs formed by CDSA of (C) SEL-1 and (D) SEL-2 in THF. PS was selectively stained with RuO_4 and appears dark.

For both SEL triblock terpolymers rather broad crystallization and melting transitions can be observed for the PE middle block ($T_c(\text{PE}) \approx 30^\circ\text{C}$ – 32°C , $T_m(\text{PE}) \approx 50^\circ\text{C}$ – 52°C , Table S6.1). For SEL-1 it seems that the crystallization exotherm is composed of two unresolved underlying exotherms. However, this effect was not observed for the other solvents employed in this study (Figure 6.3B). Rather broad thermal transitions are typical for pseudo PE blocks due to the presence of ethyl branches (5.8 mol-% on average), arising from the 11 mol-% 1,2-units in the respective PB precursor block (Table 6.1) [40, 52]. Due to a certain nonuniformity in the distribution of the branches within the PE chains a distribution of melting and crystallization temperatures results. Melting or crystallization transitions for the PLLA blocks are not discernable. This is in accordance with THF being a good solvent for PLLA, whereas the pseudo PE block is only soluble in THF above its melting point at elevated temperatures [52].

Accordingly, the SEL triblock terpolymers were first dissolved in THF at 65°C for 10 min, followed by cooling to the peak crystallization temperature (T_c) of the PE middle block (T_c (PE) = 30 and 32°C for SEL-1 and SEL-2, respectively) to initiate CDSA. After isothermal crystallization for 24 h, the solutions were slowly cooled to -10°C to enable crystallization of the PE chains with a higher fraction of ethyl branches, that is, lower crystallization temperature. A detailed description of the CDSA procedure can be found in Section 4. The morphology of the formed micelles was then examined by transmission electron microscopy (TEM), employing selective staining of PS with ruthenium tetroxide (RuO₄). Figure 6.2C,D reveals that wCCMs with bright appearing, semi-crystalline PE cores were formed for both SEL triblock terpolymers. The formation of wCCMs is consistent with our prior work on CDSA of polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) triblock terpolymers [52]. This study showed that wCCMs are formed in good solvents for PE, being able to molecularly dissolve the PE block at elevated temperatures, like THF or toluene. The occurrence of branches and kinks in the semi-crystalline PE core is induced by the ethyl branches in the PE block, which are formed after hydrogenation of the 1,2-PB repeating units (Table 6.1) [52, 81]. The corona of the wCCMs appears dark due to the selective staining of the PS chains and shows a patch-like structure with embedded, bright appearing PLLA patches (not stained). The microphase-separated structure of the corona arises from the moderate incompatibility of the PS and PLLA corona chains with a Flory-Huggins interaction parameter of $\chi = 0.15$ at 110°C [82], that is, similar to the behaviour observed for wCCMs with a patch-like PS/PMMA corona [52, 81, 83]. As PLLA is prone to partial electron beam degradation, the size of the PLLA patches might be somewhat underestimated from the TEM micrographs. The patchy SEL wCCMs have a strong tendency to agglomerate, which is an artifact from TEM sample preparation. Agglomeration of the wCCMs occurs upon drying on the carbon-coated TEM grid, an effect that has also been observed for other patchy wCCMs [40, 49, 52, 83].

6.2.3 CDSA in Selective Solvents for the PS Corona Block

To probe whether the PLLA blocks in the patchy wCCM corona are able to crystallize and how PLLA crystallization influences the corona structure, CDSA was conducted in solvents or solvent mixtures with decreasing solvent quality for PLLA, that is, xylene (Xyl, isomeric mixture) and mixtures with cyclohexane (CH, up to 30 vol-%). In contrast to PS, the PLLA homopolymer is insoluble in Xyl or Xyl/CH mixtures at room temperature. Only upon heating to temperatures $T > 65^\circ\text{C}$ does PLLA become soluble, as probed by solubility tests with a PLLA₁₅₂ homopolymer.

Figure 6.3A,B shows the μ -DSC heating and cooling traces for SEL-1 in Xyl, and Xyl/CH mixtures with 20 and 30 vol-% CH, respectively ($c = 10 \text{ g L}^{-1}$). The μ -DSC traces for SEL-1 in Xyl are comparable to the results obtained for THF as solvent. In both cases, crystallization and melting can only be observed for the PE middle block, whereby the peak melting temperature is slightly reduced to $T_m(\text{PE}) \approx 48^\circ\text{C}$ in Xyl (Table S6.1). This might be attributed to Xyl being a slightly better solvent for PE at elevated temperatures, resulting in a more pronounced plasticizing effect. Here, it has to be noted that stainless steel batch cells sealed with fluororubber (FKM) O-rings were employed for μ -DSC measurements. The limited “inertness” of the fluororubber against Xyl and CH gives rise to artifact peaks in the cooling (endothermic peaks) and heating (exothermic peaks) traces for temperatures below ca. 10°C (Figure S6.4). Hence, in this temperature range visible transitions were not considered. Similar observations were reported when chloroform was used as solvent [84].

In the Xyl/CH = 80/20 (v/v) mixture an additional weak endotherm appears in the heating trace at $T_m = 33^\circ\text{C}$, which gets more pronounced and shifts to higher temperatures ($T_m = 36^\circ\text{C}$) upon increasing the CH content to 30 vol-% (Figure 6.3A, Table S6.1). Hence, these endotherms can be assigned to the melting of PLLA within the patch-like SEL-1 wCCM corona. In the respective cooling traces (Figure 6.3B) crystallization can only be detected for the Xyl/CH = 70/30 (v/v) mixture ($T_c(\text{PLLA}) = 15^\circ\text{C}$), suggesting that for 20 vol-% CH crystallization of PLLA can either be not resolved or occurs during the isotherm at -15°C . The PLLA melting and crystallization temperatures are significantly reduced compared to that in the respective bulk sample (Figure S6.2), which can be attributed to a plasticizing effect of the used solvents. The estimated degrees of crystallinity for PLLA are in both mixtures well below $\alpha = 5\%$ (Table S6.1). Hence, crystallization appears to be significantly hampered by the confinement imposed by the patchy corona structure. For the PE middle block, the corresponding crystallization and melting transitions are again rather broad and slightly shifted to lower temperatures in the Xyl/CH mixtures ($T_c(\text{PE}) = 27^\circ\text{C}$, $T_m(\text{PE}) \approx 44^\circ\text{C}–45^\circ\text{C}$), which is attributed to the more pronounced plasticizing effect of CH.

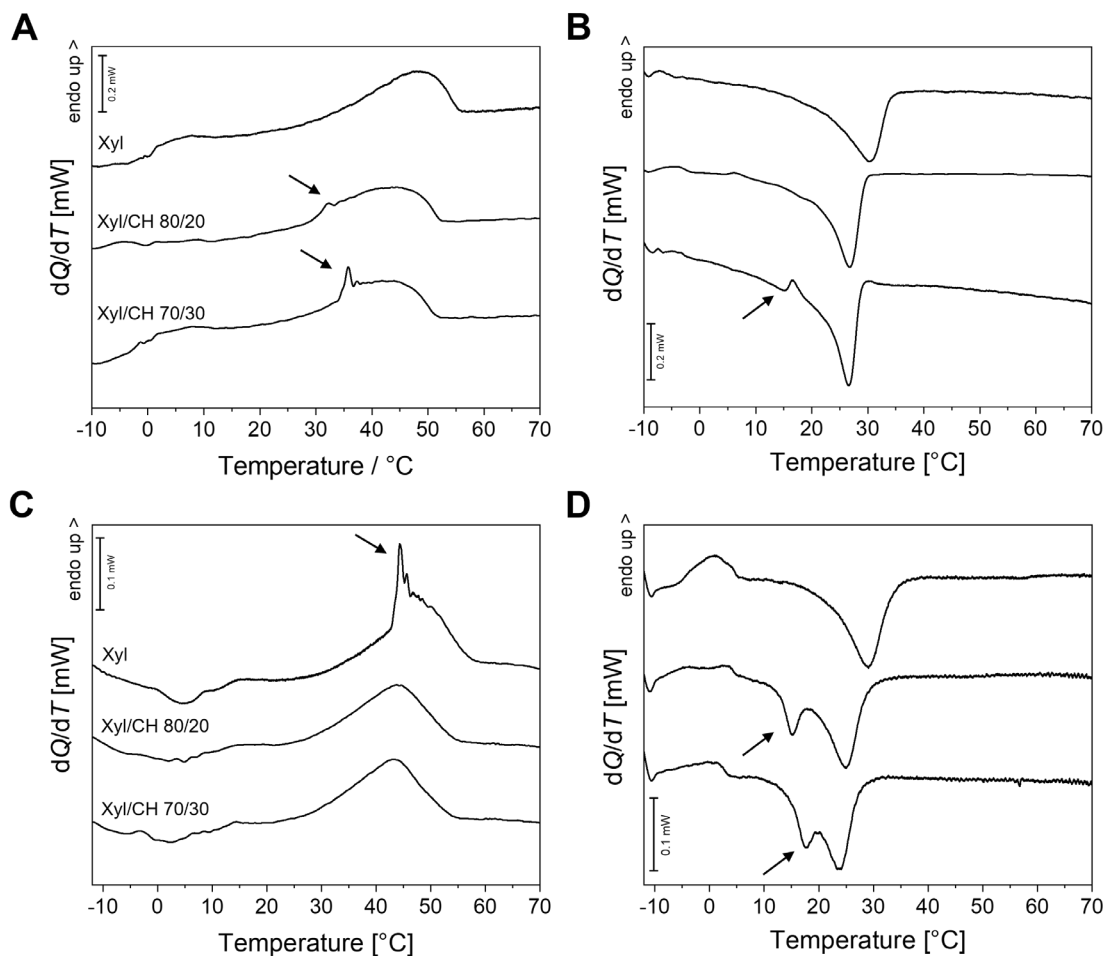


Figure 6.3 μ -DSC heating and cooling traces for (A, B) SEL-1 and (C, D) SEL-2 in Xyl, Xyl/CH = 80/20 (v/v) and Xyl/CH = 70/30 (v/v) ($c = 10 \text{ g L}^{-1}$, scanning rate: 0.5 K min^{-1}). Arrows indicate melting and crystallization transitions of the PLLA block.

For SEL-2 (Figure 6.3C,D) melting of PLLA could already be detected in pure Xyl, with the respective heating trace showing multiple weak endothermic peaks attributable to PLLA (first most intense endotherm at $T_m(\text{PLLA}) = 44^{\circ}\text{C}$, Table S6.1). This might be ascribed to the increased length of the PLLA block in SEL-2, resulting in a reduced solubility in pure Xyl. The observed multiple PLLA endotherms might be attributed either to the patchy structure of the corona, resulting in crystals of different thickness and/or perfection, or to rearrangement processes upon heating. The PE block shows a rather broad melting transition ($T_m(\text{PE}) \approx 48^{\circ}\text{C}$) being superimposed with the PLLA endotherms. In the respective cooling trace, only one exotherm attributable to PE crystallization can be detected ($T_c(\text{PE}) = 29^{\circ}\text{C}$), implying that PLLA crystallization took place during the isothermal at -15°C . In contrast to SEL-1, clear PLLA crystallization exotherms are discernible in the cooling traces of SEL-2 in Xyl/CH mixtures. The respective crystallization temperatures increase with the CH content from $T_c(\text{PLLA}) = 15^{\circ}\text{C}$ (20 vol-% CH) to $T_c(\text{PLLA}) = 18^{\circ}\text{C}$ (30 vol-% CH), whereby the degree of

crystallinity is still below 5% despite the significantly higher PLLA content in SEL-2 (Table S6.1). In the heating traces, only one broad melting transition can be observed for both Xyl/CH mixtures, which might result from comparable melting points and, accordingly, strongly overlapping PE and PLLA endotherms. It is noted that the “apparent” degree of crystallinity for the PE block calculated from the heating traces ($\alpha_{\text{app}}(\text{PE}) = 40\%–43\%$) is significantly higher compared to the degree of crystallinity obtained from the respective cooling traces ($\alpha(\text{PE}) = 33\%$), where PE and PLLA crystallization exotherms can be separated. An effect that was not observed for SEL-1 in Xyl, where only the PE block was able to crystallize with $\alpha(\text{PE}) = 64\%$ and 65% , as determined from the cooling and heating traces, respectively. This underlines the assumption that PLLA melting is “hidden” due to a strong overlap of PE and PLLA endotherms and, hence, the “apparent” degree of crystallinity derived from the heating traces is higher.

We have selected the Xyl/CH = 80/20 (v/v) mixture for further CDSA experiments and morphological studies. In pure Xyl crystallization of the PLLA block was only observed for SEL-2. Besides, for the mixture with 30 vol-% CH the PLLA crystallization exotherm strongly overlaps with the PE exotherm for SEL-2, that is, both blocks partially crystallize at the same time upon cooling. Hence, for the Xyl/CH = 80/20 (v/v) mixture the PLLA blocks are able to crystallize for both SEL triblock terpolymers and the PE and PLLA crystallization exotherms are sufficiently separated by 10°C for SEL-2. Nevertheless, for both SEL triblock terpolymers the fraction of crystalline PLLA is very low ($\alpha(\text{PLLA}) \leq 3\%$, Table S6.1). CDSA was conducted analogously to the procedure described for wCCMs prepared in THF, except that the dispersions were initially heated to 80°C. The employed peak crystallization temperatures for the PE block are listed in Table S6.1. Figure 6.4 shows the respective TEM micrographs of the structures formed by CDSA of SEL-1 and SEL-2 in Xyl/CH = 80/20 (v/v), using again selective staining with RuO₄.

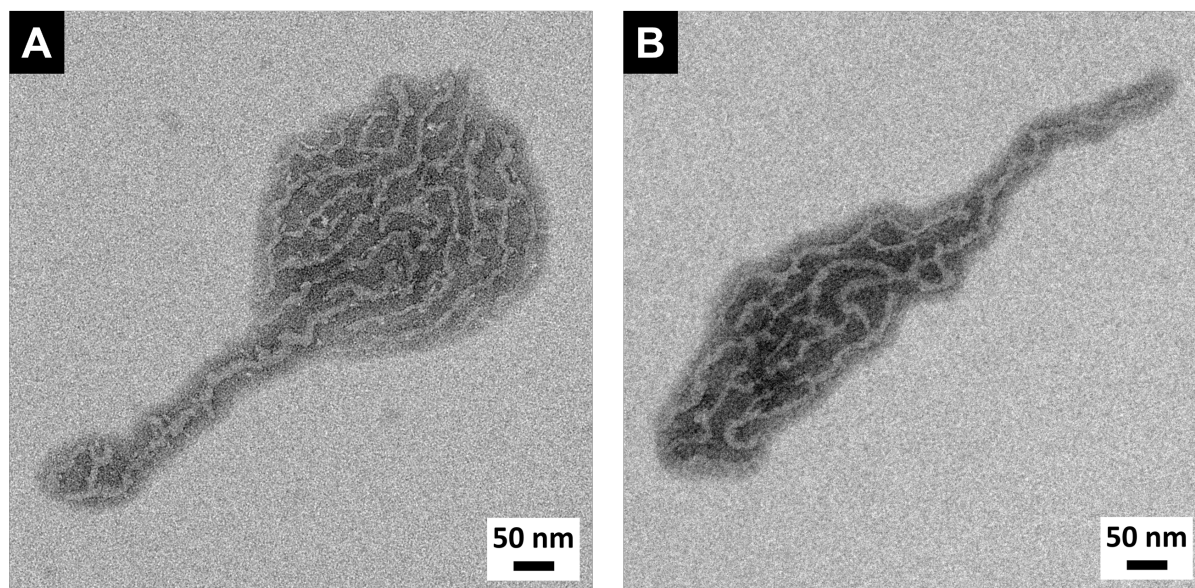


Figure 6.4 TEM micrographs of wCCMs formed by CDSA of (A) SEL-1 and (B) SEL-2 in Xyl/CH = 80/20 (v/v) mixture. PS was selectively stained with RuO₄ and appears dark.

The formation of worm-like micelles with a bright appearing PE core can be clearly deduced for both SEL triblock terpolymers. However, in contrast to the wCCMs formed in THF (Figure 6.2C,D), the PLLA patches are difficult to identify. The corona of the wCCMs appears dark due to the selective staining of the PS blocks and there are only a few small, bright appearing PLLA patches discernable. This might be attributed to the limited solubility of the PLLA corona blocks in the Xyl/CH mixture, resulting in a pronounced shrinkage/collapse of the PLLA patches. Accordingly, the collapsed PLLA patches decrease in size and will be located closer to the likewise bright appearing PE cores, which makes their detection difficult. A similar effect of decreasing patch sizes was observed for wCCMs with a patch-like PS/PMMA corona prepared in toluene, being a slightly better solvent for the PS corona blocks [52]. Moreover, the PE cores of the wCCMs shown in Figure 6.4 exhibit a pronounced undulated structure, which was not visible for the wCCMs prepared in THF. This supports the assumption of collapsed PLLA patches being located close to the PE cores.

The studies in Xyl and Xyl/CH mixtures reveal that crystallization of the PLLA block within the patch-like microphase-separated PS/PLLA corona is possible when the solvent quality for the PLLA block is reduced. However, in contrast to our prior results on CDSA of a PS-*b*-PE-*b*-PEO (SEEO) triblock terpolymer [54], which forms wCCMs with a Janus-type PS/PEO corona, crystallization is hindered due to the confinement exerted by the patchy corona structure. The latter results in strongly decreased degrees of crystallinity for the PLLA blocks in the patchy SEL wCCMs (α (PLLA) < 5%). In contrast, a significantly higher degree of crystallinity was found for the PEO block in Janus-type SEEO wCCMs (α (PEO) = 63%).

6.2.4 SCDSA of Patchy SEL wCCMs With PDLA Homopolymer

In our previous work, we have shown that SCDSA of diblock copolymer mixtures bearing enantiomeric PLLA and PDLA blocks can be utilized to form well-defined micelles with a semi-crystalline PLLA/PDLA SC core in non-solvents for the polylactide SC [78, 79]. Accordingly, using a similar approach, it should be possible to selectively load the PLLA patches in the corona of patchy SEL wCCMs driven by stereocomplexation with an enantiomeric PDLA homopolymer. This might be harnessed to add further functionality to the wCCMs, like fluorescence. To test this concept, a SEL-1 wCCM dispersion in Xyl/CH = 80/20 (v/v) was used ($c = 10 \text{ g L}^{-1}$). The solubility of the PLLA blocks in the corona patches is sufficiently limited in this solvent mixture, indicated by the ability of the PLLA blocks to crystallize (Figure 6.3A, Table S6.1). This limited solubility should also promote SC formation. Importantly, the degree of crystallinity for PLLA in the patches is sufficiently low (α (PLLA) $\approx 2\%$) and, hence, should not impair SC formation. SCDSA was induced by adding a solution of PDLA₆₂ homopolymer in THF ($c = 10 \text{ g L}^{-1}$) to the wCCM dispersion at a ratio of PLLA/PDLA units of 2/1 (w/w). A PDLA₆₂ homopolymer with a lower degree of polymerization with respect to the PLLA block in SEL-1 (S₂₉₆E₅₉₀L₃₆₈) and an excess of PLLA units were deliberately chosen to avoid a possible cross-linking of the wCCMs during SC formation. The mixture was then aged for 7 days without stirring, and the added THF was allowed to evaporate to facilitate SC formation. First, SC formation was probed by TEM (Figure 6.5). From the micrograph, it becomes evident that the overall worm-like structure of the micelles was preserved, with the PE cores again appearing bright (not stained by RuO₄). Also, cross-linking of micelles seems not to be a major issue, as the observed partial agglomeration is very similar to that observed for neat SEL-1 wCCMs (Figures 6.2C and 6.4A). In contrast, more globular assemblies might be expected in case of pronounced cross-linking.

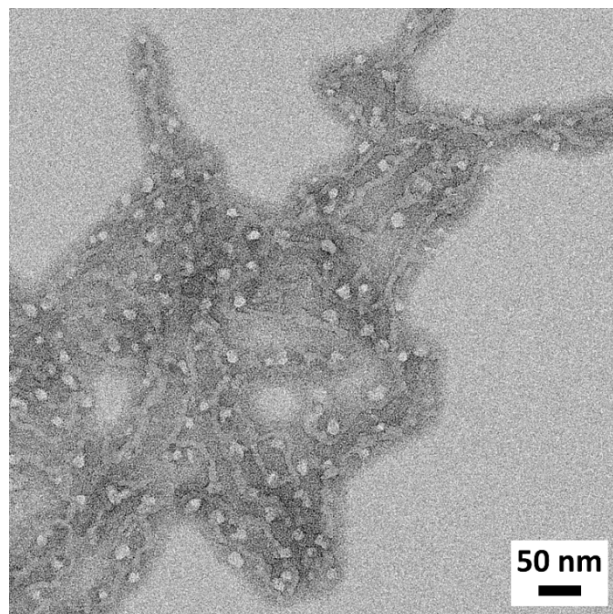


Figure 6.5 TEM micrograph of wCCMs with SC patches prepared by SCDSA of SEL-1 wCCMs with $PDLA_{62}$ homopolymer in a Xyl/CH = 80/20 (v/v) mixture. PS was selectively stained with RuO_4 and appears dark.

Notably, the corona structure differs distinctly from that of SEL-1 wCCMs prepared in THF (Figure 6.2C) and Xyl/CH = 80/20 (v/v) (Figure 6.4A). The bright patches are significantly larger and exhibit a square-like shape. They are embedded in the dark appearing PS corona (selectively stained with RuO_4), shielding the insoluble SC patches. In addition, RuO_4 is also known to preferentially stain interfaces, which results in the appearance of a darker ring around the SC patches. The area of the PLLA/ $PDLA$ SC patches, as obtained from TEM image analysis (Figure S6.5), is with $135 \pm 40 \text{ nm}^2$ about twice the area of the PLLA patches of neat SEL-1 wCCMs in THF ($73 \pm 26 \text{ nm}^2$). In comparison, the PLLA patches were very small and hard to identify for the corresponding neat SEL-1 wCCMs in Xyl/CH = 80/20 (v/v). Hence, the significant increase in size is a strong indication of successful SC formation within the patchy wCCM corona.

SC formation can be proven by infrared or Raman spectroscopy by a characteristic shift of the carbonyl stretching vibration of PLLA or $PDLA$ to lower wavenumbers upon stereocomplexation [85, 86]. Figure 6.6 compares the Raman spectra of the employed $PDLA_{62}$ homopolymer and dried SEL-1 wCCM dispersions before and after stereocomplexation. The carbonyl stretching band shifts from $\tilde{\nu} \approx 1768 \text{ cm}^{-1}$ for $PDLA_{62}$ and neat SEL-1 wCCMs to $\tilde{\nu} \approx 1750 \text{ cm}^{-1}$ for the SEL-1 + $PDLA_{62}$ SC wCCMs, proving the formation of SC patches in the wCCM corona. As the employed ratio of PLLA/ $PDLA$ units was 2/1 (w/w), the carbonyl band does not completely shift to lower wavenumbers, as there is still an excess of PLLA units in the patches that did not take part in stereocomplexation.

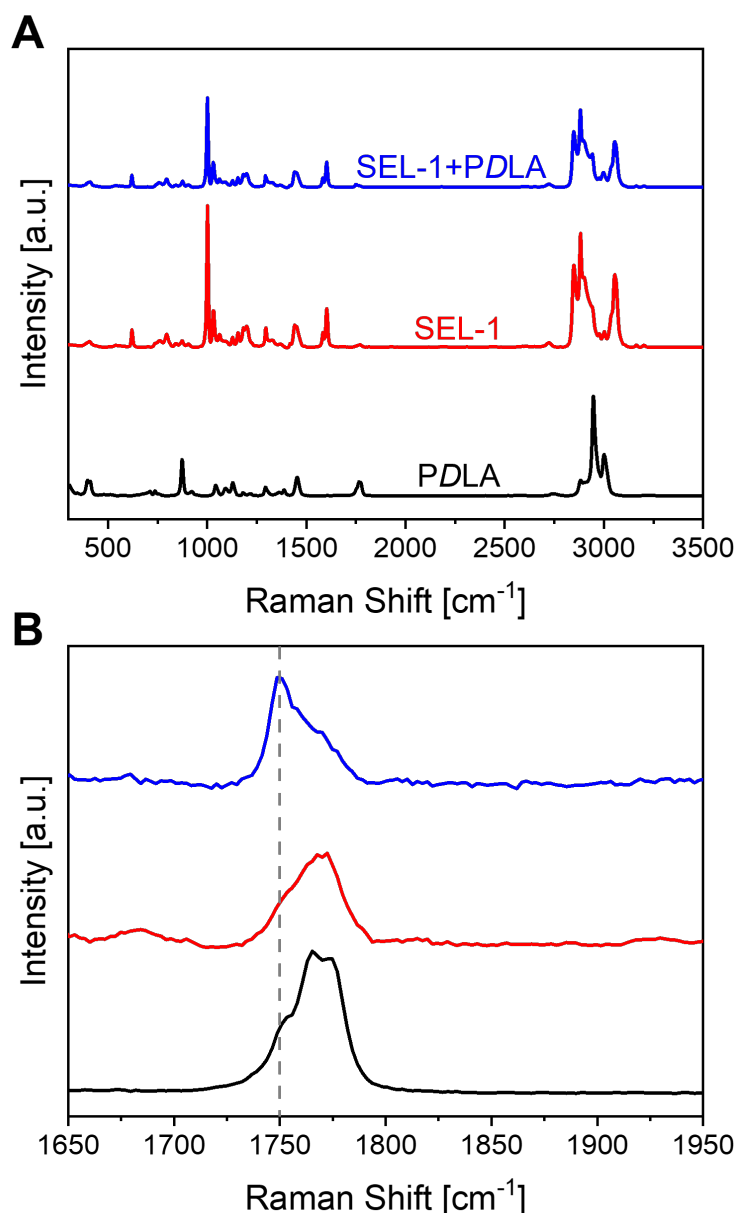


Figure 6.6 Raman spectra of PDLA_{62} homopolymer and dried SEL-1 wCCM dispersions before and after SCDSA with PDLA_{62} . (A) Full spectra and (B) zoom-ins of the carbonyl stretching vibration regime (dashed line indicates location of SC specific band).

Interestingly, when using the identical approach for SCDSA of PDLA_{62} with SEL-2 wCCMs, SC formation was not successful. In the respective TEM micrographs (Figure S6.6) large platelet-like structures are visible that most likely consist of PDLA homopolymer that crystallized upon drying the mixture on the TEM grid. In addition, the corona of the wCCMs shows hardly any patches, which is comparable to the structure found for neat SEL-2 wCCMs in $\text{Xyl/CH} = 80/20$ (v/v) (Figure 6.4B). The different behaviour of SEL-2 ($\text{S}_{296}\text{E}_{590}\text{L}_{781}$) might be attributed to the significantly longer PLLA corona block, with a degree of polymerization about twice as high as for SEL-1 ($\text{S}_{296}\text{E}_{590}\text{L}_{368}$). Accordingly, the solubility of the longer PLLA

blocks in Xyl/CH = 80/20 (v/v) is even more reduced and hinders efficient SC formation under the employed conditions.

6.2.5 Stereocomplex-Driven Fluorescence Labeling of Patchy SEL wCCMs

We utilized SCDSA to selectively introduce a fluorescent dye into the PLLA patches of SEL-1 wCCMs. This not only allows selective functionalization of the PLLA patches but also provides an elegant method to detect SC formation directly in the dispersion using fluorescence correlation spectroscopy (FCS). To this end, a rhodamine B end-functionalized PDLA homopolymer (PDLA₆₂-RB, details on synthesis are provided in the Section 4) was synthesized, and SCDSA was performed in an identical manner as described above. TEM reveals a basically identical morphology for the fluorescently labeled SEL-1 + PDLA₆₂-RB SC wCCMs (Figure S6.7) as compared to that of the non-labeled SC wCCMs (Figure 6.5). This shows that SCDSA is not altered by the presence of the fluorescent dye at the PDLA chain end.

FCS was then used to study the diffusion of the single dye-labeled polymer chains in highly diluted solutions [87], thus providing a tool to distinguish between molecularly dissolved PDLA₆₂-RB or PDLA₆₂-RB immobilized in the patches of wCCMs by stereocomplexation. According to the Stokes-Einstein relation, the diffusion coefficient is inversely proportional to the hydrodynamic radius. The significantly larger size of SC wCCMs compared to single PDLA₆₂-RB chains translates to a much larger hydrodynamic radius. Consequently, substantially reduced diffusion coefficients are expected for the SC wCCMs, leading to longer diffusion times observable in FCS measurements. Figure 6.7 compares the normalized autocorrelation of intensity data for PDLA₆₂-RB in THF (molecularly dissolved) and SEL-1 + PDLA₆₂-RB SC wCCMs in Xyl/CH = 80/20 (v/v). The results reveal that the correlation time of the PDLA₆₂-RB chains is about 3 orders of magnitude shorter than that of the micelles. This observation aligns with the expectation that micelles diffuse much more slowly. Notably, the autocorrelation data for the SEL-1 + PDLA₆₂-RB SC wCCMs exhibit no multi-step descent in the curve, indicating the absence of freely diffusing individual PDLA₆₂-RB chains or significantly larger structures that might have been formed by homo-crystallization of non-complexed PDLA₆₂-RB. Hence, in agreement with the TEM and Raman spectroscopy results discussed above, FCS confirms successful SC formation within the patches of the SEL-1 wCCMs. The important difference between the methods is that FCS can directly detect SC formation in the dispersion, whereas TEM or Raman spectroscopy can only examine the samples in the dried state.

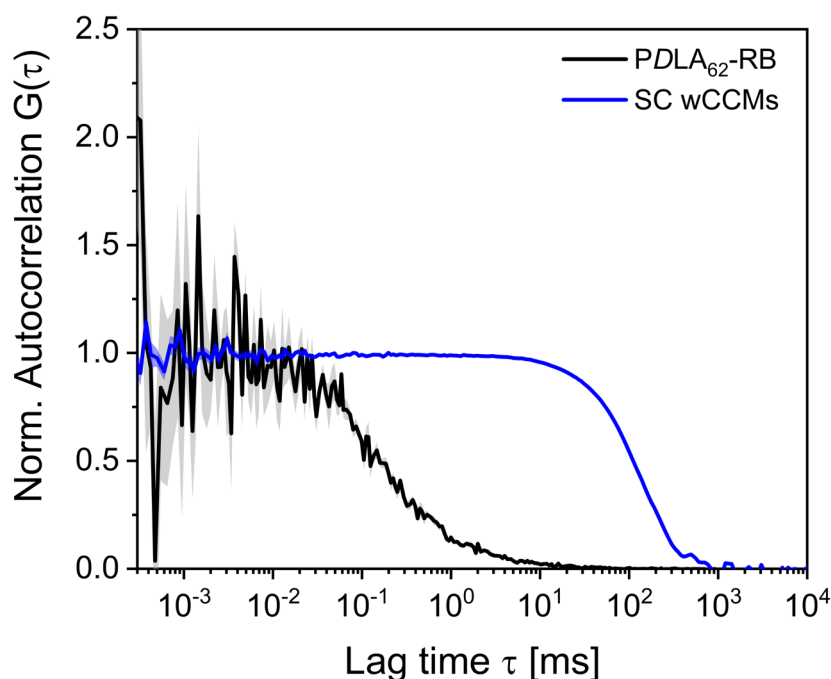


Figure 6.7 FCS autocorrelation of intensity data of PDLA₆₂-RB homopolymer in THF ($c = 1 \cdot 10^{-8} \text{ g L}^{-1}$) and SEL-1 + PDLA₆₂-RB SC wCCMs in Xyl/CH = 80/20 (v/v) ($c = 1 \text{ g L}^{-1}$). Errors are displayed as transparent areas.

6.3 Conclusion

This work shows that well-defined patchy wCCMs can be prepared by CDSA of double-crystalline polystyrene-*block*-polyethylene-*block*-poly(*L*-lactide) (PS-*b*-PE-*b*-PLLA) triblock terpolymers. CDSA to patchy wCCMs is driven by the crystallization of the PE middle block due to its insolubility in common organic solvents at room temperature. In THF, being a good solvent for the PS and PLLA corona blocks, only crystallization of the PE block is observed, resulting in wCCMs with an amorphous patchy PS/PLLA corona. However, when the solvent quality for the PLLA block is sufficiently reduced, for example, in xylene or xylene/cyclohexane mixtures, crystallization within the PLLA patches is induced without compromising the overall shape of the patchy wCCMs. Furthermore, the stereoregular PLLA patches can be selectively loaded by stereocomplexation with enantiomeric PDLA homopolymers, yielding wCCMs with PLLA/PDLA SC patches in the corona. In this way, also further functionalities can be introduced in the patchy corona as exemplified with a fluorescently labeled PDLA homopolymer. This in turn presents an elegant way to follow stereocomplexation directly in dispersion employing fluorescence correlation spectroscopy. Here, a clear shift of the autocorrelation of intensity data to longer correlation times proves the successful incorporation of the PDLA chains into the larger, slower diffusing wCCMs.

In future research, the concept of stereocomplex-driven loading can be harnessed to incorporate different (functional) guest molecules or nanoparticles into the corona of wCCMs with stereoregular PLLA patches. In addition, employing block copolymers or micelles with enantiomeric PDLA blocks/coronas might enable the construction of hierarchically structured micellar assemblies. As the efficiency of stereocomplexation is highly dependent on the employed solvent and/or temperature, access to dynamic assemblies might also be envisaged.

6.4 Experimental Section

6.4.1 Materials

All chemicals were used as received unless otherwise noted. Ethylene oxide (Linde, 3.0) was stirred over calcium hydride (CaH_2) at 0°C for 3 h before being transferred into a storage ampoule. Prior to use, ethylene oxide was additionally purified over *n*-butyllithium (*n*-BuLi) at 0°C . 1,3-Butadiene (2.5, Tyczka Industrie-Gase GmbH) was passed over columns with molecular sieves and activated alumina, followed by storage over di-*n*-butylmagnesium (Bu_2Mg) before use. Styrene ($>99\%$, Sigma-Aldrich) was stirred over Bu_2Mg under nitrogen and condensed into a storage ampoule. Dichloromethane (DCM, $\geq 99.8\%$ stabilized with amylene, analytical reagent grade, Thermo Scientific) used for lactide polymerization was dried by distillation over CaH_2 . Toluene (technical grade) for anionic polymerization was purified over 1,1-diphenyl-3-methylpentyllithium, prepared in situ by the reaction of *sec*-butyllithium (*sec*-BuLi) with 1,1-diphenylethylene (DPE), refluxed for 2–3 days under dry nitrogen, and distilled directly before use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, $>98\%$, TCI) was dried by distillation over CaH_2 . *D*- and *L*-lactide ($\geq 99.8\%$, PURASORB D and L, Corbion, Amsterdam, The Netherlands) were recrystallized from toluene and stored under argon until use. DPE ($>98\%$, TCI) was stirred with *sec*-BuLi under argon atmosphere, distilled under vacuum, and stored under argon until use. Pyridine ($>99\%$, Carl Roth) was dried successively over KOH and CaH_2 and distilled prior to use. Sulforhodamine B acid chloride (pure, Thermo Scientific), Bu_2Mg (1.0 M in heptane, Sigma-Aldrich), *sec*-BuLi (1.3 M in cyclohexane/hexane, Thermo Scientific), *n*-BuLi (1.6 M in hexanes, Thermo Scientific), benzoic acid (p.a., AlppiChem), 2-hydroxyethyl 2-bromoisobutyrate (HEBiB, 95%, Sigma-Aldrich), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, HPLC grade, Sigma-Aldrich), silver trifluoroacetate (AgTFA , $>99.9\%$, Sigma-Aldrich), deuterated chloroform (CDCl_3 , 99.8%, Deutero), tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst, $\geq 99.9\%$, Sigma-Aldrich), ruthenium(III) chloride hydrate (ReagentPlus,

Sigma-Aldrich), sodium hypochlorite solution (NaOCl, 10–15 wt% in water, Thermo Scientific), acetic acid ($\geq 99.7\%$, analytical reagent grade, Thermo Scientific), hydrochloric acid (37%, Thermo Scientific), xylene (Xyl, 99.5%, isomeric mixture, Grüssing GmbH), cyclohexane (CH, $\geq 99.8\%$, analytical reagent grade, Thermo Scientific), acetone ($\geq 99.5\%$, puriss. p.a., ACS reagent, Sigma-Aldrich), 2-propanol ($\geq 99.8\%$, puriss. p.a., ACS reagent, Sigma-Aldrich), toluene ($\geq 99.5\%$, AnalaR NORMAPUR ACS, Reag. Ph. Eur., VWR chemicals) and methanol (MeOH, $\geq 99.9\%$, analytical reagent grade, Thermo Scientific).

6.4.2 Methods

^1H NMR spectroscopy was carried out with a Bruker Ultrashield-300 spectrometer (300 MHz) at 20 or 60°C in the case of SEL triblock terpolymers. The chemical shift (δ) was determined relative to the residual solvent signal of CDCl_3 (δ (^1H) = 7.26 ppm).

SEC was conducted with an Agilent 1200 Infinity system (Agilent Technologies, Santa Clara, CA, USA) equipped with an SDV gel precolumn (particle size = 5 μm , PSS, Mainz, Germany) and an SDV linear XL gel column (particle size = 5 μm) with a porosity range from 10^2 to 10^5 Å (PSS, Mainz, Germany) using CHCl_3 (HPLC grade) as the eluent. The samples were measured at a flow rate of 0.5 mL min^{-1} at 23°C, and a refractive index (RI) detector (1260 Infinity, Agilent Technologies, Santa Clara, CA, USA) was used. Prior to analyses, all samples were dissolved and filtered through a 0.2 μm PTFE filter. The SEC system was calibrated with narrowly distributed PS standards (PSS calibration kit) and toluene (HPLC grade) was used as the internal standard.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was performed with a Bruker Daltonics autoflex maX (Bruker, Germany) equipped with a smartbeam-II solid state laser and operating in linear mode. The samples were prepared by the dried droplet method using DCTB as matrix and AgTFA as ionization agent. All components were dissolved in THF (HPLC grade) at a concentration of $c = 10\text{ g L}^{-1}$ and mixed together in a volumetric ratio of matrix/sample/ionization agent = 20/5/1.

DSC of the bulk samples was performed on a Phoenix 204 F1 (Netzsch, Selb, Germany) using aluminum crucibles with pierced lids. Measurements were done under a nitrogen atmosphere within a temperature range of -50 to 200°C (scanning rate of 10 K min^{-1}).

$\mu\text{-DSC}$ was conducted with a Setaram μDSC III at a scanning rate of 0.5 K min^{-1} . The samples ($c = 10\text{ g L}^{-1}$) were dissolved at 60°C (for THF) or 70°C (for Xyl and Xyl/CH mixtures) for 1 h and transferred into closed “batch” cells sealed with fluororubber (FKM) O-rings. The pure solvent or solvent mixture was used as a reference.

Raman spectroscopy was carried out on a confocal WITec Alpha 300 RA+ Raman imaging system equipped with a UHTS 300 spectrometer and a back-illuminated Andor Newton 970 EMCCD camera (WITec Suite SIX 6.1 software package). Raman spectra of the dried micelle dispersions and the PDLA homopolymer were acquired with an excitation wavelength of $\lambda = 532$ nm and a 100x objective (Zeiss EC Epiplan-Neofluar DIC, $NA = 0.9$), employing a laser intensity of 20 mW and an integration time of 0.5 s (50–100 accumulations). All spectra were corrected for cosmic ray spikes and subjected to a background removal routine. Samples of the micelle dispersions were prepared by dropping small amounts ($3 \times 10 \mu\text{L}$) of the dispersion onto a glass slide followed by drying in vacuo (24 h, 20 mbar).

FCS was performed on a commercial confocal microscope MicroTime 200 (PicoQuant). For excitation of the Rhodamine B dyes attached to the PDLA chains, a laser diode with a wavelength of $\lambda = 560$ nm (LDH-D-TA-560B, PicoQuant) operated in pulsed mode with a repetition rate of 20 MHz was used. The excitation intensities were adjusted to approximately 1010 W cm^{-2} for PDLA₆₂-RB in THF and 8.8 W cm^{-2} for the SEL-1 + PDLA₆₂-RB SC wCCMs in Xyl/CH = 80/20 (v/v). Radiation from the laser was directed through a single-mode optical fiber into the main optical unit, reflected by a dichroic mirror (ZT488/561rpc, AHF/Chroma) into an inverted confocal optical microscope (Olympus IX73), and focused into a quartz cuvette using a semi-apochromatic objective (LUCPLFLN60X, $NA = 0.7$, Olympus) with a long working distance (1.5–2.2 mm). The signal from the sample was transmitted to the dichroic mirror and passed through a long pass filter (561 LP Edge Basic, Semrock). The signal was detected by a single-photon counting avalanche diode (SPCM-AQRH-14-TR, Excelitas), and a time-correlated single-photon counting unit (TCSPC TimeHarp 260 PICO Dual, PicoQuant, temporal resolution of 250 ps) was used to collect fluorescence data. The microscope was calibrated with a Rhodamine 110 solution excited at $\lambda = 560$ nm, yielding a radius of $\omega_r = 504 \pm 40$ nm for the detection volume in the lateral dimension. The after-pulsing effects of the avalanche photodiode were removed by applying fluorescence lifetime correlation spectroscopy (FLCS) [88, 89]. The fluorescence data was corrected and autocorrelated using the commercial software SymPhoTime 64 (Picoquant).

TEM was carried out with a JEOL JEM-2200FS field emission TEM. The energy filtering transmission electron microscope (EFTEM) was operated at an acceleration voltage of 200 kV. Zero-loss filtered micrographs ($\Delta E \approx 0$ eV) were taken with a bottom mounted CMOS camera system (OneView, Gatan) and the images were processed with a digital image processing software (Digital Micrograph 3.11, Gatan). The diluted micelle dispersions ($c = 0.1 \text{ g L}^{-1}$, $V = 10 \mu\text{L}$) were dropped on a carbon-coated copper grid, and the residual solvent was removed

directly by blotting with a filter paper, followed by drying of the coated copper grid in vacuo (24 h, $1 \cdot 10^{-5}$ mbar). The samples were stained for 5 min with RuO₄ vapor, which was formed in situ from RuCl₃ hydrate and an aqueous NaOCl solution. Afterwards, the samples were kept in a fume hood for at least 1 h to ensure the complete removal of any unreacted RuO₄. The sizes of the PLLA patches were determined with the software Fiji using the freehand selection tool and measuring 150 patches from multiple positions [90].

6.4.2 Polymer Syntheses

6.4.3.1 Hydroxy Terminated Polystyrene-*block*-Polybutadiene Macroinitiator (SB-OH)

The SB-OH macroinitiator was prepared by sequential living anionic polymerization of styrene and 1,3-butadiene in toluene followed by end-capping with ethylene oxide as published elsewhere [80]. Briefly, styrene was polymerized at 25°C for 4 h using *sec*-BuLi as the initiator. Subsequently, butadiene was added and allowed to polymerize at 40°C for 5 h. After complete conversion, the reaction mixture was cooled to 5°C and a 5-fold molar excess of ethylene oxide was added followed by stirring for 30 min at 25°C. The polymer was terminated with a mixture of acetic acid/methanol (1/5 (v/v)) and isolated by precipitation from methanol. The product was filtered and dried in vacuo (2×10^{-2} mbar) at 40°C.

6.4.3.2 PS-*b*-PB-*b*-PLLA (SBL)

PS-*b*-PB-*b*-PLLA triblock terpolymers were prepared according to the literature [91]. To SB-OH in DCM ($c \approx 150$ g L⁻¹) the respective amount of *L*-lactide was added and stirred at 25°C for 10 min under argon. DBU (10 eq with respect to OH end groups) was added, and the reaction mixture was stirred for 10 min at 25°C. Subsequently, benzoic acid (equimolar amount to DBU) was added to stop the reaction, and the mixture was stirred for 30 min. The product was precipitated from MeOH, filtered, and dried in vacuo (1×10^{-5} mbar).

6.4.3.3 Hydrogenation

The PS-*b*-PE-*b*-PLLA triblock terpolymers were obtained by hydrogenation of the corresponding SBL precursors via homogeneous catalysis in toluene at 60°C and 60 bar H₂ pressure for 3 days using Wilkinson's catalyst (RhCl(PPh₃)₃, 1 mol% with respect to the number of double bonds in the PB block). For purification, the polymer was refluxed with small amounts of concentrated hydrochloric acid and precipitated from methanol. Additionally, SEL-1 was dissolved in toluene at 70°C and precipitated from acetone/isopropanol (1/1 (v/v)), centrifuged, and dried in vacuo (1×10^{-5} mbar).

6.4.3.4 Hydroxy Terminated and Fluorescently Labeled PDLA Homopolymer (PDLA₆₂ and PDLA₆₂-RB)

PDLA₆₂ and PDLA₆₂-RB were prepared as published in previous work [79]. Briefly, PDLA₆₂ was synthesized by organo-catalyzed ring-opening polymerization of *L*-lactide employing HEB/B as the initiator and DBU as the catalyst. PDLA₆₂-RB was obtained by esterification of the hydroxy end group with sulforhodamine B acid chloride.

6.4.4 Preparation of wCCMs and SC Loading

Preparation of wCCMs via CDSA was carried out with a Crystal 16 instrument (Technobis Crystallization Systems). The SEL triblock terpolymers were dispersed at a concentration of $c = 10 \text{ g L}^{-1}$ in the respective solvent (THF) or solvent mixture (Xyl/CH = 80/20 (v/v)) using 1.5 mL vials equipped with a small stirring bar, and the following heating and cooling protocol was conducted. First, the samples were dissolved at 60°C for 1 h, followed by erasing any thermal history at 65°C (THF) or 80°C (Xyl/CH = 80/20 (v/v)) for 10 min. While slowly stirring (50 rpm) the solutions were cooled to the crystallization temperature of the PE block ($T_c(\text{PE})$, Table S1) at a cooling rate of 0.5 K min^{-1} and held at this temperature for 24 h. Subsequently, the dispersions were cooled to -10°C at 0.1 K min^{-1} , held for 1 h, and finally heated to 20°C at 0.5 K min^{-1} .

For SCDSA experiments, PDLA₆₂ dissolved in THF ($c = 10 \text{ g L}^{-1}$, $V = 36 \mu\text{L}$ [for SEL-1] or $54 \mu\text{L}$ [for SEL-2]) was added to the SEL wCCM dispersion ($c = 10 \text{ g L}^{-1}$ in Xyl/CH = 80/20 [v/v], $V = 200 \mu\text{L}$), employing a 2:1 weight ratio with respect to the enantiomeric PLLA and PDLA blocks (amount of THF after the addition $\approx 15 \text{ vol-}\%$ for SEL-1 and $\approx 21 \text{ vol-}\%$ for SEL-2). Afterwards, the dispersion was aged at 25°C for 1 week, and the remaining THF was allowed to evaporate. Fluorescently labeled wCCMs were prepared analogously using PDLA₆₂-RB.

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Supporting Information

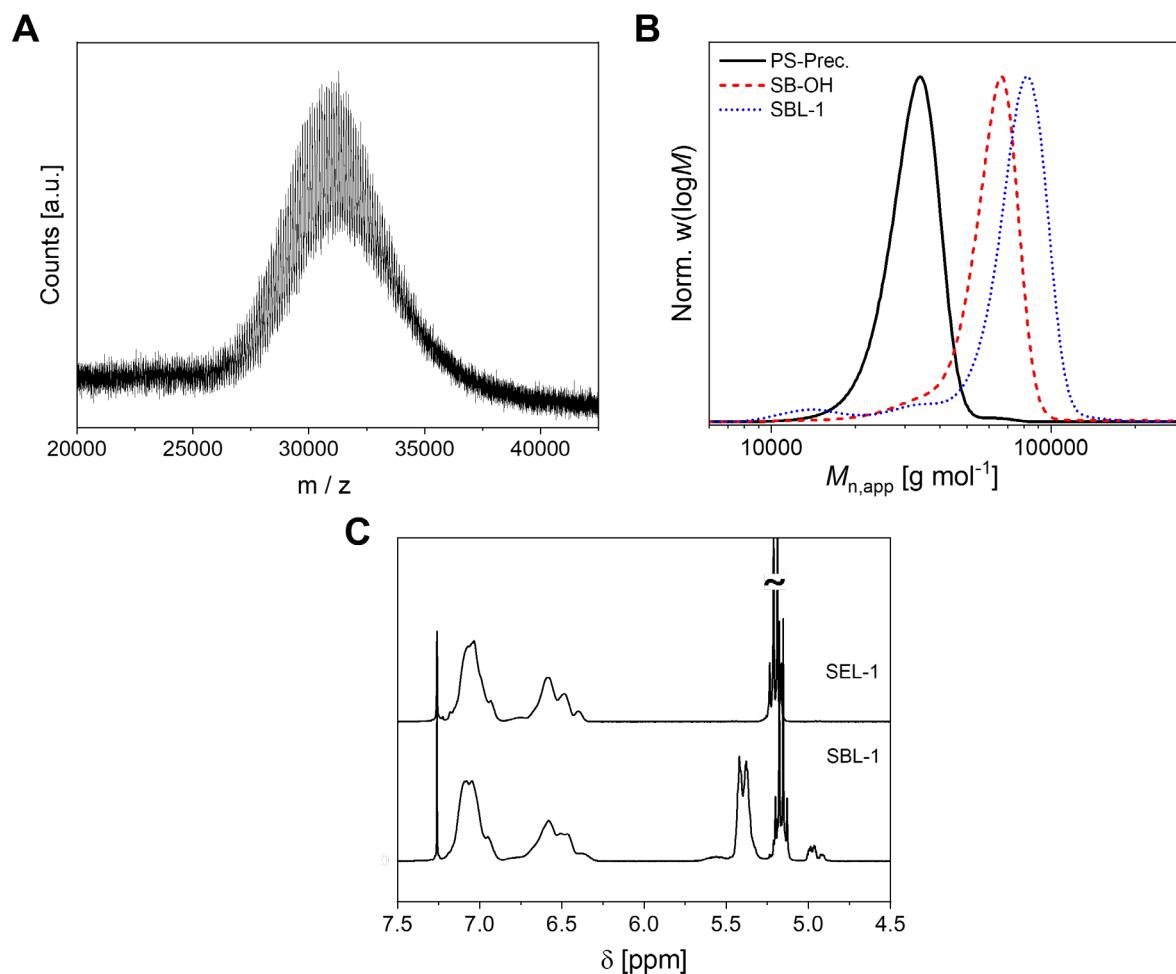


Figure S6.1 A) MALDI-ToF mass spectrum of the PS precursor (matrix: DCTB, salt: AgTFA). B) CHCl_3 -SEC traces of SBL-1 and the respective PS and SB-OH precursors. The SEC trace of SBL-1 shows a minor fraction of PLLA homopolymer formed during synthesis (peak at $V_e \approx 9.8$ mL). This was removed after hydrogenation by selective precipitation of SEL-1 in isopropanol/acetone (1/1 (v/v)). C) ^1H NMR (CDCl_3) spectra of SBL-1 and SEL-1 (measured at 60°C).

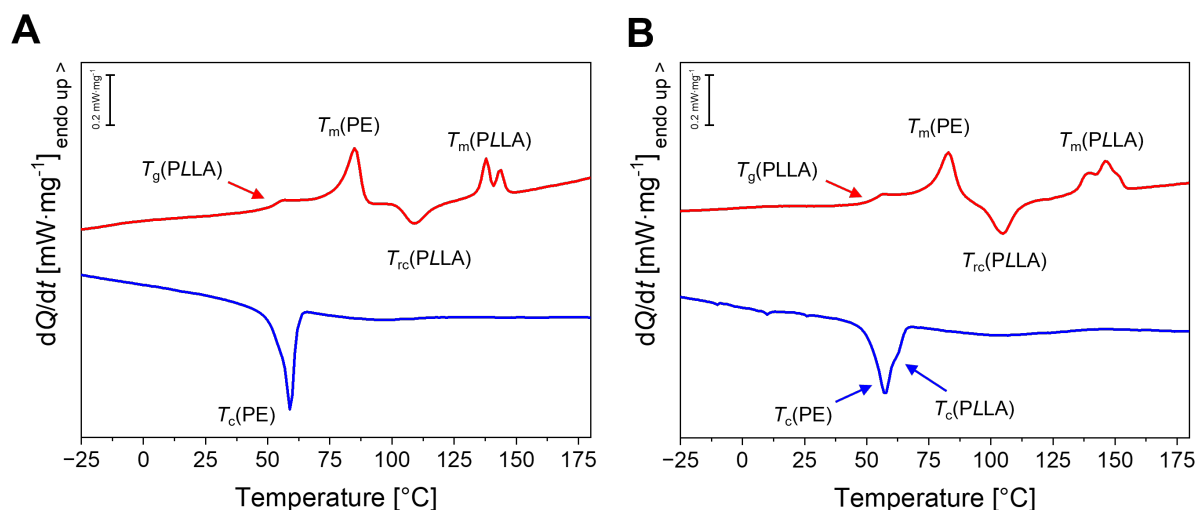


Figure S6.2 DSC cooling and second heating traces of A) SEL-1 and B) SEL-2 in bulk (scanning rate: 10 K min^{-1}): T_g = glass transition, T_m = melting, T_c = crystallization, and T_{rc} = recrystallization temperature, respectively.

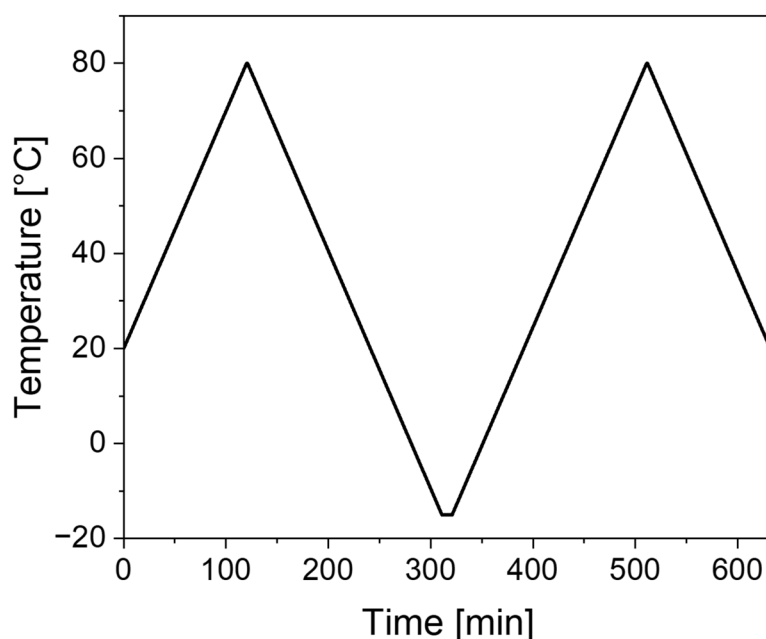


Figure S6.3 Temperature profile employed for μ -DSC measurements. In case of THF as solvent the maximum temperature was set to 65 $^{\circ}\text{C}$ (scanning rate: 0.5 K min^{-1}).

Table S6.1 Thermal properties of SEL triblock terpolymers in solution.

sample	solvent ^a	PE ^b		PLLA ^b	
		T_c / α_c [°C] / [%]	T_m / α_m [°C] / [%]	T_c / α_c [°C] / [%]	T_m / α_m [°C] / [%]
SEL-1 (S ₂₉₆ E ₅₉₀ L ₃₆₈)	THF	30 / 47	52 / 53	n.d. ^c	n.d. ^c
	Xyl	30 / 64	48 / 65	n.d. ^c	n.d. ^c
	Xyl/CH 80/20 (v/v)	27 / 59	45 / 59 ^d	n.d. ^c	33 ^e / 1.6 ^d
	Xyl/CH 70/30 (v/v)	27 / 60 ^f	44 / 60 ^d	15 / 2.9 ^f	36 ^e / 4.7 ^d
SEL-2 (S ₂₉₆ E ₅₉₀ L ₇₈₁)	THF	32 / 38	50 / 56	n.d. ^c	n.d. ^c
	Xyl	29 / 33	48 / 43 ^d	n.d. ^c	44 ^e / 3.6 ^d
	Xyl/CH 80/20 (v/v)	25 / 33 ^f	45 / 43 ^g	15 / 3.2 ^f	n.d. ^g
	Xyl/CH 70/30 (v/v)	24 / 33 ^f	44 / 40 ^g	18 / 2.7 ^f	n.d. ^g

^a THF = tetrahydrofuran, Xyl = xylene (mixture of isomers), CH = cyclohexane, polymer concentration $c = 10 \text{ g L}^{-1}$

^b T_c = peak crystallization temperature, T_m = peak melting temperature, degree of crystallinity determined from cooling (α_c) or melting (α_m) traces (PE: $\Delta H_m^0 = 289.5 \text{ J g}^{-1}$; [1] PLLA: $\Delta H_m^0 = 106 \text{ J g}^{-1}$), [2] scanning rate 0.5 °C min^{-1}

^c n.d. = not detected

^d overlapping PE and PLLA melting endotherms

^e first sharp endothermic peak attributable to PLLA melting

^f overlapping PE and PLLA crystallization exotherms

^g PLLA melting is most likely “hidden” beneath PE melting endotherm, no specific PLLA melting endotherms detectable; α_m corresponds to apparent degree of crystallinity of PE due to overlapping and not separable endotherms

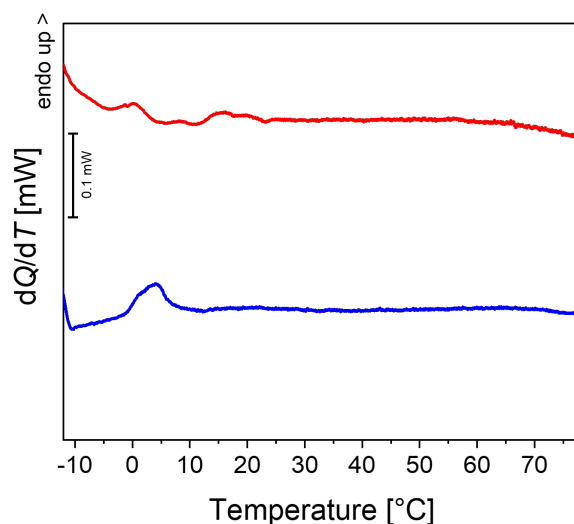


Figure S6.4 μ -DSC heating (red) and cooling (blue) traces for a neat Xyl/CH = 70/30 (v/v) mixture. Due to solvent vapor interactions with the used fluororubber (FKM) O-ring sealings, especially at higher temperatures, artifacts arise in the μ -DSC traces, e.g. endothermic peaks in cooling trace and exothermic peaks in heating trace, respectively.

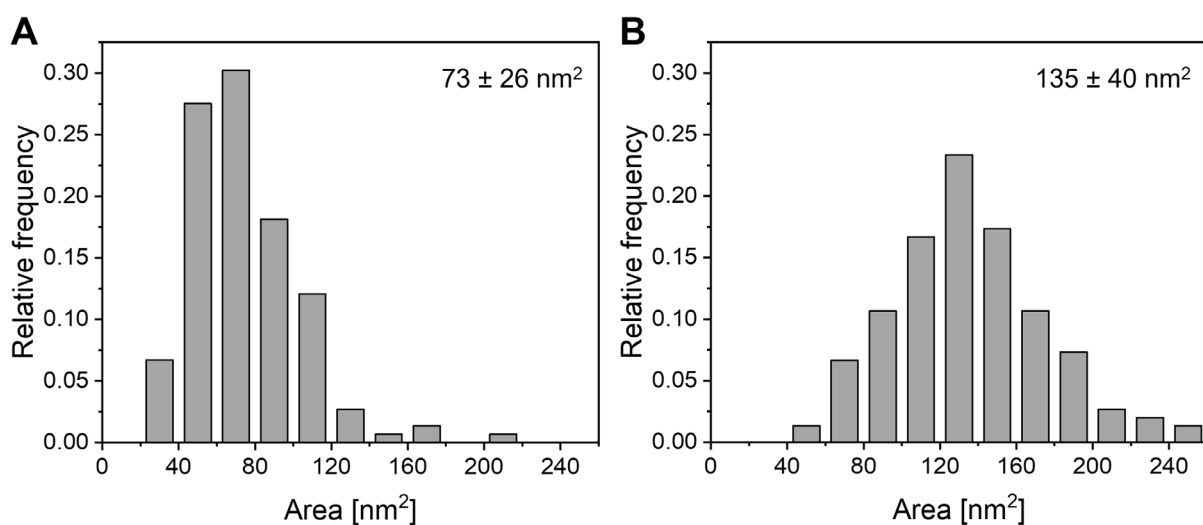


Figure S6.5 Histograms of area distributions for A) PLLA patches in SEL-1 wCCMs prepared by CDSA in THF and B) SC patches in SEL-1 + PDLA₆₂ SC wCCMs prepared in Xyl/CH = 80/20 (v/v), obtained by TEM image analysis.

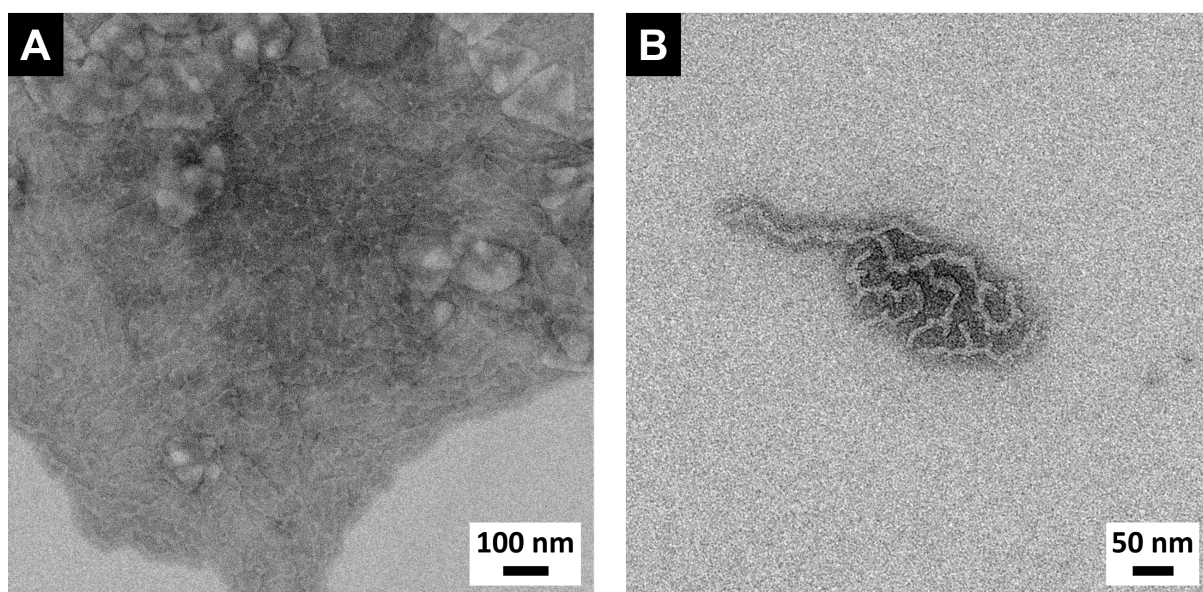


Figure S6.6 TEM micrographs of the structures formed upon addition of $PDLA_{62}$ ($c = 10 \text{ g L}^{-1}$ in THF) to a dispersion of patchy SEL-2 wCCMs ($c = 10 \text{ g L}^{-1}$), employing a ratio of PLLA/PDLA units of 2/1 (w/w). PS was selectively stained with RuO_4 vapor and appears dark.

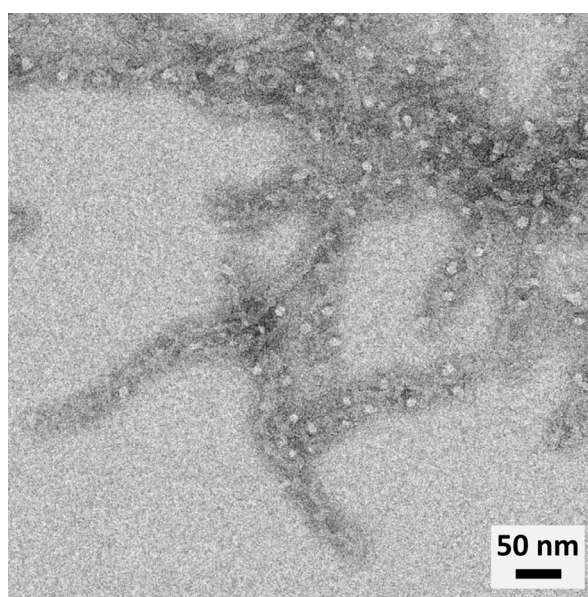


Figure S6.7 TEM micrograph of fluorescently labeled SC wCCMs prepared by SCDSA of SEL-1 wCCMs with $PDLA_{62}$ -RB homopolymer. PS was selectively stained with RuO_4 vapor and appears dark.

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7 Outlook

The modular approach of SCDSA allows an easy variation of corona-forming blocks and, consequently, corona chemistry, allowing for the fine-tuning of interfacial activity and functionality. Water-soluble polymers such as PEO or poly(methacrylic acid), obtained *via* hydrolysis of *Pt*BMA, could be employed to generate micelles with amphiphilic corona being particularly promising for stabilizing water/oil Pickering emulsions. The incorporation of nanoparticles *via* SCDSA into either the core or the corona patches may pave the way for applications in liquid-liquid interfacial catalysis. Furthermore, the preparation of micelles with a surface-compartmentalized PS/PB corona is desirable for use as compatibilizers for industrial relevant high impact PS/PB blends. To this end, alternative methods for large-scale preparation have to be developed.

Furthermore, this work enables access to patchy micelles exhibiting both spherical and platelet-like morphologies. Together with previously reported worm-like (cylindrical) patchy micelles, this broadens the range of available architectures and allows for a systematic investigation of how micellar shape influences their interfacial performance, particularly as emulsion stabilizers and compatibilizers in polymer blends.

The use of PLA-based crystalline-coil block copolymers under 3D confinement, such as within emulsion droplets, offers the potential to generate microparticles with novel morphologies. The combination of PLLA- and PDLA-based diblock copolymers can be exploited to form complex structures resembling “pseudo” triblock terpolymer morphologies *via* SCDSA in the confinement of emulsion droplets. Subsequent selective hydrolytic degradation of the PLA SC domains within the microphase-separated structures may then lead to porous microparticles with a Janus-like internal surface. Additional surface-functionalization and loading with nanoparticles may further enable their use as orthogonal catalysts in cascade reactions.

Glossary

1D	one-dimensional
$^1\text{H-NMR}$	proton nuclear magnetic resonance spectroscopy
2D	two-dimensional
3D	three-dimensional
a	degree of crystallization
A	area
AcOH	acetic acid
AFM	atomic force microscopy
ATRP	atom transfer radical polymerization
b	block
BCP	block copolymer
BuLi	butyllithium
c	concentration
CCDSA	co-crystallization-driven self-assembly
CCM	core-crystalline micelle
CDSA	crystallization-driven self-assembly
CH	cyclohexane
$\bar{D}$	dispersity
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
$D_{\text{h,app}}$	apparent hydrodynamic diameter
DLS	dynamic light scattering
DDLS	depolarized dynamic light scattering
DMAP	4-dimethylaminopyridine
DP	degree of polymerization
DSC	differential scanning calorimetry
eq	equivalent(s)
f	weight fraction
FCS	fluorescence correlation spectroscopy
FM	fluorescence microscopy
h	hour

HEBiB	2-hydroxyethyl 2-bromoisobutyrate
<i>J</i>	coupling constant
MeOH	methanol
M_n	number average molecular weight
M_w	weight average molecular weight
NA	numerical aperture
NOESY	nuclear Overhauser effect spectroscopy
P2VP	poly(2-vinyl pyridine)
PAA	poly(acrylic acid)
PB	polybutadiene
PCEMA	poly(2-cinnamoyloxyethyl methacrylate)
PCL	poly(ϵ -caprolactone)
PDLA	poly(<i>D</i> -lactide)
PDMA	poly(<i>N,N</i> -dimethylacrylamide)
PDMS	polydimethylsiloxane
PE	polyethylene
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PFS	poly(ferrocenyl dimethylsilane)
PI	polyisoprene
PLA	polylactide
PLLA	poly(<i>L</i> -lactide)
PMDETA	<i>N, N, N', N'', N'''</i> -pentamethyldiethylenetriamine
PMMA	poly(methyl methacrylate)
PnBA	poly(<i>n</i> -butyl acrylate)
PNiPAAm	poly(<i>N</i> -isopropylacrylamide)
ppm	parts per million
PS	polystyrene
PtBA	poly(<i>tert</i> -butyl acrylate)
PtBMA	poly(<i>tert</i> -butyl methacrylate)
<i>R</i>	radius
RB	rhodamine B
ROP	ring-opening polymerization

rpm	revolution per minute
r.t.	room temperature
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
<i>sc</i>	stereocomplex
SC	stereocomplex
sCCM	spherical core-crystalline micelle
SCDSA	stereocomplex-driven self-assembly
SE2	secondary electron (detector)
SEC	size exclusion chromatography
SEL	polystyrene- <i>block</i> -polyethylene- <i>block</i> -poly(<i>L</i> -lactide)
SEM	scanning electron microscopy
SLT	polystyrene- <i>block</i> -poly(<i>L</i> -lactide)- <i>block</i> -poly(<i>tert</i> -butyl methacrylate)
T_{Θ}	theta temperature
<i>t</i> BMA	<i>tert</i> -butyl methacrylate
T_c	crystallization temperature
TEM	transmission electron microscopy
T_g	glass transition temperature
TFE	trifluoroethanol
THF	tetrahydrofuran
T_m	melting temperature
v/v	volume ratio
w/w	weight ratio
WAXS	wide-angle X-ray scattering
wCCM	worm-like core-crystalline micelle
wt%	weight percent / mass fraction
Xyl	xylene
γ	interfacial tension
δ	chemical shift
ΔH_c	enthalpy of crystallization
ΔH_m	enthalpy of fusion
$\Delta H_{\text{recryst}}$	enthalpy of recrystallization

γ	interfacial tension
δ	chemical shift
Δz	vertical hight difference (z -direction)
μ -DSC	<i>micro</i> -differential scanning calorimetry
τ	lag time
$\tilde{\nu}$	wavenumber

Appendix

The following chapters present additional results from complementary research projects conducted alongside the main work of this dissertation. Although the projects remained incomplete, they reflect a significant portion of the scientific effort invested. These results are included for completeness but are not part of the submitted dissertation.

Hierarchical Self-Assembly of Patchy Stereocomplex Micelles

This section builds on the results presented in Chapter 3 and investigates the SCDSA of diblock copolymers featuring an asymmetric block length ratio of the corona-forming segments. For this purpose, $\text{PS}_{169}\text{-}b\text{-PLLA}_{56}$ and $\text{PDLA}_{72}\text{-}b\text{-PtBMA}_{592}$ were synthesized, both carrying shorter PLA blocks than the systems examined in the main study. SCDSA was performed under standard conditions: Each diblock copolymer was dissolved separately in DCM ($c = 10 \text{ g L}^{-1}$), the solutions were combined at a 1:1 weight ratio with respect to the enantiomeric PLA blocks, and the mixture was added dropwise to cyclohexane ($\text{CH/DCM} = 9/1 \text{ (v/v)}$) under stirring. After 5 days, the remaining DCM was removed by evaporation. Compared to the symmetric diblock systems, DLS revealed an increased apparent hydrodynamic diameter of $D_{\text{h,app}} = 220 \pm 90 \text{ nm}$ (vs. $104 \pm 30 \text{ nm}$ for $\text{PS}_{169}\text{-}b\text{-PLLA}_{120}/\text{PDLA}_{114}\text{-}b\text{-PtBMA}_{172}$ mixture), which can be attributed to the substantially longer PtBMA block (**Figure A1A**). Surprisingly, TEM micrographs displayed colloidal chain-like structures rather than isolated spherical micelles (**Figure A1B**). The chains do not show a continuous core and exhibit a dark PS corona, consistent with selective RuO_4 staining. The formation of these hierarchical chains is most likely an artefact introduced during TEM sample preparation. Upon drying on the carbon-coated copper grid, the long PtBMA blocks become insoluble first, collapse toward the micellar core, and promote the secondary assembly of individual micelles into chain-like aggregates.

Several attempts were made to trigger chain formation directly in dispersion, such as adding weak non-solvents or lowering the temperature to reduce the solubility of PtBMA, but the presence of anisotropic assemblies could not be conclusively verified by DLS alone. Depolarized dynamic light scattering (DDLS) would have been the method of choice for such an analysis, because it measures the rotational diffusion coefficient, which only arises for anisotropic particles possessing optical anisotropy. A detectable rotational diffusion mode in DDLS would therefore provide direct evidence for chain-like or elongated micelles, in contrast to spherical ones, which exhibit no depolarized scattering. However, DDLS instrumentation

was not available during the course of this study, preventing unambiguous confirmation of hierarchical chain formation.

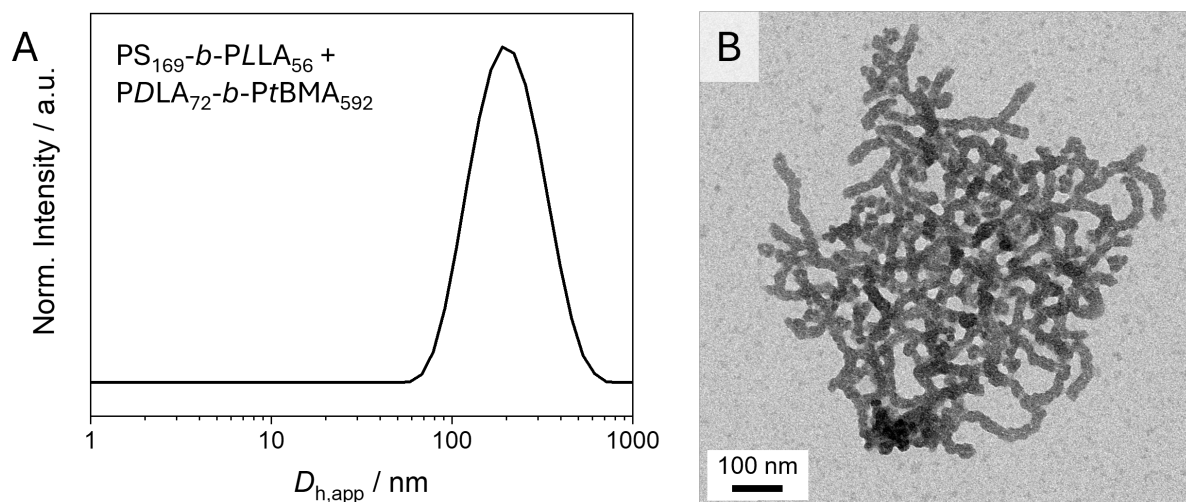


Figure A1 (A) Hydrodynamic diameter distribution from DLS for SC micelles prepared from $\text{PS}_{169}\text{-}b\text{-PLLA}_{56}$ and $\text{PDLA}_{72}\text{-}b\text{-PtBMA}_{592}$ ($c = 1 \text{ g L}^{-1}$, CH). (B) TEM micrograph of the corresponding SC micelles assembling into colloidal chains during TEM sample preparation. PS was selectively stained with RuO_4 and appears dark.

Surface-Compartmentalized Micelles by Stereocomplex-Driven Self-Assembly of Triblock Terpolymers

This work investigates the SCDSA of SLT triblock terpolymers in combination with PDLA homopolymers. In contrast to the CCDSA of SLT and PLLA described in Chapter 5, SCDSA resulted in spherical particles exhibiting a less defined surface compartmentalization. Since SCDSA of the enantiomeric $\text{PS-}b\text{-PLLA}$ and $\text{PDLA-}b\text{-PtBMA}$ diblock copolymers (cf. chapter 3) resulted exclusively in spherical micelles regardless of the self-assembly conditions, it was speculated that altering the polymer architecture might enable access to new morphologies. By combining an SLT triblock terpolymer, bearing both corona-forming blocks covalently linked to the PLLA middle block, with the corresponding PDLA homopolymer, a different crystallization behavior during SC formation was anticipated. The influence of the PLA block length and the block length ratio between the enantiomeric PLA segments on the resulting micelle morphology was examined, along with the impact of different self-assembly conditions.

SCDSA was first carried out under standard conditions. The SLT triblock terpolymer ($\text{S}_{156}\text{L}_{82}\text{T}_{132}$) and PDLA_{88} were dissolved separately in DCM ($c = 10 \text{ g L}^{-1}$), mixed at a 1:1 weight ratio with respect to the enantiomeric PLA blocks, and subsequently added to cyclohexane (CH/DCM = 9/1 (v/v)) under stirring. After 3–5 days, the remaining DCM was

removed by evaporation. DLS revealed narrowly dispersed particles with an apparent hydrodynamic diameter of $D_{h,app} = 204 \pm 65$ nm (**Figure A2A**). TEM micrographs show predominantly round particles (**Figure A2B**). In contrast to the SC micelles obtained from the diblock copolymers, neither a distinct SC core nor a well-defined surface compartmentalization is observed. Instead, the particle surface is rough and displays dark and bright regions resulting from selective staining of the PS domains with RuO_4 (PS = dark; PLLA/PDLA and PtBMA = bright). Overall, the morphology most closely resembles that of German bread dumplings. A complementary SEM image reveals particles that exhibit an even more pronounced surface roughness (**Figure A2C**). In SEM, the overall structure appears raspberry-like rather than dumpling-like. This increased roughness results from the partial degradation of the PtBMA domains under the high-energy electron beam, leaving only the PS and *sc*-PLA domains intact. In both TEM and SEM images, next to the bigger dumpling-like particles, smaller Janus micelles were detected as a side product, originating from SLT unimers that did not participate in SCDSA. These small Janus micelles do not appear in the DLS data because in the Rayleigh scattering regime, the scattering intensity scales with the sixth power of the particle radius ($I \propto R^6$), causing large particles to dominate the signal and obscure contributions from much smaller species.

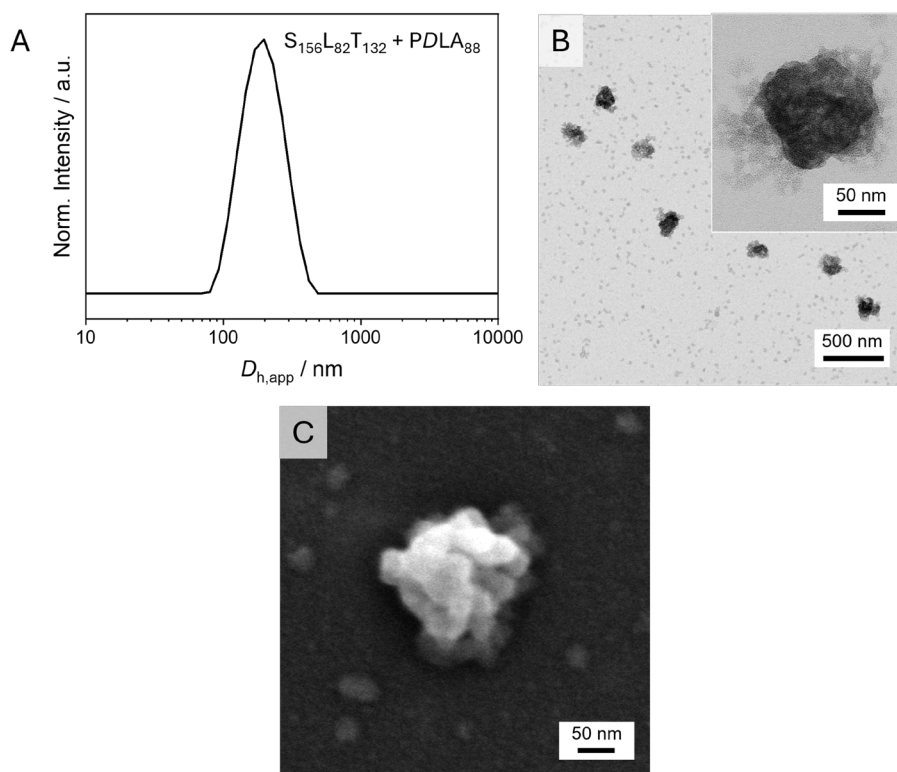


Figure A2 (A) Hydrodynamic diameter distribution from DLS for SC micelles prepared from PS_{156} -*b*- $PLLA_{82}$ -*b*- $PtBMA$ and $PDLA_{88}$ ($c = 1$ g L⁻¹, CH). (B) TEM micrograph and (C) SEM image of the corresponding SC micelles. PS was selectively stained with RuO_4 and appears dark in TEM and bright in SEM.

To test the influence of the PLA molecular weight, SCDSA of $S_{156}L_{32}T_{106}$ and $PDLA_{36}$, both having significantly shorter PLA lengths, was investigated next. Under identical conditions bigger particles were obtained, as revealed by optical microscopy. The large size of several millimeters ruled out any DLS and TEM analysis and is counterproductive for the preparation of defined micelles. Hence, the SC formation efficiency had to be lowered. It was speculated that a mismatch between the block lengths of the enantiomeric PLA would result in a less effective SC formation.

To reduce the efficiency of stereocomplex formation, $PDLA_{36}$ was replaced with the longer $PDLA_{62}$, thereby increasing the mismatch between $PLLA$ and $PDLA$ segments. SCDSA again yielded dumpling-like micelles with sizes comparable to those obtained from $S_{156}L_{82}T_{132}$ and $PDLA_{88}$. However, the relative amount of dumpling-like particles decreased, and a higher fraction of Janus micelles was observed. This can be attributed to the molar excess of $S_{156}L_{32}T_{106}$ in the mixture. Due to the mismatch in PLA block lengths, a 1:1 weight ratio with respect to the enantiomeric PLA blocks does not translate into a 1:1 molar ratio of $PLLA$ blocks and $PDLA$ chains. Consequently, less $PDLA_{62}$ homopolymer is available per $PLLA$ chain, leading to incomplete stereocomplexation and a higher fraction of unimers forming Janus micelles. To compensate, the $PDLA_{62}$ content was increased, and the $PLLA/PDLA$ ratio was systematically varied between 1/1 and 1/2 (w/w). DLS showed a clear increase in particle size with increasing $PDLA_{62}$ content (**Figure A3A**). At a $PLLA/PDLA$ ratio of 1/2 (w/w) the apparent hydrodynamic diameter reached $D_{h,app} = 470 \pm 130$ nm, being bigger than for the combination with longer and matching $PLLA/PDLA$ blocks. The signal at approximate 5000 nm is attributed to excess $PDLA_{62}$ homopolymer, which precipitated during the addition to CH. TEM analysis confirmed the formation of larger particles with a more pronounced surface compartmentalization characteristic of dumpling-like micelles (**Figure A3B**). Notably, fewer Janus micelles were observed at higher $PDLA_{62}$ loadings, indicating more efficient incorporation of $PDLA$ into the SC core. Interestingly, increasing the $PLLA/PDLA$ ratio did not affect micelle size or morphology for the combination of $S_{156}L_{82}T_{132}$ with $PDLA_{88}$, highlighting that stoichiometry sensitivity arises specifically from the shorter $PLLA$ block in $S_{156}L_{32}T_{106}$. Changing the solvents to mixtures of CH and dioxane, allowing thermal annealing at higher temperatures, did also not affect the micelle morphology or size. In this context, a temperature dependent solubility study of the different $PDLA$ homopolymer was conducted.

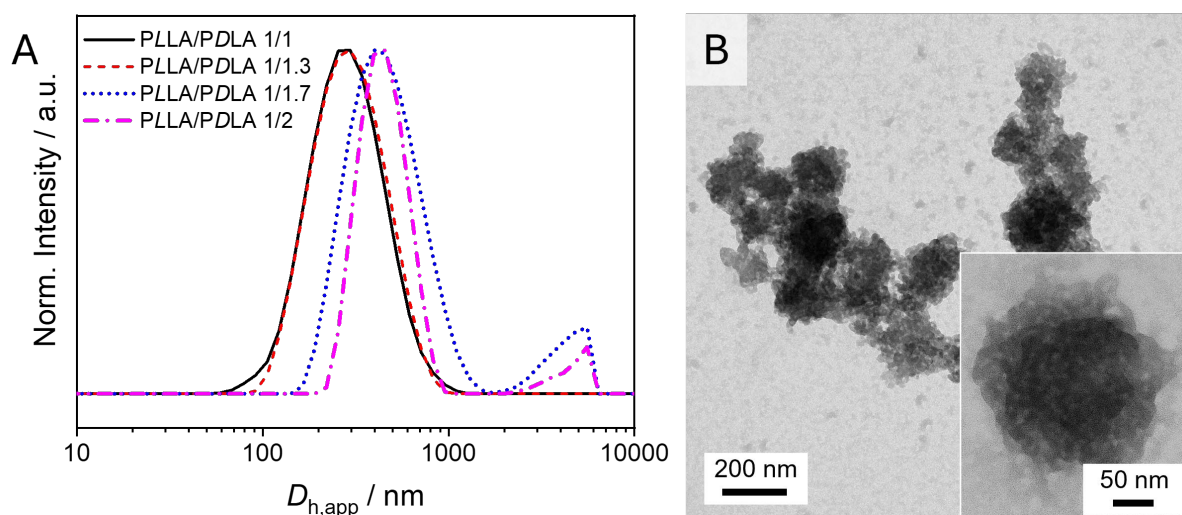


Figure A3 (A) Hydrodynamic diameter distributions from DLS for SC micelles prepared from PS_{156} - b - $PLLA_{32}$ - b - $PtBMA_{106}$ and $PDLA_{62}$ ($c = 1 \text{ g L}^{-1}$, CH) with different PLLA/PDLA (w/w) ratios. (B) TEM micrograph of the corresponding SC micelles with a PLLA/PDLA ratios of 1/2 (w/w). PS was selectively stained with RuO_4 and appears dark.

In conclusion, the SCDSA of SLT triblock terpolymers with the corresponding PDLA homopolymer leads to the formation of particles exhibiting an intriguing surface compartmentalization. However, a complete elucidation of the structure was not achievable due to limited access to advanced analytical methods. TEM tomography could enable a more detailed characterization of the particle shape and surface. Additional scattering methods, such as small-angle X-ray/neutron scattering (SAXS/SANS), would be required to resolve core–corona organization and internal domain arrangement, but it was decided not to conduct these measurements within the timespan of this work.

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