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RAFT Polymerization of a Renewable Ricinoleic Acid-Derived Monomer and Subsequent Post-Polymerization Modification via the Biginelli-3-Component Reaction

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The search for renewable monomers for radical polymerization techniques is of current interest due to the awareness of sustainability requirements in the chemical sciences. Herein, the synthesis and reversible addition-fragmentation chain-transfer (RAFT) polymerization of a renewable methacrylate monomer based on ricinoleic acid as sustainable starting material is presented. In addition, the hydroxy moiety of the ricinoleic acid is converted to an acetoacetate in order to allow for a post-polymerization modification (PPM) using the Biginelli-three-component reaction (B-3CR), rendering the presented monomer a renewable and highly flexible reactant for the synthesis of polymer materials. Consequently, RAFT polymerization yields macromolecules with a molecular weight of up to 15 000 g mol^{-1} and expectedly narrow molecular weight distributions with Đs around 1.13. The feasibility of chain extension and block copolymer synthesis is demonstrated. Eventually, the PPM of the acetoacetate moiety of the polymer repeating units using the B-3CR is proven to be efficient with conversions of up to 95% of the acetoacetates, while the modification allows for a pronounced increase of the glass transition temperature to approximately room temperature compared to the unmodified polymers (T_g = −50 °C).

1. Introduction

The availability of renewable starting materials and the subsequent conversion to suitable monomers for radical polymerization techniques have recently been critically reviewed, showing that the number of renewable monomers is limited.[1,2] Hence, the search for suitable renewable monomers for the synthesis of various polymers and materials is of current interest.

A promising monomer source is castor oil produced from the seeds of *Ricinus communis*.[3,4] Castor oil is obtained by extraction of the seeds via various processing steps, followed by several refining steps to remove free fatty acids, lipids, proteins, water, and other contaminants.[3,4] The resulting castor oil consists of triacylglycerides from glycerol and different fatty acids. Up to 90% of these fatty acids is ricinoleic acid ((9*Z*,12*R*)-12-hydroxyoctadec-9-enoic acid, 1) followed by 4–5% of linoleic acid ((9*Z*,12*Z*)-octadeca-9,12-dienoic acid) and 2–3% of oleic acid ((9*Z*)-octadec-9-enoic acid).[5] Further, small amounts of palmitic (hexadecanoic acid), stearic (octadecanoic acid), and α/γ-linolenic acid ((9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoic acid/(6*Z*,9*Z*,12*Z*)-octadeca-6,9,12-trienoic acid) are present.[5] After the saponification of castor oil, pure 1 is obtained after several extraction steps.[6]

Eventually, 1 is not only an important platform chemical for the production of several C_7, C_8, C_{10}, and C_{11} compounds by pyrolysis or caustic fusion, but is directly applicable for the preparation of different polymers, especially polycondensates.[7–15] Furthermore, the esterification of renewable carboxylic acids with radically polymerisable substrates, such as 2-hydroxyethyl acrylate, -methacrylate (2), or acrylamide is a well-known method to broaden the field of renewable monomers with reactive double bonds.[1,2] Consequently, the homo- and copolymerizations of several saturated and unsaturated fatty acid esters were investigated by free radical polymerization (FRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain-transfer (RAFT) polymerization.[16,17] The respective (meth)acrylates and acrylamides of 1 are known as well.[18–20] However, only the methacrylate has been used for the synthesis of polymers.[18] More precisely, it was applied as a comonomer (≤3.0 wt.%) in a free radical miniemulsion polymerization together with butyl acrylate and methyl methacrylate;[18] homopolymers have not been reported yet.

Moreover, multi-component reactions, such as the Biginelli-3-component reaction (B-3CR), offer promising features both synthetically and from the standpoint of sustainability.[21,22] Consequently, the B-3CR has been increasingly applied within the field of polymer chemistry in usually three different ways for a large

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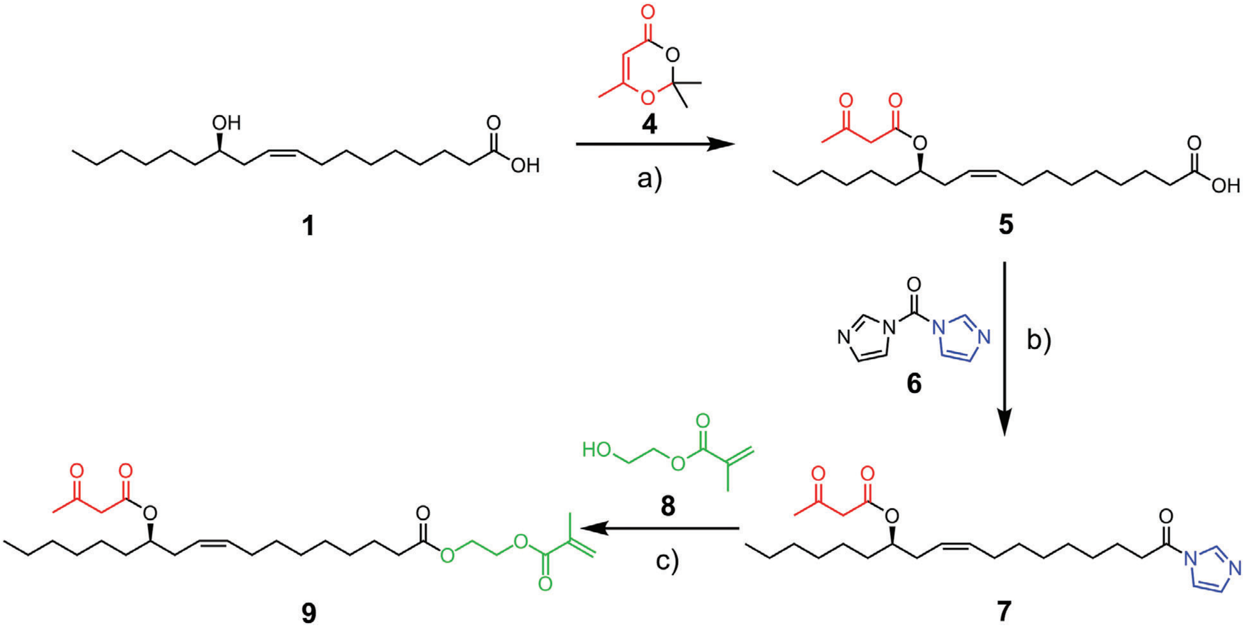


Scheme 1. Reaction sequence for the synthesis of the ricinoleic acid-based monomer 9: a) 3.0 eq 4, bulk, 95 °C, 1 h, 68%; b) 1.05 eq 6, 0.43 м in anhydrous toluene, room temperature, 16 h, quantitative (^{1}H NMR, no workup); c) 1.00 eq 8, 0.43 м in toluene, 65 °C, 8 h, 92%.

variety of applications: first, the synthesis of vinyl monomers that carry the 3,4-dihydropyrimidin-2(1*H*)-one group followed by a subsequent radical polymerization,[23–27] second, the polycondensation of bifunctional components directly via the B-3CR,[28–33] and third, the application of the B-3CR for the post-polymerization modification (PPM).[34–39] Due to the usual efficiency of the B-3CR and its sustainable character, the latter approach will be applied in this work for the straightforward modification of the resulting fatty acid based polymers, as well.

Herein, we show the feasibility of a ricinoleic acid based monomer for the synthesis of a homopolymer via RAFT polymerization. We further show the possibility for chain extension and subsequent copolymerization. Last but not least, the conversion of the hydroxy group of ricinoleic acid to an acetoacetate is used to allow for a post-polymerization using the versatile and sustainable B-3CR reaction.

2. Results

2.1. Monomer Synthesis

Monomer synthesis was conducted starting from sodium ricinoleate (3) due to its better availability compared to ricinoleic acid (1). Consequently, 1 was quantitatively obtained after protonation of 3 with 1 м HCl$_{aq}$. Second, the hydroxy group of 1 was converted to the respective acetoacetate by reaction with diketene acetone adduct (2,2,6-trimethyl-4H-1,3-dioxin-4-one, 4) at 95 °C before the methacrylate function was introduced to avoid polymerization under the necessary elevated temperatures for acetoacetate synthesis (**Scheme 1**a)). Full conversion of the hydroxy group was observed by ^{1}H NMR spectroscopy after one hour of reaction time. Notably, full conversion was reached after up to two hours for multi-gram batches yielding 68% of pure product ((12*R*,9*Z*)-12-[(3-oxobutanoyl)oxy]octadic-9-enoic acid, 5) after column chromatography. The synthesis of 5 was confirmed by NMR spectroscopy and high-resolution mass spectrometry (HRMS) (cf. supporting info including Figures S1 and S2, Supporting Information).

Subsequently, 5 was esterified with carbonyldiimidazole (6) and 2-hydroxyethyl methacrylate (8). The activation of the carboxylic acid for the subsequent esterification was preferred over a simple acid catalyzed esterification to reduce side reactions between the acetoacetate moiety of 5 and 8. The reaction consisted of two steps: first, the reaction of 5 with 6 to the acylimidazole 7 (Scheme 1b), second, without previous workup of 7, heating of the mixture to 65 °C with the subsequent addition of 8 (Scheme 1c). After 8 h of reaction time at 65 °C, the pure product (2-(methacryloyloxy)ethyl-(*R*,*Z*)-12-((3-oxobutanoyl)oxy)octadec-9-enoate, 9) was obtained with a yield of 92% after column chromatography. Notably, the direct addition of all reactants was also attempted. However, 6 reacted preferentially with 8 to form the respective carbamate.

The synthesis of pure 9 was verified by NMR spectroscopy and HRMS. The ^{1}H NMR spectrum showed the characteristic signals of 9, that is, the proton signals of the double bond of the methacrylate moiety at 6.13 and 5.59 ppm, the proton signals of the double bond of the ricinoleic acid at 5.48 and 5.31 ppm, and the signals of the CH$_2$ and CH$_3$ protons of the acetoacetate group at 3.42 and 2.26 ppm, respectively (**Figure 1**). Afterwards, the radical polymerization of 9 was investigated.

2.2. Polymerization

2.2.1. Homopolymerization and Chain Extension

To test the general reactivity of 9, a free radical polymerization (FRP) in bulk using 2,2'-azobis(2-methylpropionitrile) (AIBN) as radical initiator was performed. After 10 h, a gel-like material,

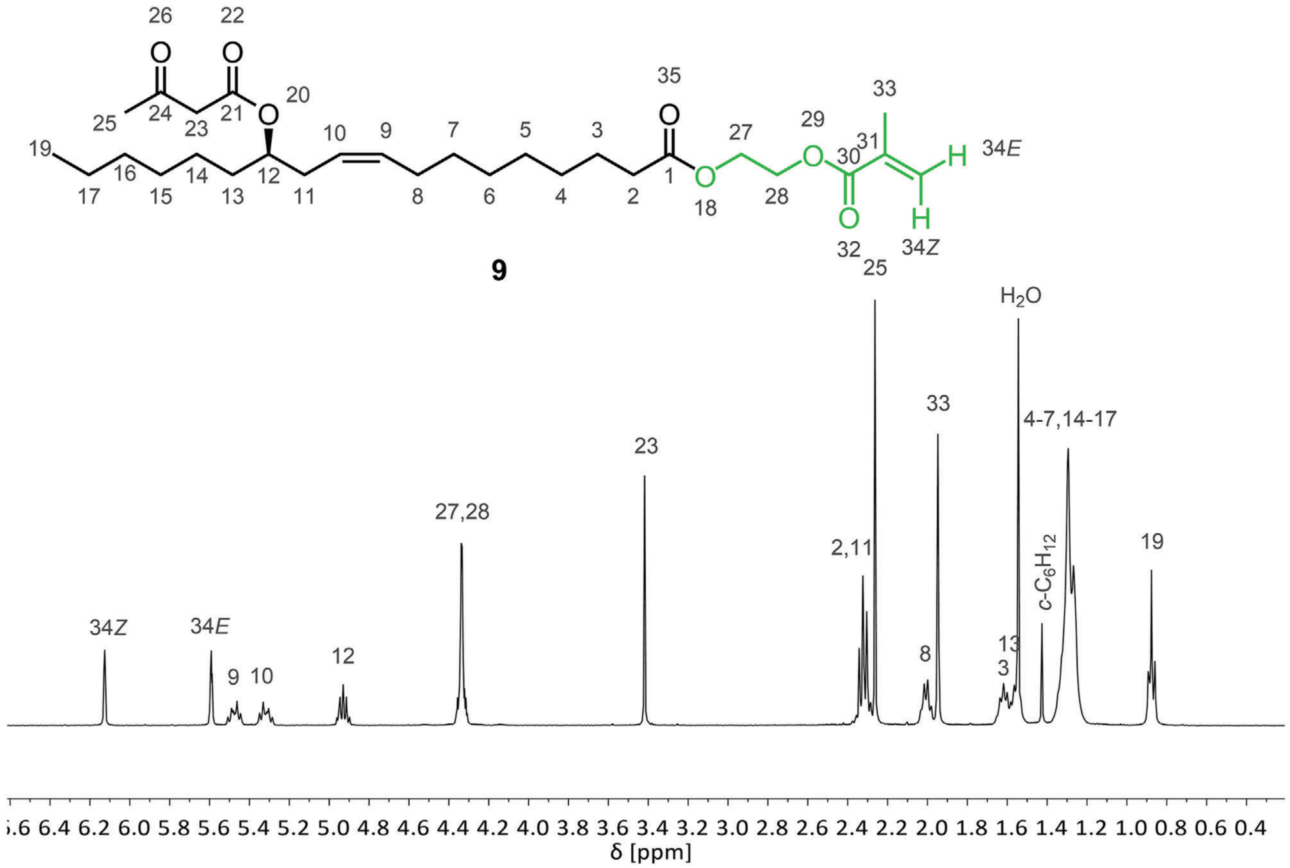


Figure 1. ^{1}H NMR spectrum of 9 in $CDCl_3$.

insoluble in $CHCl_3$, toluene, tetrahydrofuran, and hexafluoroisopropanol, was obtained indicating the successful polymerization. The insolubility was probably caused by crosslinking between the polymer chains due to chain transfer to polymer reactions. As a consequence, the RAFT polymerization of 9 was investigated as the RAFT equilibrium suppresses such side reactions.[40] The experiments were performed at different monomer concentrations in toluene at a temperature of 65 °C with AIBN as the radical initiator. Furthermore, two chain transfer agents (CTA), previously reported to allow for the control of the polymerization of methacrylates, namely 2-cyanoprop-2-yl benzodithioate (CTA1) and *S*-(2-cyanoprop-2-yl)-*S*-dodecyltrithiocarbonate (CTA2), were applied and the respective results compared.[41] The ratio of monomer to CTA to AIBN was kept at 50 to 1 to 0.1. All reaction mixtures were thoroughly degassed and backfilled with argon prior to heating to avoid inhibition by the formation of peroxy radicals with triplet oxygen.

Samples were taken after certain time intervals to screen the reaction progress via ^{1}H NMR spectroscopy and size exclusion chromatography (SEC). Thus, samples of the crude reaction mixture were directly dissolved in $CDCl_3$ or tetrahydrofuran with 2 vol% triethylamine, respectively. To calculate the conversion by NMR spectroscopy, the decrease of the integrals of the proton signals of the methacrylate double bond was observed in relation to the integrals of the double bond protons of the ricinoleic acid and the CH next to the acetoacetate.

Table 1. ^{1}H NMR and SEC results of the screening of the RAFT polymerization of 9 with CTA1 at a 7.5 M concentration.

entry[a]	reaction time [h]	Conversion [%]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,SEC}$ [g mol^{-1}]	Đ
1	1	9	2450	14 900	1.34
2	2	28	7150	31 000	1.19
3	3	45	11 350	45 800	1.25
4	5	70	17 530	115 000	2.51

[a] ratio of monomer to CTA to AIBN is 50:1:0.1. [b] $M_{n,NMR}$ is calculated using the monomer conversion.

To test for the possibility of RAFT polymerization, the polymerization of 9 was first conducted with a 7.5 M concentration of 9 in toluene using CTA1 (**Table 1**). The $M_{n,NMR}$ and $M_{n,SEC}$ increased over time, verifying the polymerization under RAFT conditions. However, the dispersities (Đ) were higher than expected for a RAFT polymerization and a large deviation between $M_{n,NMR}$ and $M_{n,SEC}$ was observed for each sample. These observations were attributed to the formation of a highly viscous solution 30 minutes after the start of the reaction. As the viscosity increases, diffusion was considered to drastically decrease, consequently decreasing chain transfer of the active polymer chain to CTA-end groups. Thus, chain transfer reactions to polymer (not end-groups) became more pronounced compared to chain transfer to CTA-end

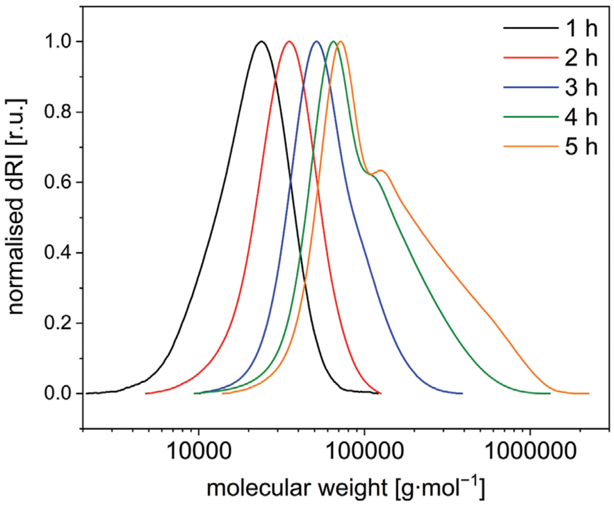


Figure 2. SEC chromatograms of the RAFT polymerization of 9 with CTA1 in a 7.5 M reaction mixture showing the development of a bimodal molecular weight distribution at reaction times longer than 2–3 h.

Table 2. ^{1}H NMR and SEC results from the screening of two different concentrations of the RAFT polymerization of 9 with CTA1.

entry[a]	Concentration [M]	Reaction time [h]	Conversion [%]	$M_{n,NMR}$[b] [g mol^{-1}]	$M_{n,SEC}$ [g mol^{-1}]	Đ
1	3.75	1	13	3400	18 100	1.27
2		2	36	9200	29 400	1.23
3		3	50	12 600	50 900	1.24
4		4	66	16 600	74 600	1.55
5	1.88	1	8	2200	5355	1.15
6		2	15	3930	6560	1.17
7		3	21	5420	7880	1.17
8		4	34	8630	9690	1.17
9		5	44	11 100	11 750	1.15
10		6	54	13 580	13 480	1.17
11		6.5	59	14 810	14 400	1.18

[a] ratio of monomer to CTA to AIBN is 50:1:0.1. [b] $M_{n,NMR}$ is calculated using the monomer conversion.

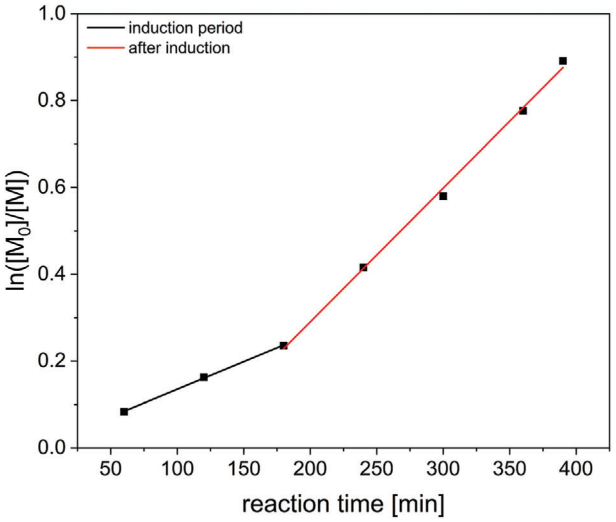


Figure 3. Pseudo-first order kinetic plot showing the relation between ln([M$_0$]/[M]) and the reaction time; a rate retarded induction period of 3 h was observed, the conversion was determined by ^{1}H NMR spectroscopy.

groups, which finally led to branching (higher Đ) and ultimately crosslinking at high conversions.

These assumptions were supported by the observation of bimodal mass distributions starting after 2–3 h of reaction time and the formation of a partly insoluble gel after approximately 4 h of reaction time (**Figure 2**, the respective dRI vs retention time plots are shown in Table S1 and Figure S4, Supporting Information). Finally, a deviation between $M_{n,NMR}$ and $M_{n,SEC}$ is naturally caused by the calculation of $M_{n,SEC}$ using linear poly(methyl methacrylate) standards due to their different hydrodynamic volume (at the same molecular weight) compared to the sample polymer. Additionally, this deviation becomes more pronounced if the polymer architecture of the sample differs from the architecture of the standard.

Consequently, the concentration was lowered for polymerizations with CTA1 to maintain sufficient mixing throughout the polymerization process, thus preventing temperature and concentration gradients. Polymerizations with CTA1 were screened with 3.75 and 1.88 M solutions of 9 (**Table 2**). While 3.75 M concentration still showed the same problems as described above, 1.88 M mixtures led to polymers with narrow molecular weight distributions with Ds between 1.15 and 1.17. Moreover, the molecular weight linearly increased with time and $M_{n,NMR}$ and $M_{n,SEC}$ were expectedly similar, indicating a controlled polymerization. Nonetheless, a qualitative increase in viscosity of the polymerization mixture was observed for conversions above 55%. Hence, if higher conversions are intended, lower concentrations are considered beneficial. Afterwards, the application of CTA2 was investigated under optimized conditions in a 1.88 M reaction mixture (Table S2, Supporting Information). However, the higher Ds between 1.18 and 1.35 and the larger deviation between $M_{n,NMR}$ and $M_{n,SEC}$ compared to the experiments with CTA1 indicated only partial control during the polymerization. Hence, CTA1 was used for the following investigations and syntheses.

The pseudo first-order rate plot for the RAFT polymerization of 9 with CTA1 in a 1.88 M solution is given in **Figure 3**. The polymerization shows significant rate retardation of a factor of approximately 2.4 within the first 3 h compared to the rate for reaction times longer than 3 h. This is a well-known behavior of RAFT polymerizations of methacrylates with dithiobenzoate CTAs, but also for other monomer and CTA classes, while the polymerization is still in the preequilibrium phase.[42] Retardation after the induction period is also known, while it has been shown that higher CTA concentrations lead to lower polymerization rates.[40] However, this phenomenon was not further investigated for the polymerization of 9.

Afterwards, the found relation between ln([M$_0$]/[M]) and reaction time *t* was used to determine the reaction times needed to reach monomer conversions of 40%, 50%, and 60%, respectively (**Table 3**). Hence, the respective polymerization experiments were stopped after 222, 276, and 333 min. The reached conversions resembled the desired molecular weights with a deviation between

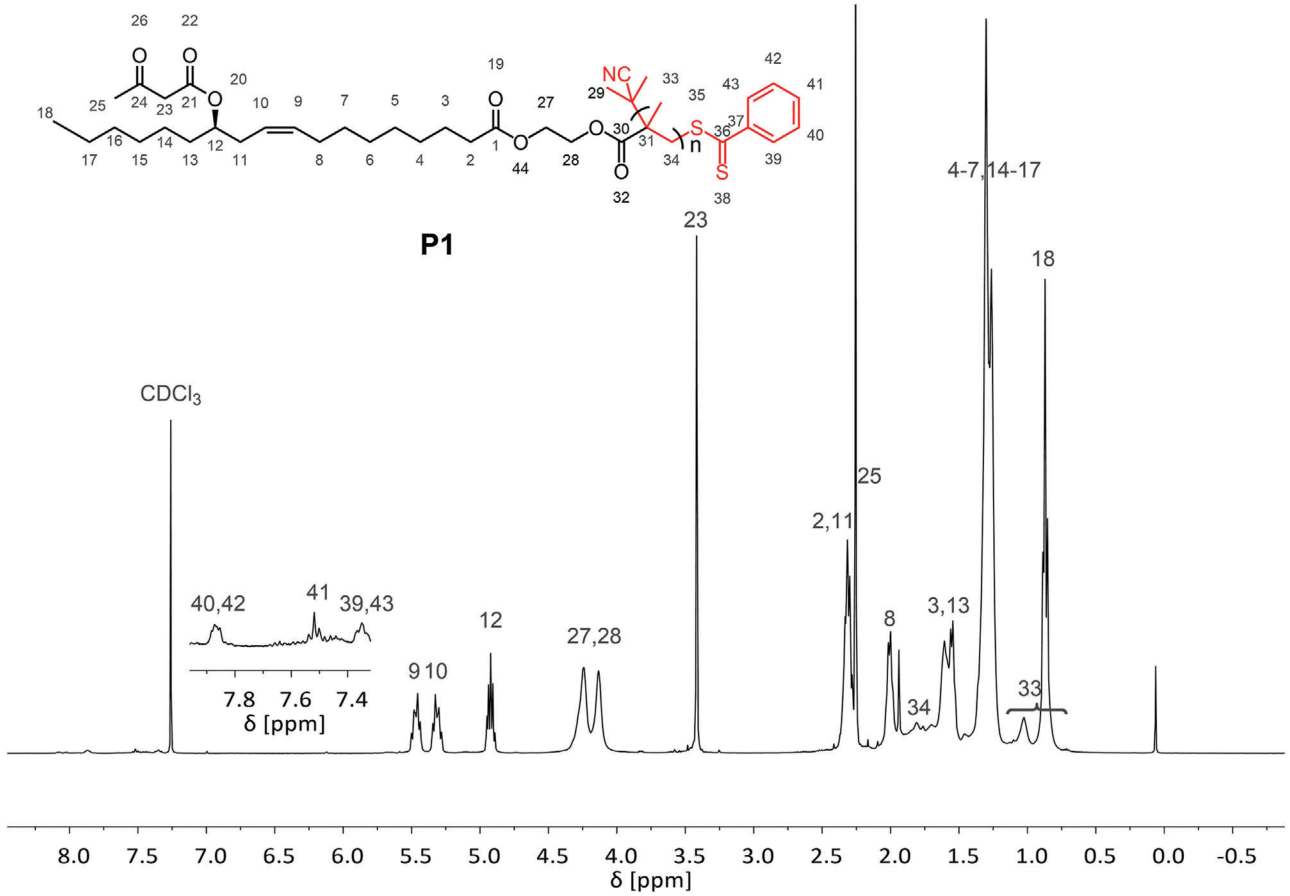


Figure 4. ^{1}H NMR spectrum of RAFT polymer P1 with a DP of 21in CDCl$_3$.

Table 3. SEC and ^{1}H NMR data for the synthesis of RAFT polymers of specific molecular weights.

entry[a)]	Reaction[b)] time [min]	Intended $M_{n,NMR}$[b)] [g mol^{-1}] (conversion [%])	$M_{n,NMR}$[c)] [g mol^{-1}] (conversion [%])	$M_{n,SEC}$ [g mol^{-1}]	Đ
1	222	10 200 (40)	10 620 (42)	11 410	1.14
2	276	12 700 (50)	11 950 (51)	11 680	1.12
3	333	15 200 (60)	14 450 (57)	13 920	1.13

[a)] ratio of monomer to CTA to AIBN is 50:1:0.1. [b)] calculated using the found relation between ln([M$_0$]/[M]) and t (Figure 3). [c)] $M_{n,NMR}$ is calculated using the signals of the dithiobenzoate end group.

1% and 3%. Furthermore, $M_{n,NMR}$ and $M_{n,SEC}$ were comparable and the Ðs of 1.12 to 1.13 verified the controlled polymerization.

Since the resulting polymers (P1) were purified, the conversions and $M_{n,NMR}$ were calculated using one of the proton signals of the dithiobenzoate end group at 7.87 ppm in relation to the signals of the internal double bonds at 5.48 and 5.31 ppm (**Figure 4**). Notably, the thermal properties of the polymers P1 were also investigated using differential scanning calorimetry (DSC) finding a consistent glass transition temperature (T_g) of −50 °C (Figure S8, Supporting Information).

The resulting polymer chains of a RAFT process still carry the, in this case, dithiobenzoate function, thus functioning as macro CTA. Consequently, chain extension and the synthesis of block copolymers are possible if the macro CTA is applied for the RAFT polymerization of another suitable monomer. A prerequisite is, however, the end group fidelity over the whole molecular weight distribution so that the polymers of each chain length are extended. To investigate the end group fidelity, P1 samples were measured by SEC using both an RI detector and a UV detector set at a wavelength of 305 nm, which is well suited to detect the absorption of the dithiobenzoate group.[43] For maximum end group fidelity, the peak shapes were expected to be identical. After correction of the data of the UV detector regarding the concentration, both distributions qualitatively showed identical peak shapes indicating high-end group fidelity (**Figure 5**).[44]

Additionally, the end group fidelity was indirectly shown by a chain extension experiment, as the presence of dead chain ends (resembling a deficiency in end group fidelity) would lead to the formation of a low molecular weight shoulder or the formation of a bimodal distribution. Thus, P1 with a degree of polymerization (DP) of 21 was used as macro CTA for the polymerization of 9 using the same conditions as above (Table 3) to confirm the feasibility of the chain extension. A ratio of monomer to macro CTA to AIBN of 50:1:0.1 was used.

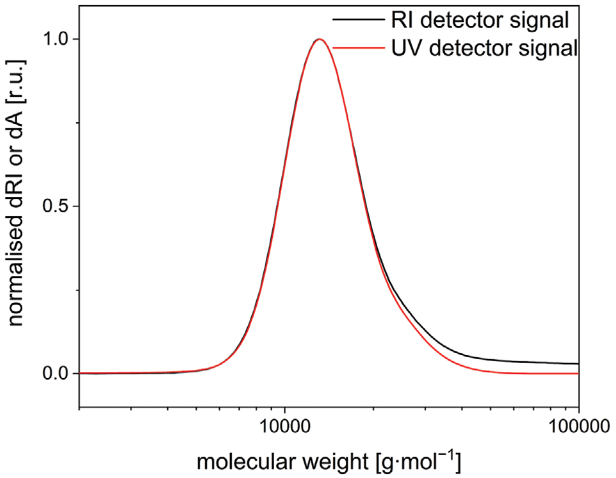


Figure 5. Example overlay of the normalized molecular weight distributions of the RI- and UV detector of P1 showing strong resemblance.

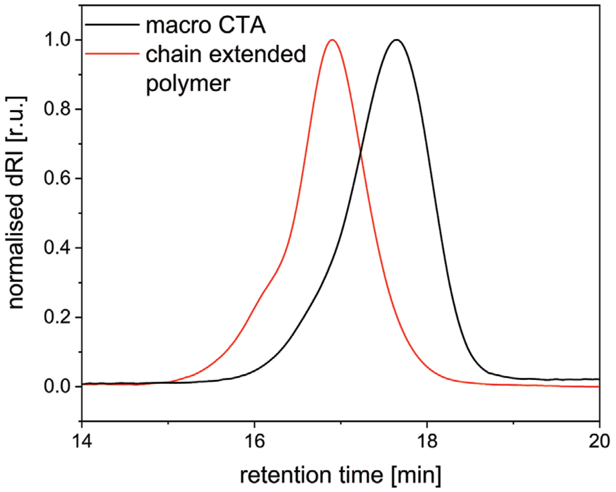


Figure 6. SEC chromatograms of the macro CTA and the chain extended polymer.

Since the inhibition phenomena at the beginning of polymerization are only reported for low molecular weight CTAs but not for macro CTAs, the polymerization rate after the induction period (cf. Figure 3) was used to calculate the reaction time for a monomer conversion of 35%.[40] A conversion of 35% was chosen to avoid an increase in viscosity and a subsequent loss of control as discussed above. Consequently, the reaction time of 144 min was determined in order to reach a final $M_{n,NMR}$ of approximately 19 300 g mol^{-1}.

The $M_{n,NMR}$ was found to be 18 730 g•mol^{-1}, corresponding to a conversion of 33%. The $M_{n,SEC}$ of 18 700 g mol^{-1} and the Đ of 1.15 verified the controlled polymerization (**Figure 6**). The formation of the slightly high molecular weight shoulder was attributed to the above-discussed increase in viscosity for higher molecular weights. The results of the chain extension experiments, therefore, confirm the high-end group fidelity of the macro CTA that was obtained by RAFT polymerization of 9, as well as the feasibility of the synthesis of block copolymers.

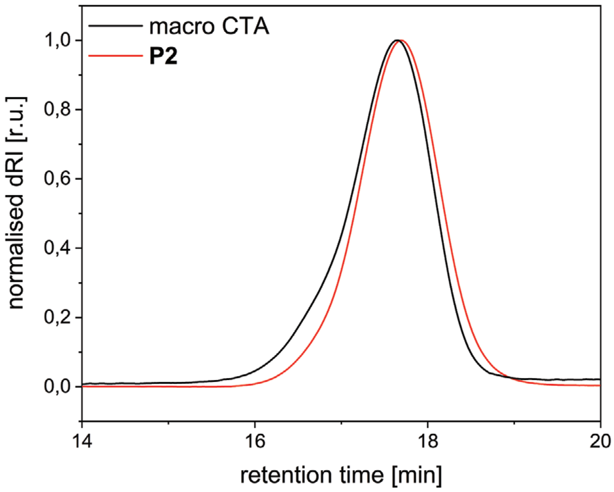


Figure 7. SEC chromatograms of the block copolymer P2 and the used macro CTA.

2.2.2. Blockcopolymer Synthesis

Consequently, a block copolymer (P2) was synthesized using methyl methacrylate (10) as monomer and P1 with a DP of 21 as macro CTA (cf. supporting information for detailed information). The same conditions as for the chain extension were used with a ratio of monomer to macro CTA to AIBN of 50:1:0.1. The synthesis of a block copolymer was confirmed by ^{1}H NMR spectroscopy showing the characteristic signals of the methyl ester of the poly(methyl methacrylate) block at approximately 3.6 ppm (**Figure 7**). While the Đ of 1.13 indicated the controlled polymerization of methyl methacrylate, the $M_{n,SEC}$ of 10 325 g mol^{-1} was smaller compared to the $M_{n,SEC}$ of the macro CTA. This was attributed to the different chemical structure of the poly(methyl methacrylate) block, which led to an overall smaller hydrodynamic volume compared to the macro CTA. The $M_{n,NMR}$ of 18 130 g mol^{-1} showed an increase of approximately 1000 g mol^{-1} indicating a DP of the poly(methyl methacrylate) block of 10.

To summarize, the ricinoleic acid-derived methacrylate monomer 9 was synthesized and its RAFT polymerization was investigated. It was shown that rather diluted reaction conditions were needed to obtain narrow molecular weight distributions. Concentrations lower than 1.88 м were found suitable to obtain Đs lower than 1.15. While the application of the dithiobenzoate (CTA1), 2-cyanoprop-2-yl benzodithioate led to Đs lower than 1.15, the trithiocarbonate (CTA2), *S*-(2-cyanoprop-2-yl)-*S*-dodecyltrithiocarbonate only led to partial control over the molecular weight. In order to apply RAFT polymers from 9 for the synthesis of block copolymers, high-end group fidelity and the possibility of a controlled chain extension are prerequisites, which were both successfully shown. As such, 9 was shown to be a suitable renewable monomer for the synthesis of homo- and block copolymers via RAFT polymerization.

The application of the incorporated acetoacetate functionality for PPM by the Biginelli reaction will be addressed in the following section.

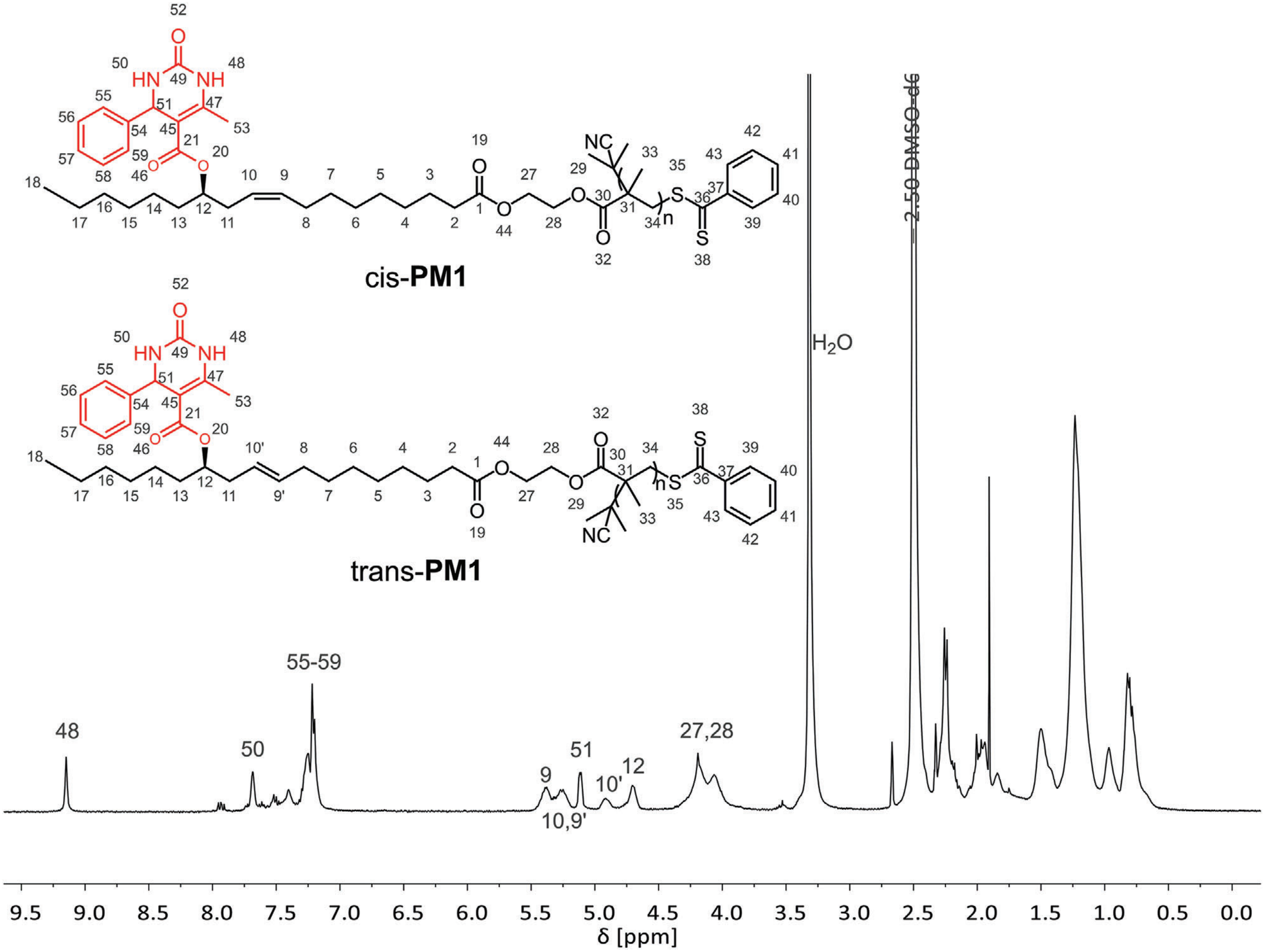


Figure 8. ^{1}H NMR spectrum of the purified polymer PM1 after PPM of P1 by Biginelli reaction: each of the cis/trans-isomers of PM1 are visible.

2.3. Post-Polymerization Modification

PPMs are a valuable tool to include functionalities in polymers or to alter the macroscopic properties of a polymer material in a way that was not possible prior to polymerization at the stage of the monomer. Thus, the PPM of the RAFT polymers P1 was investigated using P1 with a DP of 21 as example. The acetoacetate moiety that was present within the monomer structure was retained during the polymerization (cf. Figure 4) and its exploitation in a subsequent B-3CR was investigated.

Hence, P1 with a DP of 21 was dissolved in AcOH, and stirred together with 1.33 eq of benzaldehyde (11), 1.33 eq urea (12), and 0.07 eq $MgCl_2$ $6H_2O$ (13) as catalyst according to an adapted procedure of Tao et al.[36] The reaction progress was monitored by ^{1}H NMR spectroscopy, referencing the CH proton of the arising 3,4-dihydropyrimidin-2(1H)-one (DHPM) structure at 5.11 ppm to the signal of the CH adjacent to the acetoacetate of the ricinoleic acid structure (**Figure 8**). Eventually, a conversion of approximately 95% of the acetoacetate moiety after 25 h of reaction time was determined. The formation of the other typical signals of a DHPM, namely the signals of the NH-protons at 9.15 and 7.68 ppm, was also observed. After precipitation in MeOH and washing, the pure polymer PM1 was obtained with a yield of 92%.

Interestingly, the two multiplet signals of the double bond protons of 9 split into four different signals (Figure 8). It was assumed that the cis-double bond was partly isomerized to the trans-isomer. This was confirmed by the phase-edited heteronuclear single quantum correlation (HSQC) NMR spectrum of PM1 with reference to reported chemical shifts for cis/trans isomers of aliphatic olefins (Figure S15, Supporting Information).[45] The chemical shifts of the ^{13}C carbon signals of 9 and 9’ as well as 10 and 10’, respectively, resembled each other while the ^{1}H signals of the protons at 9’ and 10’ were shifted to higher ppm values compared to the chemical shifts of the protons at 9 and 10. Finally, a ratio of cis/trans of 60/40 was determined.

The SEC analysis of PM1 revealed the formation of a small shoulder towards higher molecular weights, while the main signal was shifted to lower molecular weights compared to the starting material (P1) resulting in an $M_{n,SEC}$ of 8600 g mol^{-1} ($Đ = 1.24$) compared to an $M_{n,SEC}$ of 10 200 g mol^{-1} ($Đ = 1.13$) of the starting material (**Figure 9**).

The shift of the signal towards lower molecular weights was attributed to the tendency of polymers that contain the DHPM motif to form, due to hydrogen bonding, compact coils in solution, as it was already discussed previously.[30,31] Finally, a DSC

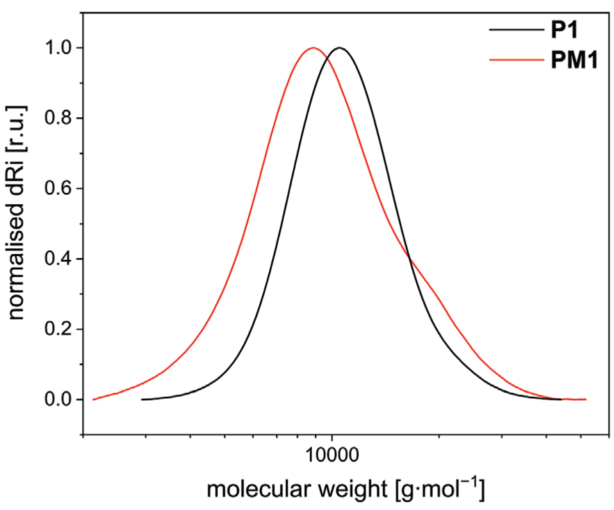


Figure 9. SEC graphs of P1 and PM1.

Table 4. Comparison of the modified polymers PM1-4.

polymer	cis/trans ratio	acetoacetate conversion [%]	$M_{n,SEC}$ [g mol^{-1}]	Đ	T_g [°C]
PM1	60/40	95	8600	1.24	−13
PM2	61/39	93	9700	1.23	29
PM3	60/40	78	11 400	1.22	−19
PM4	62/38	72	11 200	1.24	−16

analysis revealed a shift of the original T_g at −50 to −13 °C (cf. Figures S8 and S13, Supporting Information).

Afterwards, the B-3CR was repeated with anisaldehyde (p-methoxy benzaldehyde, 14) and *N*-methyl urea (15) as components to verify the feasibility of the PPM approach (**Figure 10**, cf. supporting information for detailed data). The ^{1}H NMR spectra of the resulting modified polymers PM2, PM3, and PM4 verified the formation of the expected DHPM moiety, while a conversion of the acetoacetate to the DHPM of up to 95% was determined. The data regarding cis/trans ratio, molecular weight, dispersity, and T_g is summarized in **Table 4**.

To conclude, it was shown in four examples that the Biginelli reaction is an efficient tool for the PPM of P1 reaching high conversions of up to 95% accompanied by a significant change of the T_g.

3. Conclusion

In summary, a promising renewable monomer for the controlled radical polymerization via RAFT polymerization was synthesized based on ricinoleic acid as starting material. Moreover, the hydroxy group of ricinoleic acid monomer was acetoacetylated in order to allow the PPM of the resulting polymers by the Biginelli reaction. The RAFT polymerization was optimized with respect to the concentration and the applied chain transfer agent, finally yielding polymers with a molecular weight of up to 15 000 g mol^{-1} and narrow molecular weight distributions (Ðs around 1.13). Furthermore, the suitability of the resulting material for chain extension and thus block copolymer synthesis was demonstrated by the determination of the end group fidelity of the RAFT polymers, the subsequent chain extension under RAFT conditions, and the synthesis of a block copolymer with poly(methyl methacrylate) as second block. Finally, the PPM of the acetoacetate moiety within the homopolymers was investigated using the Biginelli reaction. Conversions of up to 95% of the acetoacetate moiety towards the desired DHPM motif were shown, while increasing the T_gs of the unmodified polymers by up to 80 °C. Overall, our novel ricinoleic acid-based methacrylate monomer was deemed a promising starting material for the synthesis of various polymer materials.

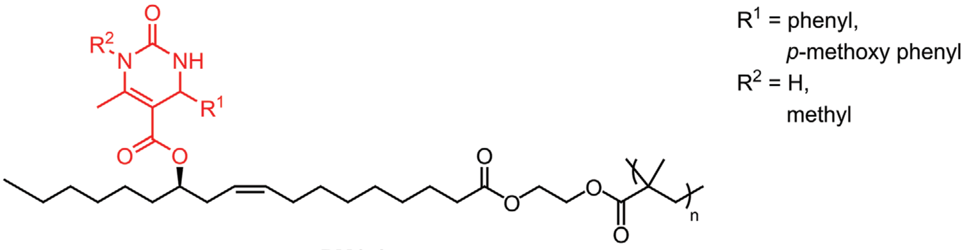
4. Experimental Section

Materials: Sodium ricinoleate (TCI, 80%), diketene acetone adduct (Sigma, 95%), AIBN (Sigma, 98%, recrystallized from acetone), carbonyl diimidazole (Sigma, 97%), 2-hydroxyethyl methacrylate (Sigma, 99%, stabilized), 2-cyanoprop-2-yl benzodithioate (Sigma, 97%), *S*-(2-cyanoprop-2-yl)-*S*-dodecyltrithiocarbonate (Sigma, 97%), anhydrous toluene (Sigma, 99.8%), urea (Sigma, 99%), *N*-methyl urea (Sigma, 97%), benzaldehyde (Sigma, 99%), *p*-anisaldeyhde (Fischer, 99%), and $MgCl_2$ $6H_2O$ (Carl Roth, tech.).

Solvents were used in technical grade if not noted otherwise.

Thin-Layer Chromatography (TLC): Fluorescent silica-coated aluminum plates were used for thin-layer chromatography. The plates were developed using Seebach stain (phosphomolybdic acid, cerium(IV) sulfate, sulfuric acid, water) to visualize UV-inactive compounds. The R_f values and used solvent mixtures were given at the respective synthesis procedure of each compound.

Column Chromatography: Flash column chromatography was performed using a method similar to that introduced by Still et al.[46] The glass column with built-in fritted glass filter was filled with a slurry of eluent (the eluent was given at the respective synthesis procedure of each compound) and stationary phase (silica, Aldrich, technical grade, 60 Å pore size, 230–400 mesh size, 40–63 µm particle size). The crude substance was applied



PM1-4

Figure 10. Chemical structures of Bigineli polymers PM1-PM4.

in a liquid state dissolved in a small amount of eluent. Pressure was applied with a manual pump.

NMR Spectroscopy: ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance NEO spectrometer at a frequency of 400.13 and 100.62 MHz, respectively. All spectra were measured at ambient temperature. For sample preparation, 10–15 mg of substance was dissolved in 0.40 mL DMSO-*d6* (99.80 atom% D) or $CDCl_3$ (99.80 atom% D). The chemical shift (δ) was given in parts per million (ppm) relative to the δ of tetramethylsilane (δ(TMS) = 0.00 ppm).

The chemical shifts of the residual DMSO-*d5* (^1H NMR: 2.50 ppm; ^{13}C NMR: 39.52 ppm) or $CHCl_3$ (^1H NMR: 7.26 ppm; ^{13}C NMR: 77.16 ppm) were used for reference. Splitting patterns were denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets), ddt (doublet of triplets), and br (broad). The respective coupling constants xJ were given in Hertz (Hz). The signals were listed from low field (large ppm) to high field (small ppm).

In addition, 2D-spectra were recorded to support signal structure assignments. The following experiments were used: ^1H,^1H-Correlated Spectroscopy (^1H,^1H-COSY), phase edited ^1H,^{13}C-Heteronuclear Single Quantum Coherence (^1H,^{13}C-HSQCed), and ^1H,^{13}C Heteronuclear Multiple Bond Correlation (^1H,^{13}C-HMBC).

Size Exclusion Chromatography (SEC): Samples were measured on a Shimadzu LS 20A system equipped with a SIL-20A autosampler and a RID-20A refractive index detector. For sample preparation, 2 mg of sample were dissolved in 2 mL tetrahydrofuran/2 vol% NEt_3. The same solvent mixture was used as mobile phase. The solvent flow was 1.00 mL min^{-1} at 30 °C. The analysis was performed on a three-column system: PSS SDV analytical (5 μm, 300•8.0 mm^2, 1000 Å), PSS SDV analytical (5 μm, 300•8.0 mm^2, 100 000 Å), and a PSS SDV analytical precolumn (5 μm, 50•8.0 mm^2). For the calibration, narrow linear poly(methyl methacrylate) standards (Polymer Standards Service, PPS, Germany) ranging from 1100 to 981 000 g mol^{-1} were used.

Furthermore, samples were measured on an Agilent 1260 Infinity II system equipped with UV/Vis-detector and RI-detector. For sample preparation, 2 mg of sample were dissolved in 2 mL tetrahydrofuran. The same solvent mixture was used as mobile phase. The solvent flow was 1.00 mL min^{-1} at 35 °C. The analysis was performed on a three-column system: SDV Lux pre-column (8•50 mm^2), SDV Lux (8•300 mm^2, 1000 Å), and SDV Lux (8•300 mm^2, 100 000 Å). The system was calibrated with linear poly(methyl methacrylate) standards (PSS, M_p: 102–981 kg mol^{-1}).

IR Spectroscopy: IR-spectra were recorded on a Bruker Alpha FTIR spectrometer equipped with Platinum ATR technology. The resulting transmittance spectra were averaged from 24 measurements. The energies of the IR bands were given as wavenumbers ν in cm^{-1}. The signals were noted from large to small wavenumbers.

High-Resolution Mass Spectrometry (HRMS): High-resolution mass spectra were recorded on a Finnigan MAT 95 spectrometer using electron ionization (EI) or fast atom bombardment (FAB). The signal of the singly charged radical cation of the analyte was referred to as $[M]^{\bullet +}$, the protonated singly charged cation of the molecule was referred to as $[M+H]^+$.

Differential Scanning Calorimetry (DSC): DSC experiments were performed on a DSC821e (Mettler Toledo) calorimeter. Samples were prepared by compressing 15–20 mg of sample in a 100 µL aluminum crucible or 2–5 µg of substance in a 40 µL crucible. The measurements were performed under nitrogen atmosphere with two heating cycles in the temperature range of −70–100 °C with a cooling rate of 15 K min^{-1} and a heating rate of 30 K min^{-1}.

For the calculation of the thermal transitions, the second heating cycle was used. The T_gs were determined using the inflection points of the respective second-order transitions.

Synthesis of (12R,9Z)-12-[(3-Oxobutanoyl)Oxy]Octadec-9-Enoic Acid (5): (9*Z*,12*R*)-12-Hydroxyoctadec-9-enoic acid (14.0 mmol, 1.00 eq) and diketene acetone adduct (2,2,6-trimethyl-4*H*-1,3-dioxin-4-one, 3.00 eq) were mixed in an open round bottom flask and stirred for 1 h at 95 °C. Afterwards, the mixture was subjected to column chromatography using silica gel; eluent: *c*-C_6H_{12}:EtOAc = 90:10 + 1 vol% AcOH; R_f(product): 0.70 in *c*-C_6H_{12}:EtOAc = 90:10 + 1 vol% AcOH; yield: 68% (3.64 g, 9.51 mmol, dark orange oil).

^1H-NMR (400 MHz, DMSO-d_6): δ (ppm) = 11.96 (s, 1H, H_{19}), 5.51 – 5.41 (m, 1H, H_9), 5.39–5.27 (m, 1H, H_{10}), 4.85–4.76 (m, 1H, H_{12}), 3.56 (s, 2H, H_{23}), 2.27 (dd, $^3J_{H11;H12;H10}$ = 7.8, 5.9 Hz, 2H, H_{11}), 2.19 (t, $^3J_{H3;H4}$ = 7.3 Hz, 2H, H_3), 2.17 (s, 3H, H_{25}), 2.04–1.96 (m, 2H, H_8), 1.55–1.42 (m, 4H, $H_{4,13}$), 1.36–1.17 (m, 16H, $H_{5\text{-}7,14\text{-}18}$), and 0.89–0.83 (m, 3H, H_{19}).

^{13}C-NMR (101 MHz DMSO-d_6): δ (ppm) = 201.40 (C_{24}), 174.45 (C_2), 166.88 (C_{21}), 132.25 (C_9), 124.26 (C_{10}), 74.00 (C_{12}), 49.77 (C_{23}), 33.64(C_3), 32.89 (C_{13}), 31.34 (C_{11}), 31.11 ($C_{4\text{-}7,14\text{-}18}$), 30.02 ($C_{25}$), 28.91 ($C_{4\text{-}7,14\text{-}18}$), 28.58 ($C_{4\text{-}7,4\text{-}18}$), 28.51 ($C_{4\text{-}7,14\text{-}18}$), 28.50 ($C_{4\text{-}7,14\text{-}18}$), 28.42 ($C_{4\text{-}7,14\text{-}18}$), 26.96 ($C_8$), 24.57 ($C_{4\text{-}7,14\text{-}18}$), 24.47 ($C_{4\text{-}7,14\text{-}18}$), 21.96 ($C_{4\text{-}7,14\text{-}18}$), and 13.89 ($C_{19}$).

HRMS (FAB): m/z for $C_{22}H_{38}O_5H^+$ $[M+H]^+$: calculated: 383.2792; found: 383.2794.

Synthesis of 2-(Methacryloyloxy)Ethyl (12R,9Z)-12-[(3-Oxobutanoyl)Oxy]-Octadec-9-Enoate (9): (12*R*,9*Z*)-11-[(3-oxobutanoyl)oxy]octadec-8-enoic acid (38.98 mmol, 1.00 eq) was dissolved in 90 mL of toluene. After the addition of carbonyldiimidazole (1.05 eq), the mixture was stirred at room temperature for 16 h. Subsequently, 2-hydroxyethyl methacrylate (1.00 eq) was added to the mixture and the stirring was continued for 8 h at 65 °C. The crude product was purified by column chromatography over silica gel; eluent: *c*-C_6H_{12}:EtOAc = 90:10; R_f(product): 0.78 in *c*-C_6H_{12}:EtOAc = 50:50; yield: 92% (17.7 g, 35.9 mmol, colorless oil).

^1H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.15–6.10 (m, 1H, H_{34E}), 5.61–5.57 (m, 1H, H_{34Z}), 5.52–5.42 (m, 1H, H_9), 5.37–5.27 (m, 1H, H_{10}), 4.97–4.88 (m, 1H, H_{12}), 4.38–4.29 (m, 4H, $H_{27,28}$), 3.42 (s, 2H, H_{23}), 2.35–2.29 (m, 4H, $H_{2,11}$), 2.26 (s, 3H, H_{25}), 2.04–1.97 (m, 2H, H_8), 1.97–1.93 (m, 3H, H_{33}), 1.66–1.59 (m, 2H, H_3), 1.59–1.52 (m, 2H, H_{13}), 1.38–1.20 (m, 16H, $H_{4\text{-}7,14\text{-}17}$), and 0.92–0.84 (m, 3H, H_{19}).

^{13}C-NMR (101 MHz $CDCl_3$): δ (ppm) = 200.72 (C_{24}), 173.70 (C_1), 167.25 (C_{30}), 166.97 (C_{21}), 136.11 (C_{31}), 133.03 (C_9), 126.14 (C_{34}), 124.08 (C_{10}), 75.54 (C_{12}), 62.61 ($C_{27/28}$), 62.02 ($C_{27/28}$), 50.59 (C_{23}), 34.28 (C_2), 33.64 (C_{13}), 31.97 ($C_{4\text{-}7,14\text{-}17}$), 31.85 ($C_{4\text{-}7,14\text{-}17}$), 30.23 ($C_{25}$), 29.64 ($C_{4\text{-}7,14\text{-}17}$), 29.31 ($C_{4\text{-}7,14\text{-}17}$), 29.25 ($C_{4\text{-}7,14\text{-}17}$), 29.24 ($C_{4\text{-}7,14\text{-}17}$), 29.20 ($C_{4\text{-}7,14\text{-}17}$), 27.48 ($C_8$), 25.41, 25.03 ($C_3$), 22.71, 18.41 ($C_{33}$), and 14.20 ($C_{19}$).

HRMS (FAB): m/z for $C_{28}H_{46}O_7H^+$ $[M+H]^+$: calculated: 495.3316; found: 495.3318.

General procedures for the RAFT polymerization, the chain extension, the blockcopolymer synthesis, and the PPM were given. Detailed information, spectra, and chromatograms are given in the Supporting Information.

RAFT Polymerization: All RAFT polymerizations were conducted according to the same general procedure if not denoted otherwise. The optimized procedure for the RAFT polymerization of 2-(methacryloyloxy)ethyl (12*R*,9*Z*)-12-[(3-oxobutanoyl)oxy]octadic-9-enoate (168) with 2-cyanoprop-2-yl benzodithioate as CTA was given as follows:

2-(Methacryloyloxy)ethyl (12*R*,9*Z*)-12-[(3-oxobutanoyl)oxy]octadic-9-enoate (168, 1.01 mmol, 50.0 eq) and 2-cyanoprop-2-yl benzodithioate (1.00 eq) were dissolved in 495 µL toluene in 5 mL glass vial. Afterwards, 44 µL of a AIBN stock solution (0.10 eq, 0.0075 mg µL^{-1} in toluene) were added and the vial was closed with a rubber septum. The mixture was degassed with argon for 15 min. Subsequently, the mixture was stirred under argon at 65 °C for several hours, depending on the desired molecular weight. Afterwards, the reaction mixture was cooled in an ice bath for 10 min, opened to the atmosphere, and precipitated in 40 mL MeOH. The mixture was three times decanted and backfilled with 40 mL MeOH, each. After the last decantation, the MeOH was removed under high vacuum. Finally, the purified polymer was stored under the absence of light at 4 °C.

^1H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.54–5.42 (m, H_9), 5.37–5.26 (m, H_{10}), 4.97–4.88 (m, H_{12}), 4.24 (s, H_{23}), 4.13 (br s, $H_{27/28}$), 3.42 (br s, $H_{27/28}$), 2.38–2.27 (m, $H_{2,11}$), 2.26 (s, H_{25}), 2.06–1.97 (m, H_8), 1.90–1.67 (br, H_{34}), 1.67–1.58 (m, H_3), 1.58–1.51 (m, H_{13}), 1.39–1.20 (m, $H_{4\text{-}7,14\text{-}17}$), 1.10–0.79 (br m, H_{33}), and 0.87 (t, $^3J_{H18,H17}$ = 6.7 Hz, H_{18}).

Chain Extension: For the chain extension of the RAFT polymer (169), 169 was applied as macro CTA ($M_{n,NMR}$ = 12 011 g mol^{-1}, 0.0202 mmol, 1.00 eq). Subsequently, 795 µL of toluene and 2-(methacryloyloxy)ethyl (12*R*,9*Z*)-12-[(3-oxobutanoyl)oxy]octadic-9-enoate (168, 1.01 mmol, 50.0 eq) were added. Afterwards, 44 µL of an AIBN stock solution (0.10 eq, 0.0075 mg µL^{-1} in toluene) were added and the mixture was degassed with argon for 15 min. Subsequently, the mixture was stirred under argon at 65 °C for 2.4 h (35% monomer conversion). Afterwards, the reaction mixture was cooled in an ice bath for 10 min, opened to the atmosphere, and precipitated in 40 mL MeOH. The mixture was decanted three times and backfilled with 40 mL MeOH, each. After the last decantation the MeOH was removed under high vacuum. Finally, the purified polymer was stored under the absence of light at 4 °C. The final polymer showed a $\mathrm{M}_{n,NMR}$ of 18 700 g mol^{-1} (35% monomer conversion) and a $\mathrm{M}_{n,SEC}$ of 18 700 g mol^{-1} with Đ = 1.15.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.54–5.42 (m, H_9), 5.37–5.26 (m, H_{10}), 4.97–4.88 (m, H_{12}), 4.24 (s, H_{23}), 4.13 (br s, $H_{27/28}$), 3.42 (br s, $H_{27/28}$), 2.38–2.27 (m, $H_{2,11}$), 2.26 (s, H_{25}), 2.06–1.97 (m, H_8), 1.90–1.67 (br, H_{34}), 1.67–1.58 (m, H_3), 1.58–1.51 (m, H_{13}), 1.39–1.20 (m, $H_{4\text{-}7,14\text{-}17}$), 1.10–0.79 (br m, H_{33}), and 0.87 (t, $^3J_{H18,H17} = 6.7$ Hz, H_{18}).

Blockcopolymer Synthesis: The block copolymer synthesis was performed using 169 as macro CTA and methyl methacrylate as monomer. Methyl methacrylate was filtered over basic aluminum oxide prior to usage. The macro CTA ($\mathrm{M}_{n,NMR}$ = 17 020 g mol^{-1}, 0.0202 mmol, 1.00 eq) was dissolved in 795 µL of toluene. Afterwards, methyl methacrylate (1.01 mmol, 50.0 eq) and 44 µL of an AIBN stock solution (0.10 eq, 0.0075 mg µL^{-1} in toluene) were added and the mixture was degassed with argon for 15 min. Subsequently, the mixture was stirred under argon at 65 °C for 5.6 h. Afterwards, the reaction mixture was cooled in an ice bath for 10 min, opened to the atmosphere, and precipitated in 40 mL MeOH. The mixture was decanted three times and backfilled with 40 mL MeOH, each. After the last decantation the MeOH was removed under high vacuum. Finally, the purified polymer was stored under the absence of light at 4 °C. The final polymer (170) showed a $\mathrm{M}_{n,NMR}$ of 18 130 g mol^{-1} and a $\mathrm{M}_{n,SEC}$ of 10 325 g mol^{-1} with Đ = 1.13.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.46–5.36 (m, H_9), 5.31–5.20 (m, H_{10}), 4.91–4.81 (m, H_{12}), 4.18 (br s, $H_{27/28}$), 4.07 (br s, $H_{27/28}$), 3.64–3.48 (m, H_{44}), 3.35 (s, H_{23}), 2.32–2.21 (m, $H_{2,11}$), 2.19 (s, H_{25}), 1.99–1.91 (m, H_8), 1.86–1.60 (m, $H_{31,45}$), 1.60–1.52 (m, H_3), 1.52–1.45 (m, H_{13}), 1.32–1.14 (m, $H_{4\text{-}7.14\text{-}17}$), 1.05–0.72 (m, $H_{33,35}$), and 0.86–0.75 (m, H_{18}).

Post-Polymerization Modification (PPM): The PPMs were conducted according to the same general procedure while either benzaldehyde or anisaldehyde and urea or *N*-methyl urea were used leading to PM1-4. As follows, the PPM with benzaldehyde and urea as an example: P1 ($\mathrm{M}_{n,NMR}$ = 10 150 g mol^{-1}, 9.85 µmol , corresponds to 0.197 mmol acetoacetate, 1.00 eq) was dissolved in 0.8 mL AcOH in a 5 mL vial. Subsequently, the aldehyde component (1.33 eq), urea (1.33 eq), and $MgCl_2$ 6 H_2O (0.0667 eq) were added. After dissolution, the mixture was stirred at 100 °C for 20 h. Afterwards, the polymer was precipitated in 40 mL H_2O. The suspension was three times decanted and backfilled with 40 mL MeOH, each. After the last decantation, the remaining MeOH was removed under high vacuum yielding the final polymer.

PM1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.15 (s, H_{48}), 7.68 (s, H_{50}), 7.48–7.16 (m, $H_{55\text{-}59}$), 5.48–5.32 (m, H_9), 5.31–5.18 (m, $H_{9',10}$), 5.16–5.08 (m, H_{51}), 4.97–4.86 (m, $H_{10'}$), 4.77–4.63 (m, H_{12}), 4.31–3.93 (m, $H_{27,28}$), 2.32–2.12 (m, $H_{2,11}$), 2.08–1.76 (m, H_8), 2.08–1.61 (m, H_{34}), 1.60–1.38 (m, $H_{3,13}$), 1.39–1.05 (m, $H_{4\text{-}7,14\text{-}17}$), 1.06–0.60 (br, H_{33}), and 0.89–0.63 (m, H_{18}).

PM2: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.10 (s, H_{48}), 7.60 (s, H_{50}), 7.21–7.05 (m, $H_{55,59}$), 6.93–6.71 (m, $H_{56,58}$), 5.49–5.32 (m, H_9), 5.33–5.21 (m, $H_{9',10}$), 5.10–5.03 (m, H_{51}), 5.01–4.87 (m, $H_{10'}$), 4.80–4.65 (m, H_{12}), 4.34–3.99 (m, $H_{27,28}$), 3.68 (s, H_{60}), 2.36–2.16 (m, $H_{2,11}$), 2.12–1.38 (m, $H_{3,8,13,34}$), 1.38–1.09 (m, $H_{4\text{-}7\text{-}14\text{-}17}$), 1.03–0.89 (m, H_{33}), and 0.87–0.70 (m, H_{18}).

PM3: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.91 (s, H_{50}), 7.48–7.13 (m, $H_{55\text{-}59}$), 5.48–5.32 (m, H_9), 5.31–5.17 (m, $H_{9',10}$), 5.15–5.09 (m, H_{51}), 4.99–4.88 (m, $H_{10'}$), 4.82–4.67 (m, H_{12}), 4.34–3.94 (m, $H_{27,28}$), 3.08 (s, H_{48}), 2.46 (s, H_{53}), 2.35–2.17 (m, $H_{2,11}$), 2.10–1.77 (m, $H_{8,34}$), 1.59–1.40 (m, $H_{3,13}$), 1.39–1.05 (m, $H_{4\text{-}7,14\text{-}17}$), 1.06–0.60 (br, H_{33}), and 0.89–0.63 (m, H_{18}).

PM4: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.83 (s, H_{50}), 7.14–7.06 (m, $H_{55,59}$), 6.86–6.74 (m, $H_{56,58}$), 5.48–5.32 (m, H_9), 5.35–5.18 (m, $H_{9',10}$), 5.12–5.03 (m, H_{51}), 5.01–4.87 (m, $H_{10'}$), 4.82–4.65 (m, H_{12}), 4.34–3.91 (m, $H_{27,28}$), 3.68 (s, H_{60}), 3.07 (s, H_{48}), 2.45 (s, H_{53}), 2.36–2.16 (m, $H_{2,11}$), 2.11–1.78 (m, $H_{8,34}$), 1.59–138 (m, $H_{3,13}$) 1.38–1.04 (m, $H_{4\text{-}7\text{-}14\text{-}17}$), 1.03–0.89 (m, H_{33}), and 0.87–0.70 (m, H_{18}).

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

Biginelli reaction, controlled radical polymerization, multi-component reactions, post-polymerization modification, renewability, reversible addition-fragmentation chain-transfer polymerization

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