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Evaluating Polymerization Methods and Deprotection Strategies for Making Water Soluble Poly(acrylic acid) with Hydrolyzable Breaking Points

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Poly(acrylic acid) (PAA) is a hydrophilic polymer widely utilized in various everyday applications, but it may persist in the environment due to its stable carbon-carbon (C-C) backbone. This work presents a detailed comparative study of introducing hydrolyzable ester breaking points into the PAA backbone using different radical copolymerization methods (bulk versus solvent and batch versus semi-batch) with varied feed ratios of *tert*-butyl acrylate (tBA) and 2-methylene-1,3-dioxepane (MDO) followed by the investigation of the removal of *t*-Bu group for getting free acid functionality in copolymers under different conditions. A detailed comparison of polymerization approaches (bulk versus solution, batch versus semi-batch) revealed that solution polymerization at 100 °C with *tert*-butyl peroxide provided high ring-opening efficiency (71%) and uniform molecular weight distribution. The study optimized deprotection processes for tBA to acrylic acid, achieving complete hydrolysis under mild conditions using 5 equivalents of trifluoroacetic acid in dichloromethane. The resultant polymers displayed pH and temperature dependent solubility and significant degradation under alkaline conditions, with the formation of oligomers (400–700 Da for 35% MDO content) suitable for microbial assimilation. These findings highlight a scalable pathway for creating environmentally degradable PAA alternatives with tailored properties for functional applications.

1. Introduction

Water-soluble vinyl polymers with carbon-carbon (C-C) backbones and functional side-chain substituents are widely used as commodity and specialty polymers in applications such as paper binders, personal care products, laundry products, emulsifiers, etc.[1] Depending on their use and disposal method, these water-soluble polymers can enter the environment through wastewater streams or go to wastewater treatment facilities, where they may adsorb onto sewage sludge and eventually be discarded through landfilling or incineration. Synthetic water-soluble polymers can exert adverse lethal effects on microorganisms as shown recently by some of us.[2]

To make vinyl polymers more environmentally friendly, ensuring their degradation under environmental conditions or in wastewater treatment plants, easily fragmentable functional groups (breaking points) are introduced onto the C-C backbone.[3–5] This is done with the expectation that the vinyl polymers will remain stable during the use phase but will fragment into low molecular weight, water-soluble, and bio-assimilable fragments by cleavage at the intentionally introduced breaking points

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during the disposal phase. In the subsequent step, these low molecular weight fragments will be assimilated by microorganisms.[6] Systematic studies have demonstrated the biodegradation of low molecular weight oligomers of poly(acrylic acid) (PAA) compared to their high molecular weight counterparts, highlighting the potential of the concept of introducing breaking points into the vinyl polymer backbone.[7,8]

Making vinyl polymers with breaking points is getting more and more important due to the increasing concern about environmental pollution by persistent non-degrading plastics.[3,9,10] In most cases, easily hydrolyzable ester groups are introduced as breaking points by copolymerizing cyclic ketene acetals (CKAs) with vinyl monomers.[3,9,11] While the chemistry involved in synthesizing and copolymerizing CKAs using a radical initiator is straightforward, each new comonomer pair demands thorough investigation. These investigations concentrate on the copolymerization behavior of the specific CKA with the selected vinyl monomer and the resulting copolymer's microstructure, aiming for statistical copolymers.[12] If the breaking points are not evenly distributed along the carbon-carbon backbone, the fragmented high molecular weight polymer residues may not be bio assimilable.

As CKA parts in copolymers introduce hydrophobicity, using this chemistry to create water-soluble vinyl polymers with ester breaking points is expected to generate a new problem: compromising the water solubility of the polymers. In our previous work, copolymers of oligo(ethylene glycol) methacrylate and 5,6-benzo-1,3-dioxepane (BMDO) demonstrated temperature-dependent water solubility.[13] These polymers were soluble only up to a certain temperature and became insoluble upon heating, exhibiting lower critical solution temperature (LCST)-type behavior. The critical temperature ranged from 31 to 67 °C, depending on the copolymer composition. Similarly, Kikuchi et al. observed LCST-type thermoresponsive behavior in copolymers of 2-hydroxyethyl acrylate and N,N-dimethylacrylamide with MDO.[14] Also, copolymers of acrylamide (AAm) with MDO were water-soluble only above a critical temperature, showing upper critical solution temperature (UCST)-type thermoresponsivity.[15] The homopolymer of AAm is otherwise water-soluble without showing thermoresponsivity. Dove and Gibson introduced ester units onto the poly(vinyl alcohol) (PVOH) backbone by copolymerizing vinyl chloroacetate with MDO followed by deacetylation, but no details are given about the effect of MDO on the water solubility of PVOH.[16]

Poly(acrylic acid) (PAA) is another commercially available and widely used water-soluble polymer. Attempts to directly polymerize acrylic acid (AA) with CKAs in an attempt to make degradable PAA failed due to the rapid addition of a proton from the carboxylic acid to the double bond of CKAs, which generates another polymerizable monomer in situ, resulting in the absence of the desired copolymer structure.[17–19] We demonstrated several years ago the unsuitability of monomers with easily transferable hydrogen in copolymerization with CKAs taking the copolymerization of (meth)acrylic acid and BMDO as an example.[17] Similar behavior was shown during the copolymerization of 2-hydroxyethyl methacrylate (HEMA) with a free hydroxy group and CKA.[20] Therefore, vinyl monomers with functional groups containing transferable protons, such as -COOH, -OH, and -NH_2, should be protected before copolymerization with CKAs. In the post-polymerization process, these groups can then be deprotected to generate the desired polymer. Silyloxy groups for hydroxy and *t*-butyl for carboxy groups are commonly used protection groups.

t-Butyl acrylate (tBA), a protected form of acrylic acid (AA), is a commercially available monomer commonly used in copolymerization with cyclic ketene acetals (CKAs) instead of directly employing AA. This approach enables the formation of polymers with ester units in the backbone and acid functionalities in the side chains, which can be revealed after deprotection under acidic conditions.[18,19] The effect of copolymerization on the water solubility of poly(acrylic acid) (PAA) has not been thoroughly investigated in previous studies. Introducing hydrophobic CKA comonomer units into PAA is expected to influence its water solubility behavior. While modifying water solubility through the incorporation of breaking points may enable new applications, it could also render the polymers unsuitable for their original purposes. In degradable copolymers, preserving the original functions of polymers such as PAA requires not only achieving the correct microstructure (i.e., a statistically controlled distribution of ester units) but also maintaining their water solubility.[21]

Furthermore, the formation of ring-retained structures through the 1,2-vinyl addition of growing radicals onto the CKA monomer, alongside the ring-opening reaction, complicates this task.[22,23] Addressing this challenge necessitates optimizing the comonomer ratio and polymer structure to balance water solubility while ensuring the desired statistical distribution of breaking points along the polymer backbone. Additionally, optimizing the deprotection process is essential for efficiently converting *tert*-butyl groups into free carboxyl groups with minimal amounts of deprotecting agents under mild conditions to promote sustainability. The existing literature[18] reports the use of very high amounts (40 equivalents) of trifluoroacetic acid (TFA) for the deprotection of tBA in copolymers of tBA and MDO.

To address these issues, this study presents a detailed investigation of the radical copolymerization of tBA with MDO across a broad feed composition range at different temperatures. We examined the effects of polymerization methods (bulk versus solution, batch versus semi-batch) and deprotection conditions on the final polymer structure. The polymerization method correlated with the efficiency of the ring-opening reaction. Hydrolysis behavior and the resulting segment lengths of the copolymers under alkaline conditions confirmed the presence of randomly distributed breaking points, aligning with structural estimations obtained through other analytical methods. Furthermore, we investigated how the incorporation of breaking points influences the water solubility of the copolymers.

2. Results and Discussion

MDO was synthesized in a two-step process using our previously published procedure[24] and characterized using ^{1}H-NMR. The synthetic details and ^{1}H-NMRs are given in supporting information (Section S1, Figures S1 and S2, Supporting Information). The free radical copolymerization of MDO and tBA was conducted in bulk at 60 °C using AIBN as an initiator with different comonomer feeds. The reaction conditions are detailed in Table S1 (Supporting Information) (entries **P1-7**). Following

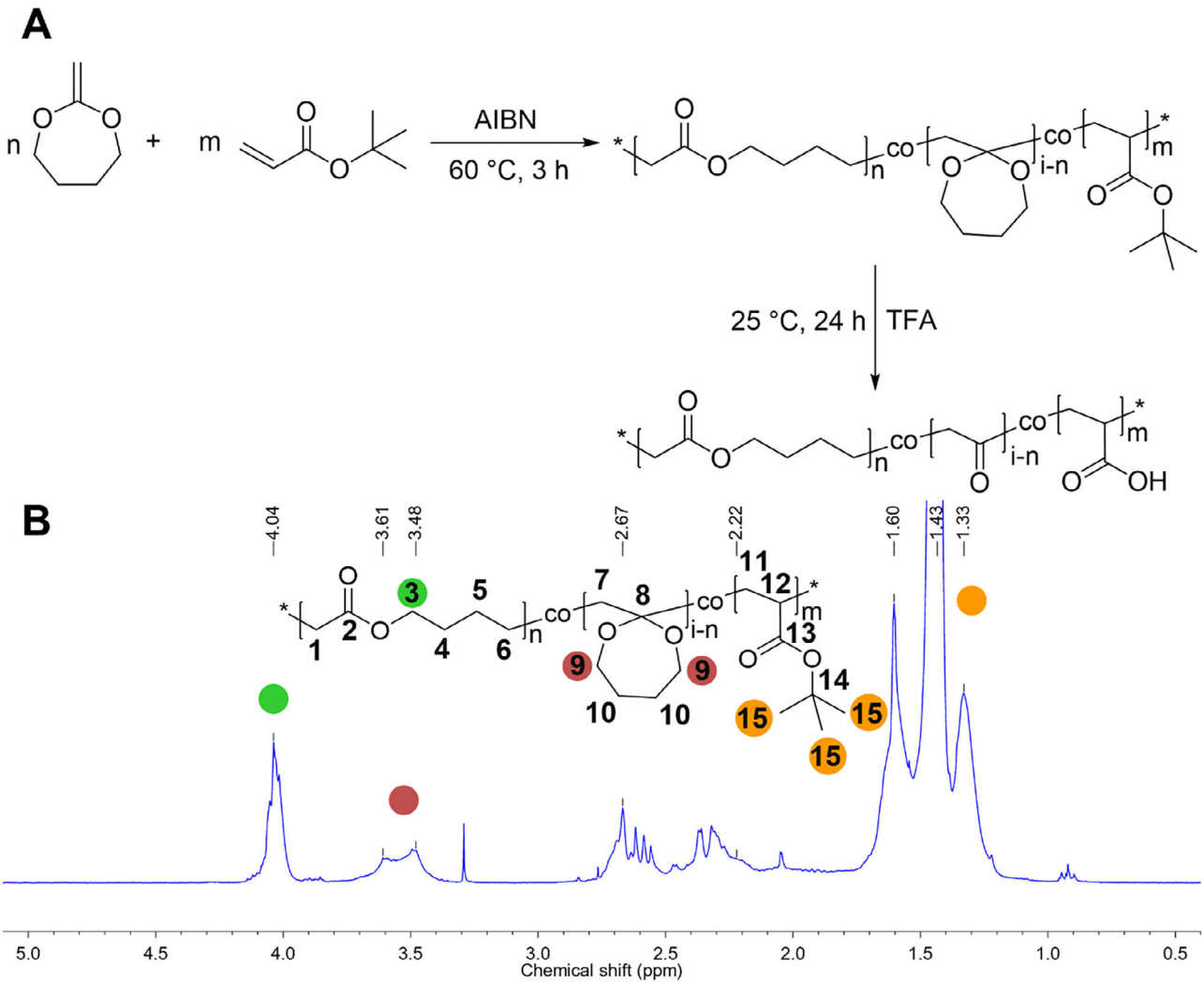

Figure 1. A) Reaction scheme illustrating the two-step preparation of poly(2-methylene-1,3-dioxepane-co-acrylic acid) (PMDO-co-PAA) by radical polymerization in bulk. B) ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of PMDO-co-PtBA (50:50 comonomer feed; **P3**, Table 1).

polymerization, the acrylate groups were deprotected, yielding poly(2-methylene-1,3-dioxepane-co-acrylic acid) (PMDO-co-PAA) (**Figure** 1A). Under similar conditions, the corresponding homopolymers were also prepared.

The ^{1}H-NMR of one of the representative samples of PMDO-co-PtBA is shown in Figure 1B. The characteristic signals of ring-opened MDO (green) at 4.04 ppm, ring-retained MDO (red) at 3.48–3.74 ppm and tBA (orange) at 1.43 ppm were observed and marked in Figure 1B.[18] The remaining methylene signals appeared as overlapping peaks at 1.3, 1.6, and between 2.2 and 2.8 ppm. The homopolymer of MDO exhibits a characteristic methyl signal at 0.9 ppm, originating from the backbiting reaction, as demonstrated in our previous work (**Figure** 2A).[25] In the copolymers, the backbiting reaction was not significant, as indicated by the presence of a negligibly small signal at 0.9 ppm.

The ^{13}C-NMR spectra of PMDO, PtBA, and PMDO-co-PtBA (Figure S3A–C, Supporting Information) were compared to assigning the signals to the carbons of the copolymer. The ester carbon of the PMDO repeating unit (signal **2**) exhibited a slightly lower chemical shift compared to the homopolymer. In the ^{13}C-NMR of the copolymer (Figure S3B, Supporting Information), new signals were found at 102 and 62 ppm, which were not observed in the spectra of PMDO or PtBA. All other carbon signals appeared at the same chemical shift as in the corresponding homopolymer. 2D HMQC-NMR of the copolymer (Figure S4, Supporting Information) correlated the ^{1}H signal at 3.63 ppm with the ^{13}C signal at 62 ppm, the expected chemical shifts for ring-retained PMDO units. The correlation of other signals confirming the copolymer structure is described in supporting information, section S3 and Figures S5 and S6 (Supporting Information).

The copolymer composition was determined using the peak integrals of the characteristic signals for ring-opened, ring-retained, and tBA, as tabulated in **Table** 1. Detailed information on the composition determination from ^{1}H-NMR (Figure S7, Supporting Information) can be found in supporting information, section S4. Copolymers with varying molar ratios (50:50 to 10:90) of MDO and tBA were obtained from copolymerization, starting with feed compositions of MDO ranging from

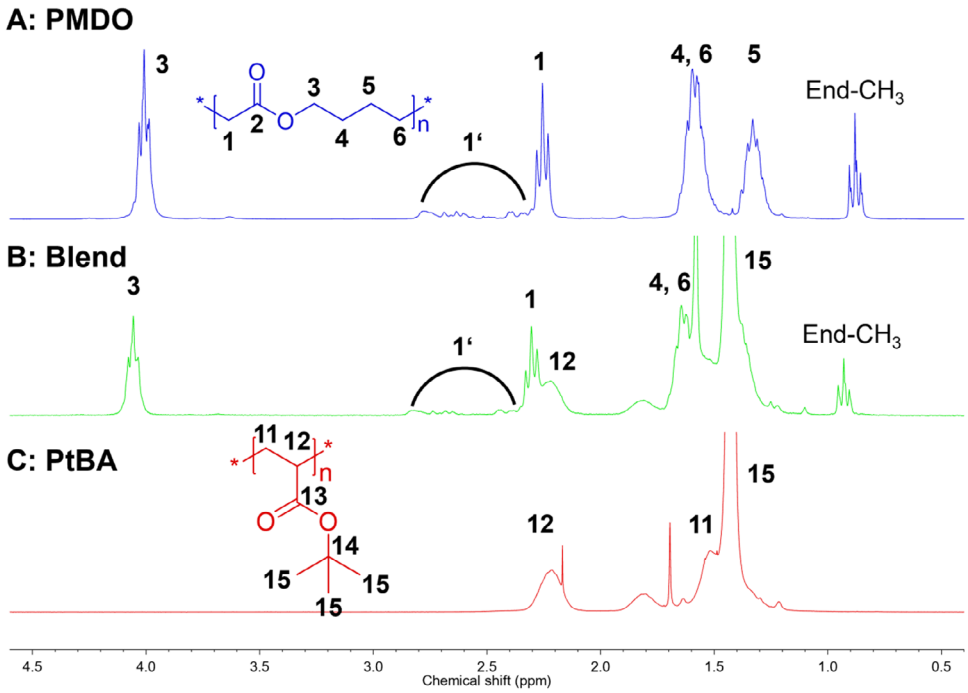

Figure 2. 1H-NMR (300 MHz, $CDCl_3$) of A) PMDO (blue); B) a blend of PtBA and PMDO (green), and C) PtBA (red).

80:20 to 10:90 (Table 1). For copolymers with feed ratios of 30:70 MDO: tBA and higher, the composition closely resembled the monomer feed. Although the ring-opening efficiency (*RO*) slightly decreased with increasing tBA concentration, it remained above 60%. In general, CKAs can undergo polymerization via radical initiation through different pathways, ring-opening (ester formation), ring-retaining (acetal formation), or a combination of both depending on factors such as initiator concentration, polymerization temperature, CKA structure, and ring size.[5,26]

Due to the absence of a solvent, the reaction proceeded very quickly. After 3 min, the Norrish-Trommsdorff effect (glass effect) was observed, indicated by a sharp increase in viscosity, followed by the sudden boiling of the reaction mixture. The SEC curves of all samples revealed multimodal distributions with very broad profiles. Therefore, instead of reporting the average molecular weights, peak average molecular weights (M_p) are reported. The M_p values ranged from 25 to 50 kDa (supporting information, section S4, Figure S8, Supporting Information). SEC measurements were not possible for the copolymers with comonomer feeds of χ_{tBA} = 80% and 90%, as the resulting polymers only swelled in organic solvents and were insoluble. The glass effect most likely caused cross-linking. The next task was to prove the formation of copolymers and rule out the formation of a mixture of two homopolymers (blend). A 2D HMBC-NMR spectrum for the samples was measured to identify the cross-couplings and thus confirm bond formation between MDO and tBA units (Figure S9, Supporting Information). Although the ester units from ring-opened MDO and tBA could be differentiated at 172 and 174 ppm, respectively, the 2D HMBC-NMR analysis did not unambiguously confirm any cross-coupling between the different repeating units. Due to overlapping peaks, successful copolymerization could not be definitively proven by this method.

Therefore, as an indirect method, the ^{1}H-NMR spectrum of the copolymer (**P3**, Table 1, Figure 1B) was compared to a blend of PMDO and PtBA of similar composition (Figure 2). In the ^{1}H-NMR spectrum of PtBA (Figure 2C), all signals were located in the range of 1.3–2.4 ppm and could be easily assigned via HMQC (Figure S5, Supporting Information) and peak integrals. The spectrum of the blend of both polymers (Figure 2B) showed the signals of both homopolymers. The protons of the homopolymers did not exhibit any change in chemical shifts when mixed as a blend. However, the ^{1}H-NMR spectrum of PMDO-co-PtBA (Figure 1B) showed very different signals within the range of 1.2–2.8 ppm. A new set of signals was found between 2.1-2.9 ppm, which were assigned to positions **1** and **12** in the copolymer, using ^{13}C-NMR and HMQC (Figures S3B and S4, Supporting

Table 1. Copolymer compositions and ring-opening efficiency (RO) determined by ^{1}H-NMR and T_g measured by DSC for copolymers of MDO and tBA prepared by bulk polymerization using different monomer feeds at 60 °C with 1 mol% AIBN.

Entry	χ_{tBA}[a)] [mol%]	Copolymer Composition [%]			*RO* [%]	T_g [°C]
		PMDO (open)	*PMDO (retained)*	*PtBA*		
P1	20	43	12	45	75	−32
P2	40	34	8	58	79	−13
P3	50	26	9	65	78	−9
P4	60	24	7	69	76	1
P5	70	20	7	73	74	7
P6	80	11	6	84	66	24
P7	90	6	4	90	63	41

a) *tert*-butyl acrylate comonomer feed.

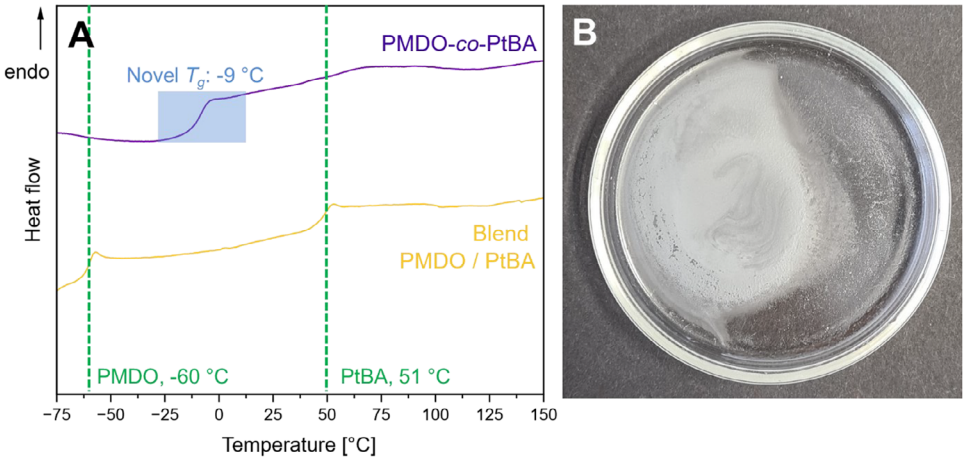

Figure 3. A) DSC measurements of PMDO-co-PtBA (65% PtBA, 35% PMDO; top curve, purple, **P3**), prepared in bulk, 1 mol% AIBN, 60 °C with χ_{tBA} = 50% comonomer feed and of PMDO / PtBA blend (60% PtBA, 40% PMDO; bottom curve, orange). B) Image of inhomogeneous PMDO / PtBA blend film.

Information). The higher chemical shift of these signals, compared to their shifts in the homopolymers (2.30 ppm for signal **1** in Figure 2A and 2.21 ppm for signal **12** in Figure 2C), strongly indicates a different chemical environment, suggesting successful copolymerization.

Solvent casting a PMDO/PtBA blend (40:60 PMDO : PtBA molar ratio) resulted in an inhomogeneous film (**Figure 3B**), demonstrating the immiscibility of both polymers. The blend exhibited two glass transition temperature values (T_g), corresponding to PMDO (−60 °C) and PtBA (51 °C) (Figure 3A, orange curve). In contrast, the copolymer displayed a single T_g at −9 °C (Figure 3A, purple curve), further confirming the formation of a copolymer.

The T_g of the copolymers varied with composition due to the significant difference in T_g between PMDO and PtBA (Table 1). A copolymer with 50% PMDO had a T_g of −32 °C, while a copolymer with 90% PtBA had a T_g of 41 °C. This variation allows for tailoring the glass transition temperature by adjusting the monomer feed composition.

Due to the lack of control in bulk polymerization, solution polymerization was studied. The reaction parameters are tabulated in Table S1 (Supporting Information), entries **P9-10**. The monomers were polymerized at 60 °C with 2 mol% AIBN in toluene (monomer concentration 33 wt%, **P9**). No Trommsdorff effect was observed. The resulting SEC curve (**Figure 4**, blue) showed lower dispersity compared to the sample (**P8**) prepared by bulk polymerization under similar conditions (60 °C, 2 mol% AIBN, Figure 4, black curve). Structural characterization of the copolymer (**Figure 5B**) by NMR revealed characteristic peaks from ring-opened MDO, ring-retained MDO, and tBA. No signals of PtBA or PMDO homopolymer were found. Although the PMDO ratio in the copolymer remained constant, the *RO* decreased to 47% in solution polymerization, compared to 72% for the corresponding polymer prepared in bulk (**P8**) (**Table 2**).

This effect was also observed by Jackson et al.[18] The decrease in *RO* is attributed to improved temperature regulation facilitated by the solvent, which makes 1,2-vinyl addition with ring-retained structure preferable to ring-opening. Generally, the literature also reports the dependence of *RO* on concentration and temperature during CKA polymerizations.[3,24] Lower concentration promotes ring-opening efficiency, while lower temperatures can reduce it. In this scenario, the impact of temperature on *RO* surpassed the influence of concentration when comparing both polymerization processes. The presence of higher amounts of ring-retained MDO units resulted in a higher T_g (20 °C). The effect of solvent polymerization was also noticed in the reduced degree of branching (*DB*), as evident from the intensity of the peak at ≈0.9 ppm in ^{1}H-NMR. The bulk copolymer showed a *DB* of 8% in comparison to 2%–3% for samples prepared by solution polymerization. Determination of *DB* is further described in the supporting information, section S5 and Figures S10 and S11 (Supporting Information). Better reaction control in solution decreased transfer reactions, thus lowering *DB*.

To improve the *RO* in solution polymerization, the reaction was conducted at 100 °C using 2 mol% tert-butyl perox-

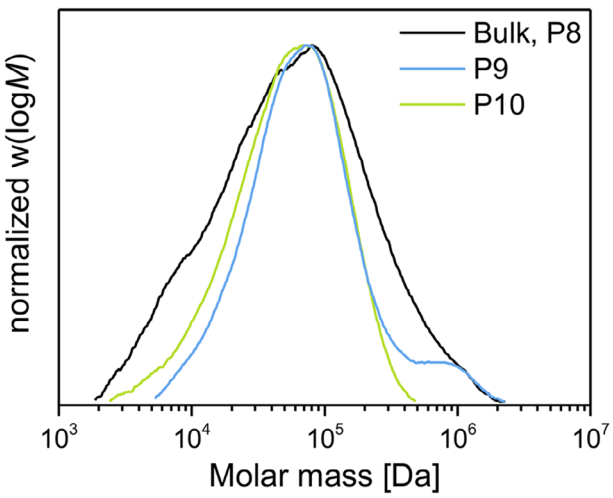

Figure 4. SEC curves, measured in THF with polystyrene as the internal standard, of PMDO-co-PtBA, prepared from χ_{tBA} = 50% comonomer feed. **Black**: 60 °C, AIBN, 2 mol% in bulk (entry **P8**); **blue**: 60 °C, AIBN, 2 mol% in solution (entry **P9**); **green**: 100 °C, DTBP, 2 mol% in solution (entry **P10**).

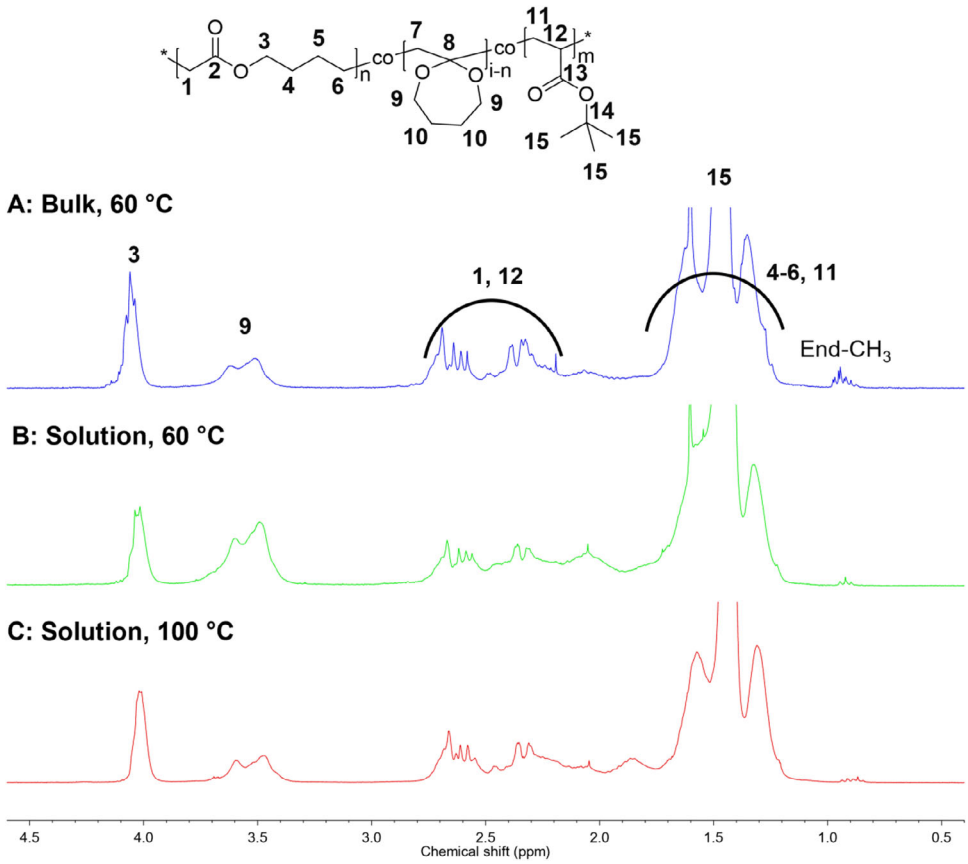

Figure 5. ^{1}H-NMR (300 MHz, $CDCl_3$) of PMDO-co-PtBA, prepared from a χ_{tBA} = 50% comonomer feed in A) bulk at 60 °C with 2 mol% AIBN (entry **P8**); B) solution at 60 °C with 2 mol% AIBN (entry **P9**) and C) solution at 100 °C with 2 mol% DTBP (entry **P10**).

ide (DTBP) as the initiator (**P10**). This resulted in a copolymer composition similar to that of bulk polymerization, with almost the same *RO* efficiency (71%) (Table 2). The *RO* efficiency was much higher than that observed during solution polymerization at 60 °C. Additionally, a monomodal molecular weight distribution ($Đ$ = 1.8) was obtained in SEC (Figure 4, green) with an M_p of 74 kDa. The T_g was 11 °C. As the PMDO ratio was similar for all copolymers, part of the change in T_g was attributed to the amount of ring-retained PMDO repeating units. The difference between **P8** and **P10** can be explained by the amount of low molecular weight fractions. As evident in the SEC curve of the bulk copolymer (Figure 4, black), it consisted of a higher amount of low molecular weight chains compared to the copolymer prepared at 100 °C in solution. The shorter chains in bulk can function as an internal plasticizer.

The desired PMDO-co-PAA was yielded from deprotection of PMDO-co-PtBA, by acidic hydrolysis with trifluoroacetic acid (TFA) (Table S2, Supporting Information). The success of the reaction was verified via ^{1}H-NMR (**Figure 6A**), by comparing the acid proton signal (12.18 ppm) to any residual *tert*-butyl signal (1.35–1.45 ppm). The composition was determined with the signal of -C$\underline{H_{222}}$O(CO)- from PMDO-ester units (3.96 ppm) and the acid signal of PAA (12.18 ppm). Since no signal at ≈3.6 ppm was observed that might have originated from the acid hydrolysis of

Table 2. Copolymer composition, ring-opening efficiency (*RO*), glass transition temperature (T_g), peak molecular weight (M_p) and degree of branching (*DB*) of PMDO-co-PtBA copolymers, prepared from χ_{tBA} = 50% comonomer feed in bulk and solution at 60 °C and at 100 °C in solution.

Entry	Method	Initiator / mol%	Composition [%]			*RO* [%]	T_g [°C]	M_p [kDa]	*DB* [%]
			PMDO (open)	*PMDO (retained)*	*PtBA*				
P8	Bulk, 60 °C	AIBN / 2	27	11	62	72	−9	80	8.0
P9	Solution, 60 °C	AIBN / 2	16	20	64	47	20	71	2.1
P10	Solution, 100 °C	DTBP / 2	23	8	69	71	11	74	3.2

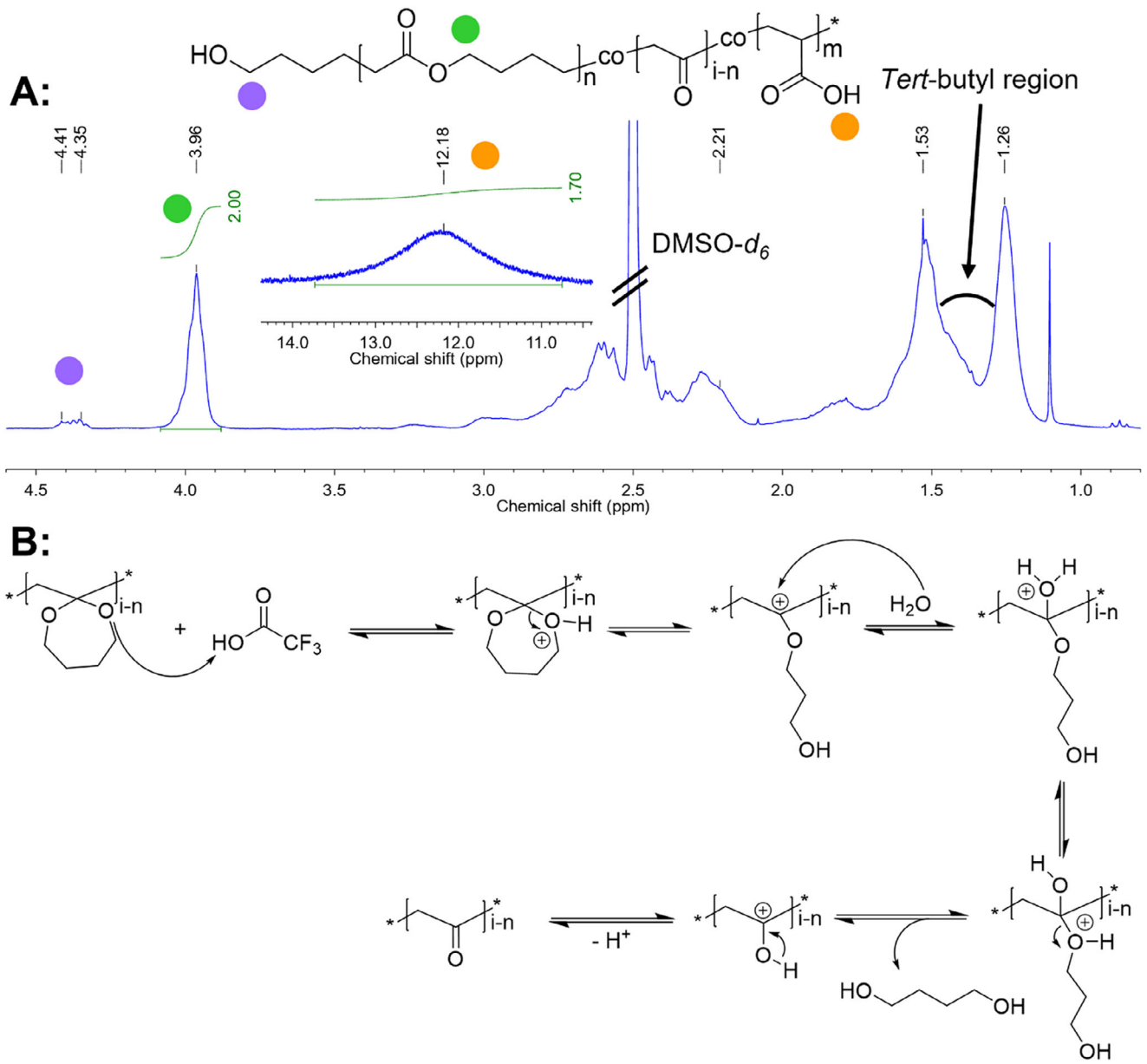

Figure 6. A) ^{1}H-NMR (300 MHz, DMSO-d_6) of poly(2-methylene-1,3-dioxepane-co-acrylic acid) (PMDO-co-PAA). B) Proposed mechanism of the deacetalization reaction of ring-retained PMDO.

the backbone ester units during deprotection step, the major reaction in the presence of TFA was the deprotection of tBA groups leading to free carboxyl groups. Furthermore, the signal of ring-retained PMDO units at 3.7 ppm (see Figure 1B) was not detected. ^{13}C-NMR (Figure S12, Supporting Information) was employed to prove the absence of the acetal and formation of a new repeating unit, as proposed in Figure 6B. The ^{13}C-NMR showed the absence of carbon **9** (see Figure S3B, Supporting Information) at 62 ppm and carbon **8** at 102 ppm, corresponding to the methylene group next to the acetal oxygens and the quaternary carbon of the ring, respectively. Furthermore, a new signal was detected at 207 ppm, corresponding to a ketone, one of the expected products of deacetalization.[18,19,27]

Different conditions were studied for the deprotection of tBA, aiming to use milder conditions with high efficiency. These conditions and their conversion rates are tabulated in Table S2 (Supporting Information). In the first run, the deprotection procedure of Jackson et al.[18] was followed, corresponding to entry **D1** in Table S2 (Supporting Information). However, full hydrolysis was not achieved after 1 h as reported by them. According to ^{1}H-NMR, only a 3% conversion was achieved. The reaction time was consequently increased to 24 h, resulting in full hydrolysis (entry **D2**).

In further attempts to reduce the amount of TFA and decrease material waste, 95% conversion was achieved with 32 equivalents of TFA (entry **D3**). However, at 20 equivalents, only 13% of the PtBA was converted after 24 h (**D4**), increasing to 37% after 48 h

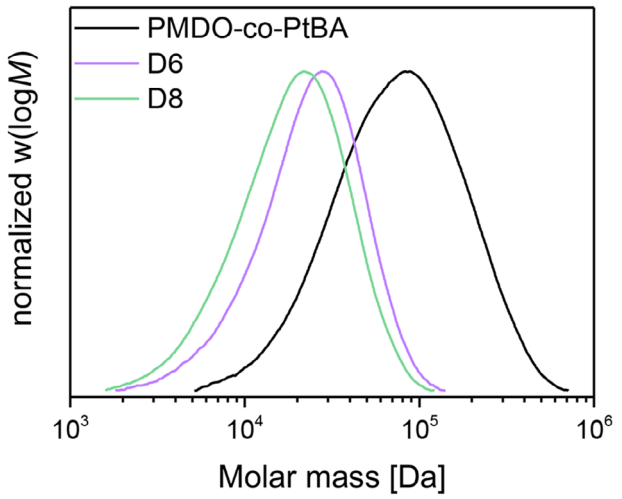

Figure 7. SEC curves, measured in THF with polystyrene as internal standard, of methylated PMDO-co-PAA after deprotection (entry **D6**: 26 eq TFA, DCM, 24 h; entry **D8**: 5 eq TFA, DCM, 24 h) in comparison to untreated PMDO-co-PtBA (**P10**, black, M_p = 85 kDa).

(**D5**), indicating that roughly 30 equivalents of TFA are necessary. Changing the solvent from THF to DCM had a drastic effect on deprotection efficiency. By switching to DCM, full hydrolysis was observed at 5–25 equivalents of TFA after 24 h (entries **D6-D12**).

To study the effect of deprotection on the backbone hydrolysis of PMDO-co-PAA, molecular weights were compared before and after deprotection (**Figure 7**). PMDO-co-PAA was methylated prior to SEC measurements to allow the use of the same eluent (THF) as for PMDO-co-PtBA as carried out in the literature.[18] The ^{1}H-NMR spectrum of the methylated copolymer is displayed in Figure S13 (Supporting Information). After deprotection, a reduction in molecular weight from M_p = 85 to 21 kDa was observed, for example, for entry **D8**. This significant decrease cannot be attributed to the cleavage of backbone ester units. Instead, it might be due to structural changes in the repeating units of the copolymers, specifically the hydrolysis of the acetal from ring-retained units of MDO to ketone. Additionally, the bulky *tert*-butyl ester was replaced by a methyl ester. Both factors strongly influence the hydrodynamic volume of the copolymer and its interaction with the column material. Therefore, molecular weights before and after deprotection cannot be directly compared.

Utilizing the optimal polymerization conditions (100 °C and 2 mol% DTBP, Table S1 (Supporting Information), entry **P10**), a kinetic study was conducted to gain insight into copolymer architecture. An exemplary ^{1}H-NMR of the reaction mixture is displayed in Figure S14 (Supporting Information), with an assignment of signals tabulated in Table S3 (Supporting Information). Detailed information about calculations is explained in supporting information, section S7. Multiple experiments on the copolymerizations of CKA and vinyl comonomers, such as methyl methacrylate (MMA), styrene, and vinyl-pyrrolidone, have shown low copolymerizability of CKAs[22,28] (e.g., r_{MMA} = 34.12; r_{MDO} = 0.05723[29]). Free radical copolymerization of these systems usually yields a mixture of polymer chains with different copolymer compositions. The faster polymerizing monomer (acrylate) is predominately consumed in the beginning, while CKA is more consumed at higher conversions.[12,30] The acrylate segment length is higher in chains formed at low conversions. Copolymerization of MDO with vinyl acetate (VAc) and derivates, on the other hand, revealed r_{MDO} = 1.53 and r_{Vac} = 0.47[31] and pseudo linear kinetics using free radical and controlled polymerization techniques. This led to smaller degradation products.[31,32]

The individual monomer conversions of tBA and MDO over time for **P10** are presented in **Figure 8** (left). The tBA is quickly converted, achieving a final conversion of 86%. In contrast, MDO is converted at a slower rate, reaching a final conversion of 43% after 3 h. To study the effect of the polymerization method on polymer microstructure, further, the polymerization method was changed to a semi-batch process (Table S1, Supporting Information, entry **P13**) in which two mixtures of A) the faster propagating monomer (tBA) in toluene and of B) the initiator (DTBP) in toluene are simultaneously added to the reaction vessel, charged with MDO and initiator in toluene. The amount of initiator is split between both mixtures to always ensure a stable initiator: monomer ratio in the polymerization mixture. The individual monomer conversions of tBA and MDO at different times of copolymerization of **P13** prepared by the semi-batch process are shown in Figure 8, right. In semi-batch polymerization, the conversions of both monomers are progressing slower and in a more linear manner. Similar MDO conversions were reached with semi-batch and batch, while the final tBA conversion was lower with semi-batch in 3 h. Homopolymer-

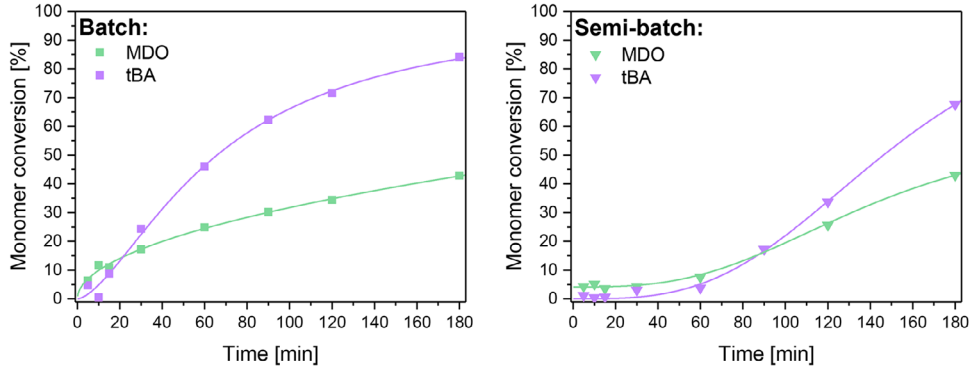

Figure 8. Kinetic study of the batch (squares) and semi-batch (triangles) polymerization of MDO (green) and tBA (purple), χ_{tBA} = 50% comonomer feed at 100 °C with 2 mol% DTBP in toluene.

Table 3. Tabulated values of monomer conversions and the ratio of the two monomers incorporated into the macromolecular chains over time. The data are derived from Figure 8. The last column pictorially represents the relative numbers of the two monomers normalized to an arbitrary total of 10. Pink spheres depict tBA, while green spheres depict MDO.

Time interval From-to [min]	Conversion [%]		Total monomer conversion after the end of the time period [%]	Ratio tBA: MDO	tBA / 10 total monomer units
	tBA	MDO			
Batch, P10					
0–30	24	17	20.5	1.4:1	5.8
30–60	22	8	35.5	2.8:1	7.3
60–90	16	5	46	3.2:1	7.6
90–120	10	4	53	2.5:1	7.1
120–150	7	4	58.5	1.8:1	6.3
150–180	5	5	63.5	1:1	5.0
Semi-batch, P13					
0–30	1	5	3	0.2:1	1.7
30–60	4	8	6	0.5:1	3.3
60–90	17	17	17	1:1	5.0
90–120	34	26	30	1.3:1	5.6
120–150	53	36	44.5	1.5:1	6.0
150–180	68	43	55.5	1.6:1	6.1

ization of MDO or tBA during batch or semi-batch polymerization was checked using ^{1}H-NMR (Figure S10C (Supporting Information) (batch) and D (semi-batch). As explained above, both PMDO and PtBA homopolymers show signals that are distinguishable from the newly formed signals within 2.1–2.9 ppm of the copolymer (Figure 5). In Figure S10C,D (Supporting Information), no signals of the homopolymers could be found. Also, DSC measurements only showed one T_g for batch and semi-batch (Figure S15, Supporting Information). The absence of the T_g of both homopolymers further solidifies the result from ^{1}H-NMR.

The data from Figure 8 are analyzed differently, comparing the ratio of the two monomers consumed over definite time intervals for both batch and semi-batch processes. This comparison is depicted in **Table 3**. It is evident from the data that each process incorporates both monomers at all stages of polymerization. Additionally, the average ratio of tBA to MDO incorporated into the macromolecular chain over time is only slightly higher

Table 4. Ring-opening efficiency (*RO*) and copolymer composition in %; glass transition temperature T_g, peak molecular weight M_p and dispersity $Đ$ of PMDO-co-PtBA for different polymerization methods (χ_{tBA} = 50% comonomer feed, 100 °C, 2 mol% DTBP, 3 h).

Entry	Method	*RO* [%]	Composition [%]			T_g [°C]	M_p [kDa]	$Đ$
			PMDO [open]	*PMDO [retained]*	*PtBA*			
P10	Batch	71	23	9	68	10	70	1.89
P13	Semi-batch	73	23	9	68	14	50	1.71

in the batch process than in the semi-batch process. The evolution of monomer consumption over time for the batch process shows a stabilization of the tBA to MDO ratio at ≈2.5–3.0:1 after 30 min, which changes to ≈1:1 toward the end of polymerization. In the semi-batch process, the tBA to MDO ratio is slightly lower and remains similar at conversions 17%–55%. Below, low tBA feed favored the polymerization of MDO. Semi-batch process exhibited a lower composition drift compared to batch polymerization, which predicts a narrower oligomer distribution after hydrolysis. A random distribution is yielded if both monomers are incorporated at a similar rate. From the data, it is evident that both batch and semi-batch processes yield macromolecular chains with a random distribution of the two comonomers. The segment length of tBA repeating units is slightly longer in the batch process compared to the semi-batch process.

The final composition, *RO*, T_g and M_p of **P10** and **P13** are listed in **Table 4**. The dispersity was reduced by semi-batch without lowering M_p, as suggested by SEC measurements of both copolymers (**Figure 9A**). Their monomodal distributions further prove successful copolymerization during batch and semi-batch. Other properties of batch copolymer; T_g, *RO* and composition, could be preserved in the semi-batch process.

The hydrophilicity of four different PMDO-co-PAA copolymers (65% (**P3**), 75% (**P5**), and 83% (**P12**) PAA units), deprotected according to Table S2, Supporting Information, entry **D8**) was assessed at different pH levels at 25 °C with a concentration of 2 mg mL^{-1} and compared to PMDO and PAA homopolymers. Since PAA contains acid side groups, water solubility is facilitated at elevated pH levels. pH 8 and 10 buffer solutions, as well as a pH 10 aqueous KOH solution, were employed to evaluate solubility. All experiments are listed in Table S4 (Supporting Information). Due to its hydrophobicity, PMDO did not dissolve in any of the tested media. The copolymers did not dissolve in Milli Q water, contrary to PAA (Figure S16, Supporting Information). However, in pH 8 and pH 10 buffer solution, copolymers with PAA content >50% dissolved. The required time for dissolving depended on the PAA content. **P12** dissolved within 10 min at pH 10 and 40 min for the pH 8 buffer solution. While **P5** dissolved within 10 min for both buffer solutions, **P3** required 1 h to fully dissolve in the pH 8 buffer medium and 45 min at pH 10 at room temperature. **P1** did not fully dissolve, even after shaking for 24 h. After filtration, a residual mass of 1.3 mg (pH 8) and 3.7 mg (pH 10) of original ca. 20 mg was yielded. PAA quickly dissolved in all tested media. Thereby, the pH of the aqueous KOH solution dropped from 10 to 4. When testing **P5** in this medium, the pH dropped as well, but the copolymer did not fully dissolve. Since the same copolymer was soluble in the pH 10 buffer solution, this further indicates pH-dependent solubility. The pH drop, induced by the dissociation of the acid side groups, limits solubility, which can be overcome by utilizing buffer systems.

When testing solubility, differences in solubilization time were observed between copolymers prepared via bulk and solution polymerizations. Copolymers with similar PAA contents (63%–65%) but different preparation methods (bulk (**P3**), solution (**P11**), semi-batch (**P13**)) were tested with Milli Q, pH 8, and pH 10 buffer solution (Figure S17, Supporting Information). While **P3** required up to 1 h for a full solution, as described above, **P11** dissolved within 5–10 min for both buffers. **P13** behaved similar to **P11**. Apart from composition, solubility behavior can also be explained by differences in molecular weight. SEC measurements of all three copolymers (Figure 9B) showed a much broader distribution for the bulk copolymer compared to the solution and semi-batch. While bulk yielded a lot more low molecu-

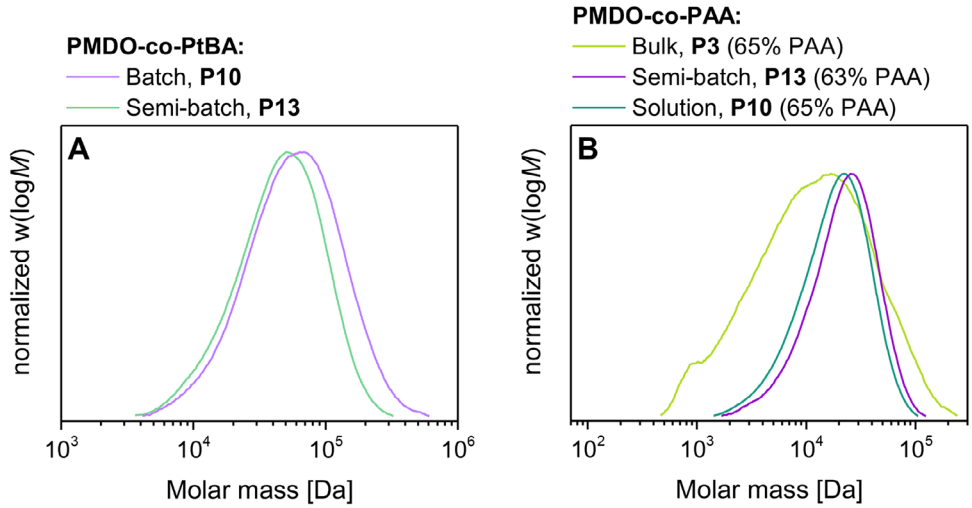

Figure 9. SEC curves, measured in THF with polystyrene as internal standard A) of PMDO-co-PtBA prepared at 100 °C, 2 mol% DTBP via batch (**P10**, purple) and semi-batch (**P13**, green). B) of methylated PMDO-co-PAA prepared via bulk (**P3**, light green); semi-batch (**P13**, dark purple) and solution (**P10**, blue).

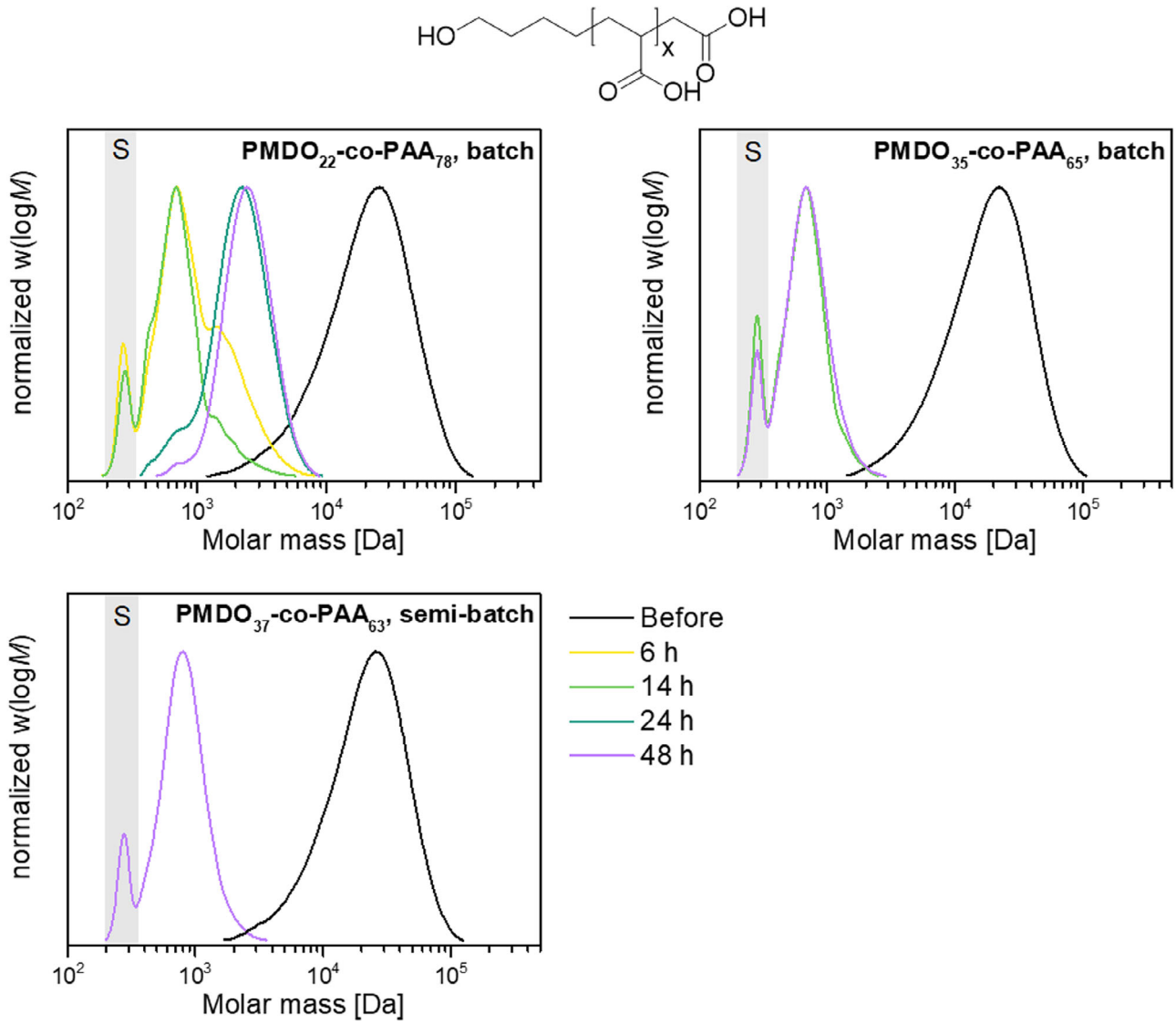

Figure 10. Proposed structure of hydrolyzed PMDO-co-PAA and SEC curves in THF, with polystyrene as internal standard (labelled *S* and marked in grey), of the hydrolytic degradation of PMDO-co-PAA (methylated before measurement) after 6 h (yellow); 14 h (green); 24 h (blue); 48 h (purple) at 20 °C and before degradation (black). From left to right: 22% PMDO to 35% PMDO batch copolymers. Bottom left: 37% PMDO semi-batch copolymer.

lar weight fractions, also higher molecular weights were achieved which can lead to prolonged solution time. However, the high amount of shorter chains should facilitate solubility.

As no copolymers were soluble in pH 6 Milli Q water at 25 °C, their solubility was further investigated at 60 °C (Figure S18, Supporting Information). The polymer mixtures were stirred for a total of 48 h. After 15 min, **P12** formed a turbid dispersion, while **P11** and **P5** required 24 h to disperse. The polymer dispersions were stable for at least 3–5 h after cooling to room temperature.

Two PMDO-co-PAA samples, prepared by batch (Table S1, Supporting Information, entries **P11-12**) and deprotected according to Table S2, entry **D8**, consisting of 35% and 22% PMDO, were hydrolyzed under alkaline conditions for 6–48 h at 20 °C with a 0.7 M aqueous KOH solution. The reaction parameters are tabulated in Table S5 (Supporting Information). SEC measurements (**Figure 10**, top left and right) were carried out after methylation of the hydrolyzed polymers to allow the use of the same eluent (THF) as for PMDO-co-PtBA. The conditions for methylation are listed in Table S6 (Supporting Information). The highest peak was chosen as M_p. Degree of polymerization, X_p, was derived from the peak molar mass after methylation by first subtracting the molar mass of the end groups, the proposed structure is displayed in Figure 10, that would result from ester hydrolysis. The M_p and X_p of the main molecular weight fraction of each sample are listed in **Table 5**. A significant molecular weight reduction was observed after only 6 h. Some molecular weights were found in the region of the internal standard (marked in grey as *S*). Stronger degradation rate after a longer reaction time was not observed.

For the sample, containing 22% PMDO, smaller segments were found after 6 and 14 h, compared to 24 and 48 h. It is

Table 5. Peak molecular weight M_p and corresponding X_p of the highest peak in SEC of two PMDO-co-PAA samples, hydrolyzed for 6, 14, 24 and 48 h at 20 °C.

Copolymer	t [h]	M_p [Da]	X_p
35% PMDO, batch, **P11**	14	679	6
	48	690	6
22% PMDO, batch, **P12**	6	676	6
	14	684	6
	24	2243	25
	48	2471	27
37% PMDO, semi-batch, **P13**	48	801	8

probable that the oligomers found at shorter reaction times were further degraded to even smaller molar masses, undetectable by SEC, with only longer chains remaining (M_p = 1200–2600 Da, X_p = 13–28). Another explanation is the formation of chains with different compositions during polymerization. Composition drift can be observed by the multimodal curves of this sample after hydrolysis. For the 35% PMDO-containing sample, only molar masses within 400–700 Da (X_p = 3–7) were detected. This is very promising for further biodegradation, as previous studies proved the necessity of small PAA segments (3–4 repeating units) for sufficient degradation.[7] This shows that the acrylate segment length in the copolymer can be influenced by the comonomer feed. The monomodal distribution of the SEC curve also suggests a low influence of composition drift on the PAA segment length in the beginning of polymerization.

Finally, a copolymer, prepared by semi-batch and consisting of 37% PMDO (Table S1, Supporting Information, entry **P13**; deprotected according to Table S2, Supporting Information, entry **D8**) was hydrolyzed for 48 h at 20 °C and compared to the corresponding batch polymer. The SEC curves after hydrolysis in Figure 10 (bottom left) showed only oligomers. M_p were close to the corresponding batch copolymer samples (Table 5). Since batch and semi-batch samples did not show a significant difference in molecular weight, the delayed addition of tBA did not yield smaller segment process.

3. Experimental Section

Materials: Azobisisobutyronitrile (AIBN, ≥ 98.0%), 2-bromo-1,1-diethoxyethane (97%), *tert*-butyl peroxide (Luperox DI, DTBP, 98%) and 2,6-di-*tert*-butyl-4-methyl-phenol (BHT, ≥ 99.0%) were purchased from Sigma–Aldrich Co. Aliquat 336, average molecular weight 442 Da, calcium hydride (93%) and *para*-toluene sulfonic acid, monohydrate (99%) were purchased from Acros Organic. 1,4-Butanediol (> 99.0%), *tert*-butyl acrylate (tBA, > 98.0%), stabilized with 4-methoxyphenol, 1,1,1-trifluoroacetic acid (TFA, > 99.0%) and trimehtylsilyldiazomethane (10% in hexanes, 0.6 M) were purchased from Tokyo Chemical Industry. Calcium chloride was purchased from Grüssing GmbH. Potassium hydroxide, analytical grade, was purchased from Bernd Kraft. Potassium *tert*-butoxide (KO^tBu, 97%) was purchased from Thermo Scientific. Hydrochloric acid (37%) was purchased from Fisher Chemical. Sodium carbonate (≥99%, water free) and sodium sulphate (≥ 99%, anhydrous) were purchased from Carl Roth GmbH + Co. KG. pH 8 and 10 buffer solutions were purchased from VWR Chemicals. Deuterated chloroform (99.8%) and deuterated dimethyl sulfoxide (DMSO, 99.8%) were purchased from Deutero. If not stated differently tetrahydrofuran (THF) was analytical grade. Dichloromethane (DCM), chloroform and toluene were analytical grade.

AIBN was recrystallized in methanol. 1,4-Butanediol was dried over $CaCl_2$ overnight and freshly distilled under vacuum. 2-Bromo-1,1-diethoxyethane was freshly distilled under vacuum. *Iso*-hexane and methanol (technical grade) were distilled. tBA was passed over a basic alumina column to remove the stabilizer. Toluene was dried over calcium hydride overnight, subsequently distilled under inert gas and stored over a 3 Å molecular sieve.

Analysis: *Nuclear magnetic resonance spectroscopy (NMR)*: The ^{1}H and ^{13}C-NMR data were acquired using a Bruker-Avance 300 MHz spectrometer at 300 MHz (^{1}H-NMR) and 75 MHz (^{13}C-NMR), respectively. The residual peak of the deuterated solvent was used as an internal standard. The spectra were evaluated with MestReNova (version: 6.1.0.6224).

Differential scanning calorimetry (DSC): The thermal properties were measured with a NETZSCH DSC 204 F1 Phoenix, using aluminum crucibles from THEPRO. The samples (8-10 mg) were heated from −80 to 150 °C with 10 K min^{-1} for PMDO and PMDO-co-PtBA. PDMO-co-PAA samples were heated from −20 to 100 °C with 10 K min^{-1}. The evaluation was conducted using the software Proteus 8.0.

Thermogravimetric analysis (TGA): The thermogravimetric data were generated using a TG 209F1 Libra thermobalance from NETZSCH. The samples (5 mg) were heated from 20–600 °C in an aluminum crucible at a heating rate of 10 K min^{-1} under nitrogen. For isothermal measurements, the sample was heated to 100 °C with 10 K min^{-1} and held at 100 °C for 1 h under nitrogen. The evaluation was performed using the software Proteus 8.0.

Size-exclusion chromatography (SEC): The molecular weight distribution was determined via size-exclusion chromatography (SEC). For this purpose, a 1200 series GPC from Agilent Technologies was used. Detection was performed with an RI detector. The data were evaluated with the help of the software PSS WinGPC UniChrom. For PMDO, PMDO-co-PtBA and methylated PMDO-co-PAA, the sample was dissolved with a 2 mg mL^{-1} concentration in tetrahydrofuran (HPLC grade) with toluene (HPLC grade) as the internal standard and filtered through a 0.22 µm PTFE filter before analysis. Measurements were carried out at a 1 mL min^{-1} flow rate. A PSS SDV with a particle size of 5 µm was used as the pre-column. The main column was PSS SDV with a 5 µm particle size. Polystyrene standards from PSS were used for calibration.

General: MDO synthesis, all polymerizations and methylation reactions were carried out under inert gas atmosphere (Argon 5.0) in standard Schlenk technique. If not stated differently, the chemicals were used as supplied. If not stated differently, deionized water was used. Spectra/Por 6 tubes pre-wetted in 0.1% Na-azide solution with a molecular weight cut-off of 1000 Da were utilized for dialysis of hydrolyzed copolymer samples. Spectra/Por 3 tubes stored dry and preserved with glycerin with a molecular weight cut-off of 3500 Da were utilized for dialysis of PAA. The tubes were stored in deionized water for min. 3 h and washed thoroughly with deionized water before use. MDO was synthesized according to literature[24] and was further described in supporting information.

Polymer Synthesis: *Poly(2-methylene-1,3-dioxepane)*. A Schlenk tube was charged with MDO (1.582 g, 13.86 mmol) and AIBN (23.0 mg, 0.14 mmol, 1 mol%). The mixture was degassed with three freeze-pump-thaw cycles. The solution was polymerized at 60 °C for 72 h and subsequently stopped by rapid cooling in liquid nitrogen and opening the tube to air. The polymer mixture dissolved in chloroform and precipitated in cold *iso*-hexane. The polymer was washed once with *iso*-hexane and dried at 70 °C under vacuum. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 4.03-4.08 (m, 2 H, OC*H2*); 2.28-2.33 (t, J = 7.48 Hz, 2 H, O = CC*H2*); 1.61-1.66 (m, 4 H, C*H2*); 1.36-1.40 (m, 2 H, CH_2CH2CH_2) ppm.

Poly(tert-butyl acrylate). A Schlenk tube was charged with tBA (0.906 g, 7.07 mmol) and AIBN (11.8 mg, 0.72 mmol, 1 mol%). The mixture was degassed with three freeze-pump-thaw cycles and polymerized at 60 °C for 3 h. The polymer was dissolved in DCM and dispersed in methanol. The polymer was isolated by centrifugation (1000 rpm, 15 min, 25 °C) and dried at 50 °C under vacuum. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 2.21 (m, 1 H, CH_2CH); 1.51, 1.77 (m, 2 H, C*H2*CH); 1.42 (s, 9 H, $CHC(CH3)_3$) ppm.

Poly(acrylic acid). Into a Schlenk flask, acrylic acid (2.169 g, 30.10 mmol) was dissolved in THF (5 mL) and Milli Q water (16 mL). After adding AIBN (49.0 mg, 0.30 mmol, 1 mol%), the solution was degassed three times via freeze-pump-thaw and stirred at 70 °C for 6 h. The polymerization was stopped by rapid cooling in liquid nitrogen and opening the flask to air. The mixture was diluted with of Milli Q water (9 mL) and dialyzed against deionized water (Spectra/Por 3, MWCO 3500 Da) for 2 days and the water was changed 4 times. The solution was reduced before lyophilization for 3 days. **^{1}H-NMR** (300 MHz, D_2O): δ = 2.39 (m, 1 H, C*H*CH_2); 1.63-1.93 (m, 2 H, C*H2*CH) ppm.

Copolymerization of MDO and tBA – Batch bulk/solution. A Schlenk tube was charged with tBA, MDO and the initiator. For solution polymerization, anhydrous toluene was added. The mixture was degassed with three freeze-pump-thaw cycles. The solution was polymerized in a preheated oil bath at 60 (AIBN) / 100 °C (DTBP) for 3 h. During kinetic experiments, aliquots were collected at given time increments and inhibited by mixing with a BHT-$CDCl_3$ solution before analysis via ^{1}H-NMR. The polymerization was stopped by rapid cooling in liquid nitrogen and opening the tube to air. The polymerization mixture was precipitated in a cold 1:11 H_2O : MeOH solution, washed, and dried under a vacuum at 70 °C for 4 days. Various copolymers were prepared by changing the molar ratio of the two monomers as shown in Table S1 (Supporting Information).

Copolymerization of MDO and tBA – Semi-batch. Into a Schlenk tube, tBA and toluene were added. A different Schlenk tube was loaded with half the DTBP and toluene. A 100 mL three-neck flask was charged with MDO, toluene (33 wt.% monomer concentration) and half the DTBP. All mixtures were degassed with three freeze-pump-thaw cycles. The three-neck flask was stirred in a 60 °C preheated oil bath while the tBA and DTBP-solution were continuously added over the course of 3 h. (Flowrate tBA-solution: 1.9 mL h^{-1}; DTBP-solution: 5.27 µL min^{-1}) NMR aliquots were collected at given time increments and inhibited by mixing with a BHT-$CDCl_3$ solution before analysis. After the complete addition of both solutions, the polymerization was stopped by rapid cooling in liquid nitrogen and opening the tube to air. The polymerization mixture was precipitated in a cold 1:11 H_2O : MeOH solution, washed and dried under vacuum at 70 °C. Reaction parameters are listed in Table S1 (Supporting Information).

Deprotection of PMDO-co-PtBA: To a solution of PMDO-co-PtBA in DCM, TFA was added in one portion and the mixture was stirred at 25 °C for 24 h. Reactions, carried out in THF-solutions, were cooled to 0 °C before adding TFA. The polymer was isolated by precipitation in ice cold water, washed until the precipitation medium reached a pH = 4 and dried under vacuum at 60 °C. **^{1}H-NMR** (300 MHz, DMSO-d_6): δ = 12.18 (s, 1 H, COO*H*); 4.35-4.41 (m, 2 H, HOC*H2*); 3.96 (m, 2 H, COOC*H2*) ppm.

Hydrophilicity of PMDO-co-PAA: In a snap lid glass, ca. 20 mg of polymer (PMDO; PAA; PMDO-co-PAA) were mixed with water (10 mL, pH 6), buffer solution (pH 8; pH 10) or a pH 10 aqueous KOH solution to yield a concentration of 2 mg mL^{-1}. The mixture was vigorously shaken for 1 h and periodically checked. The success of solution was determined via images. For the experiments **H3-6 and H8**, residual mass was determined by removing the stir bar from the mixture and dissolving the stuck polymer, prior to drying under vacuum at 50 °C. For **H16** and **H24**, undissolved polymer was removed via filtration. The polymer was washed with water to remove excess buffer and dissolved in ethanol, prior to drying under vacuum at 50 °C. The exact polymer masses and volumes of solvent used can be found in Table S4 (Supporting Information).

Hydrolytic Degradation of PMDO-co-PAA: PMDO-co-PAA was dissolved in aqueous KOH solution (0.7 M) and stirred at 20 °C for 6; 14; 24; 48 h. The pH of the mixture was then lowered to 2–7 with concentrated HCl and dialyzed (Spectra/Por 6, MWCO 1000 Da) against deionized water for 2 days. The dialysis medium was changed 4 times. The solution in the dialysis tube was reduced under vacuum and finally dried via lyophilization. The exact conditions are listed in Table S5 (Supporting Information). Prior to SEC analysis, the recovered polymer samples were methylated.

Preparation of PMDO-co-PAA for SEC Analysis: 25 mg PMDO-*co*-PAA was dissolved in 1 mL Milli Q water and 2 mL THF. Trimethylsilyldiazomethane solution was added dropwise. After full methylation, the solution turned yellow and the solution was reduced under vacuum. When primarily water was left, the sample was dried via lyophilization. The conditions of every methylation are listed in Table S6 (Supporting Information). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 4.03 (m, 2 H, OC*H2*); 3.69 (m, 3 H, OC*H3*) ppm.

PMDO/PtBA Blend Preparation: PMDO (19 mg) and PtBA (46 mg) were dissolved in DCM. The solution was poured on a glass dish and allowed to dry under atmospheric conditions overnight. For DSC measurements, PMDO (3.32 mg) and PtBA (4.77 mg) were weighed into an aluminum crucible and dissolved in DCM. The solution was carefully stirred and allowed to dry at 25 °C for 8 h, before further drying under vacuum at 60 °C overnight. To ensure complete removal of the solvent, an isothermal TGA measurement at 100 °C was conducted of the specimen, before measuring DSC.

Supporting Information

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

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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.

Keywords

copolymerization, 2-methylene-1,3-dioxepane, acrylic acid, hydrolysis, hydrophilic, radical ring-opening polymerization, semi-batch

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