Synthesis and Characterization of Novel Epoxy- and Oxetane-Functional Reversible Addition−Fragmentation Chain Transfer Agents

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ABSTRACT: Novel reversible addition−fragmentation chain transfer (RAFT) agents with epoxy- and oxetane-functional groups have been synthesized. Two different methods were used to synthesize the epoxy-functional RAFT agent. An acid-functional chain transfer agent was reacted with either epichlorohydrin (EPI) or glycidol to obtain the epoxy-functional RAFT agent. The epoxy-functional RAFT agent synthesized using EPI had a higher yield. Similarly, the oxetane-functional RAFT agent was obtained by reacting a monofunctional reactive oxetane (3-ethyl-3-hydroxymethyl oxetane) (EHMO) with the acid-functional RAFT agent. The presence of epoxy and oxetane groups on the RAFT agent was confirmed using ^{1}H and ^{13}C nuclear magnetic resonance techniques. Several acrylate monomers and styrene were polymerized using the novel RAFT agents, and in each case the polydispersity was below 1.1. Poly(butyl acrylate) (PBA) synthesized using the epoxy-functional RAFT agent was reacted with acrylic acid to obtain an acrylate-functional PBA. The oxetane-functional RAFT agent was copolymerized with EHMO to obtain a trithiocarbonylthio macromonomer, which was used for controlled free-radical polymerization of butyl acrylate to obtain a PBA graft copolymer.

Introduction

Functional polymers synthesized by controlled free-radical polymerization (CRP) methods have gained significant attention in recent years. CRP techniques such as atom transfer radical polymerization (ATRP),[1] nitroxide-mediated polymerization,[2] and reversible addition−fragmentation chain transfer (RAFT)[3] have been extensively used for the synthesis of functional polymeric materials. These polymers can be synthesized by using monomers with functional groups or by using functional initiators.[4] Polymers with different functional groups like carboxylic acid,[5,6] hydroxyl,[7] amine,[8] activated ester,[9] propargyl,[10] and carbon−carbon unsaturated group[11] have been previously synthesized using CRP techniques. Functional polymers have been used for synthesis of various block copolymers with controlled architecture and molecular weights.[12] Homo and block copolymers with controlled architecture and molecular weights have potential in applications such as dispersing agents, adhesives, drug delivery, etc.[13] Aromatic amine-functional poly(methyl methacrylate) which can be used in the synthesis of polyamide and polyimide graft copolymers has been synthesized by ATRP using aminophenyl-functional initiators.[4] Polymers with epoxy groups in the side chains have been previously made using ATRP for coatings and adhesive applications.[14] Star polymers with different end-functional groups like hydroxyl, epoxy, amino, and cyano using functional ATRP initiators have been previously synthesized.[15]

RAFT has been successfully used for polymerization of vinyl monomers,[16] styrenics,[17] acrylates,[18] and methacrylates[19] and is often conducted under simple conditions, which do not require vacuum lines, inert conditions, or highly dried reagents.[20] RAFT occurs through a sequence of addition−fragmentation equilibrium reactions (Scheme 1) using a thiocarbonylthio compound [RSC(Z)═S].[21] There is a rapid equilibrium between the active propagating radicals and the dormant polymeric thiocarbonylthio compounds, which provides equal probability for all chains to grow and also allows for the synthesis of polymers with narrow polydispersity and controlled molecular weights. While it is undesired, the termination of active chains can occur and the dead polymer can be isolated as a stable material. Most polymer chains retain the R and Z groups from the RAFT agent at the ends of the polymer.[9] Functional polymers from RAFT can be made by introducing functional groups on the R and Z end groups. It has been reported that there are disadvantages of functionalizing the Z end group due to the presence of the labile C−S bond, which can be hydrolyzed and hence it is difficult to retain the functionality of interest at the end of the polymer chain.[22]

Block copolymers from RAFT agents with the carboxylic acid group on the R end which can be condensed with hydroxyl-terminated blocks to form an ester linkage have been previously synthesized.[7] Synthesis of block copolymers using this method depends on the ease of the esterfication step. In most cases, higher temperature conditions and long reaction times are required for complete conversion of the functional groups. On the other hand, the versatility of the cyclic ether group enables facile reactions with alcohols, amines, and carboxylic acid-functional blocks. Polymers with epoxy-functional groups have been extensively used for protective coatings,[23] adhesives,[24] and sealants.[25] Epoxy groups can be homopolymerized by using appropriate catalysts and can also be polymerized by cationic UV curing.[26] Oxetanes are also important cyclic ether monomers that undergo ring-opening polymerization to yield functional polyethers. Oxetane-functional oligomers are widely used for cationic UV curing applications.[27,28] They can also be homopolymerized to make graft polymers or reacted with carboxylic acid-functional polymers. Oxetane-based polymers have lower shrinkage and high flexibility,[28] which enables their use for

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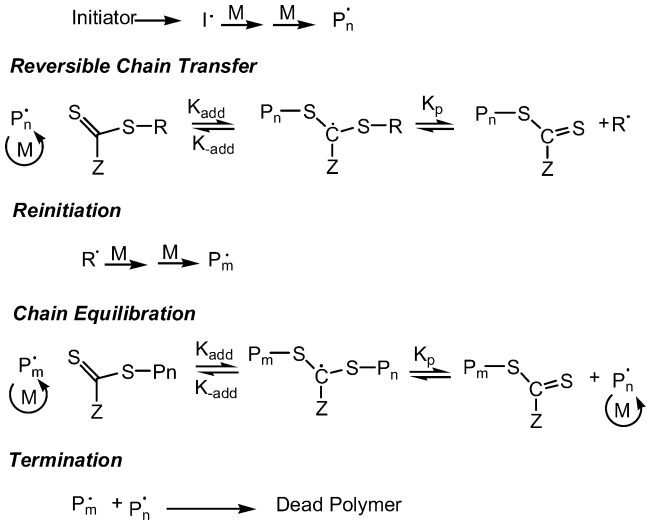
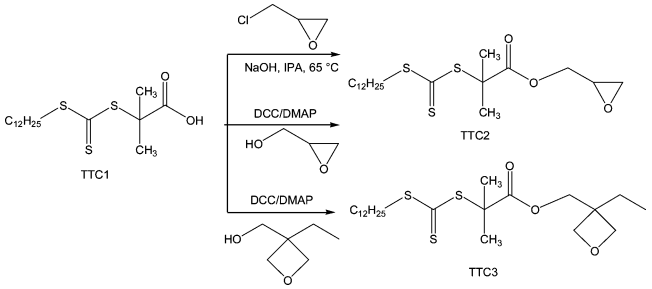
Scheme 1. Mechanism of RAFT Polymerization



Scheme 2. Synthesis of Epoxy (TTC2)- and Oxetane (TTC3)-Functional RAFT Agents



coatings and adhesives.[29] Thus, the synthesis of polymers having cyclic ether end groups is of interest in this work.

Herein, we report the synthesis of novel epoxy and oxetane-functional trithiocarbonate RAFT agents that would enable the synthesis of polymers having the respective functional end groups. Several acrylate monomers and styrene were used to synthesize the representative homo and block copolymers using the novel RAFT agents. These end groups can either be homopolymerized to form the graft copolymers or be easily linked with other functional oligomers to form the block copolymers. The ring structures of the epoxy and the oxetane were unaffected during the free-radical polymerization of monomers.

Results and Discussion

Carboxylic acid-functional RAFT agent (TTC1) was synthesized as described by Lai et al.[6] The acid group on TTC1 was reacted by two different methods to synthesize the epoxy-functional RAFT agent (TTC2) as shown in Scheme 2. For the first route, the overnight reaction of TTC1 with excess epichlorohydrin (EPI) at 65 °C in isopropanol (IPA) solvent and sodium hydroxide (NaOH) base was carried out to yield the epoxy-functional RAFT agent. The solution was filtered to remove the sodium chloride salt formed during the reaction followed by removal of excess EPI and IPA to yield a yellow-brown waxy solid. The crude product was eluted through a silica gel column using hexanes/ethyl acetate (98:2 v/v) to yield the pure chain transfer agent (CTA) TTC2 as a yellow-brown oil, yield 67%. Alternatively, TTC2 was also synthesized from TTC1 via an esterification reaction with glycidol (GLY) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) coupling agent and 4-dimethylaminopyridine (DMAP) base. This reaction was

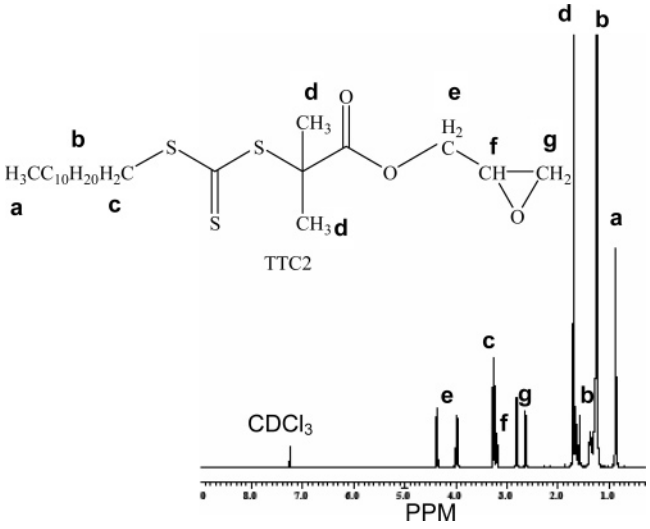


Figure 1. ^{1}H NMR of epoxy-functional RAFT agent (TTC2).

carried out for 72 h in dichloromethane (DCM) solvent. Upon removal of DCM in vacuo, the crude product was eluted through a silica gel column using hexanes/ethyl acetate (95:5 v/v) to yield the pure CTA as a yellow-brown oil, yield 44%. (Alternatively, by using molar amounts of DMAP, the reaction can be carried out in 24 h.) ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy were used to confirm the identity and purity of the compounds produced by both methods.

The ^{1}H NMR spectrum of TTC2 is shown in Figure 1. It shows peaks at 1.2−1.5 ppm, which are attributed to the dodecyl protons. The peak at 0.87 ppm is due to the C**H**$_3$−C$_{10}$H$_{20}$− group (peak "a" in Figure 1). The resonance at 3.25 ppm is due to −C$_{10}$H$_{20}$−C**H**$_2$− group designated as "c" in the proton spectrum. The resonance at 1.7 ppm is due to the methyl protons on the tertiary carbon designated as "d" in the spectrum. The peaks between 3.9 and 4.4 ppm are due the −O−C**H**$_2$− group next to the epoxy ring. The peaks at 3.2 and 2.6−2.83 ppm are due to the epoxy ring protons. The key peak integral area values for protons "a", "g", "f", "c", and "e" of TTC2 are 3.05, 1.01 and 0.97, 1.0, 1.96, and 1.0 and 1.01, respectively, which correlate well with the theoretical values.

Esterification of TTC1 with 3-ethyl-3-hydroxymethyl oxetane (EHMO) in the presence of DCC and molar amounts of DMAP in DCM solvent yielded the RAFT agent TTC3 as shown in Scheme 2. The crude product obtained after removal of DCM in vacuo was eluted through a silica gel column using hexanes/ethyl acetate (90:10 v/v) to yield the pure CTA TTC3, yield 57%. ^{1}H and ^{13}C NMR and FTIR spectroscopy were used to confirm the identity and purity of the compound.

Figure 2 shows the ^{1}H NMR spectrum of TTC3. The resonance at 0.87 ppm, designated as "a" in the figure, is due to the methyl protons at the two ends of the molecule. The peaks at 1.2−1.5 ppm, due to different dodecyl protons on the Z end group of the RAFT agent, are marked as "b" in the figure. The methylene protons next to the trithiocarbonate group which are designated as "c" can be seen at 3.25 ppm. The methyl proton on the tertiary carbon can be seen at 1.64 ppm, similar to the TTC2. The methylene protons next to the carbonyl group at 4.2 ppm are designated as "f". The peak for methylene protons marked as "e" is difficult to see as it lies at approximately 1.25 ppm and hence is overlapped by the dodecyl proton peaks. Finally, the oxetane proton peak can be seen at 4.4 ppm. The key peak integral area values for protons "a", "c", "f", and "g" of TTC3 are 5.96, 2.0, 2.0, and 4.06, respectively.

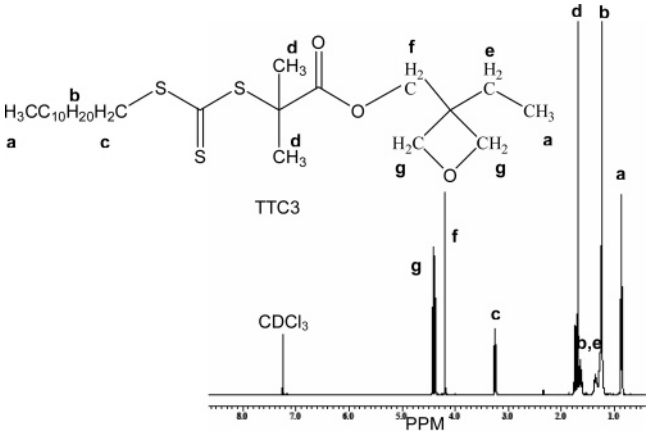


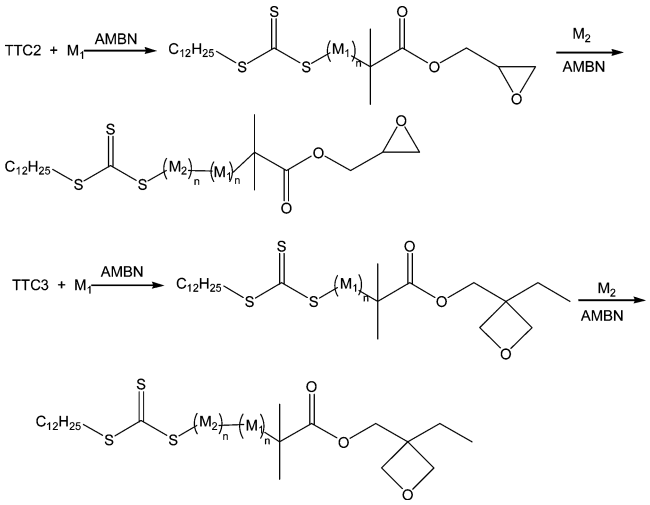
Figure 2. [1]H NMR of oxetane-functional RAFT agent (TTC3).

Table 1. Homopolymerization of Monomers[a] Using TTC2 and TTC3

monomer (g)	TTC 2 or 3 (mg)	AMBN (mg)	M_n GPC	M_w/M_n GPC	M_n MALDI	conversion (%)
BA (0.25)	2 (22.9)	4.2	5718	1.08	5107	100
2-EHA (0.25)	2 (22.9)	4.2	4421	1.09	4631	98
LA (0.25)	2 (22.9)	4.2	5511	1.07	5324	100
STY (0.25)	2 (22.9)	4.2	2741	1.08	2457	100
BMA (0.25)	2 (22.9)	4.2	8492	1.28		100
BA (0.5)	3 (50.9)	8.5	5996	1.07		100
2-EHA (0.5)	3 (50.9)	8.5	5199	1.07	4624	100
LA (0.5)	3 (50.9)	8.5	5621	1.06	4563	100
STY (0.5)	3 (50.9)	8.5	4248	1.10		100

[a] BA = butyl acrylate, 2-EHA = 2-ethylhexyl acrylate, LA = lauryl acrylate, STY = styrene, BMA = butyl methacrylate, and AMBN = 2,2′-azobis(2-methylbutyronitrile).

Scheme 3. Homo and Block Copolymerization of Monomers Using TTC2 and TTC3



Several acrylates and styrene were polymerized using the epoxy and oxetane-functional RAFT agents and for each case the polydispersity was less than 1.1 (Table 1). All acrylates were polymerized for 2 h and styrene was polymerized for 24 h. All reactions were conducted at 60 °C with 2,2′-azobis(2-methylbutyronitrile) (AMBN) as the initiator. Scheme 3 shows the homo and block copolymerization of monomers using TTC2 and TTC3. The conversion of all monomers was greater than 95% using both CTAs. Figure 3 shows a plot of conversion versus time for the polymerization of butyl acrylate using TTC2. It was observed that the polymerization of most acrylates was complete within 2 h for both TTC2 and TTC3.

Figure 4 shows the relationship of M_n with conversion for the polymerization of butyl acrylate ($M_{nTH} = 5000$). The linear increase in the molecular weight demonstrates the living nature of the polymerization.

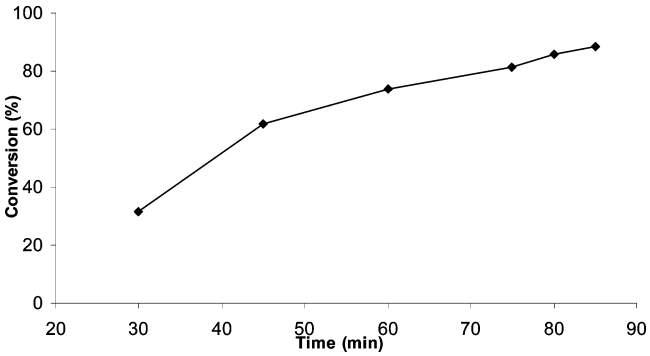


Figure 3. Conversion vs time for RAFT polymerization of BA (($M_{nTH} = 5000$) in toluene at 60 °C using TTC2.

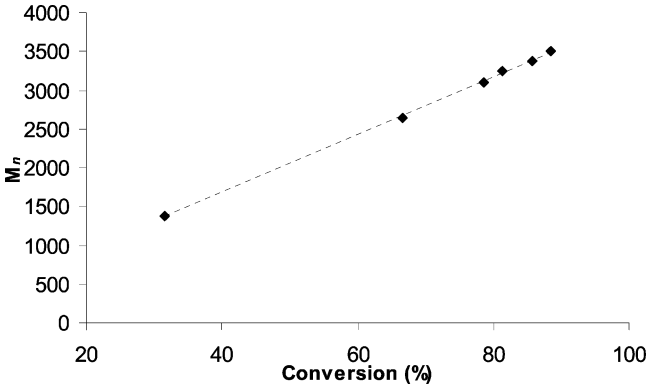


Figure 4. M_n vs conversion for RAFT polymerization of BA($M_{nTH} = 5000$) in toluene at 60 °C using TTC2.

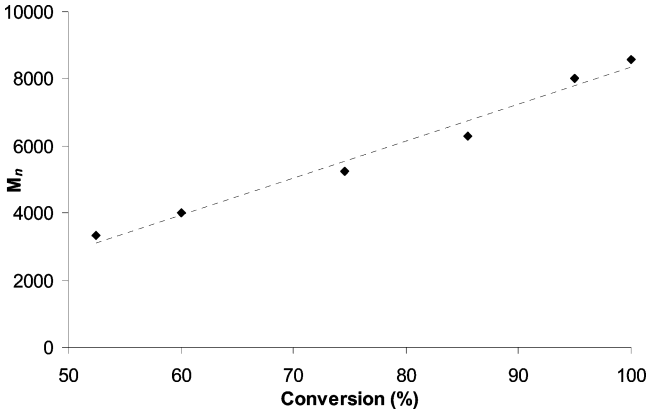


Figure 5. M_n vs conversion for RAFT polymerization of LA ($M_{nTH} = 10\,000$) in toluene at 60 °C using TTC3.

Likewise, Figure 5 shows a linear increase in M_n with percent conversion for the polymerization of lauryl acrylate (LA) using TTC3.

Homopolymers synthesized using TTC2 and TTC3 were characterized using matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry, [1]H NMR, and FTIR spectroscopic methods. MALDI has been used for quantitative analysis of polymers with internal standards.[30] Sodium iodide (NaI) was used as a cationizing agent for the MALDI experiments. The molecular weights of the polymers obtained using MALDI-TOF are in agreement with the molecular weights obtained from GPC. MALDI of poly(2-ethylhexyl acrylate) (P(2-EHA)) synthesized with TTC2 (Figure 6 a,b) shows a series of peaks spaced by 184 mu, which is the mass of 2-EHA. Analysis of the spectrum shows a series of several

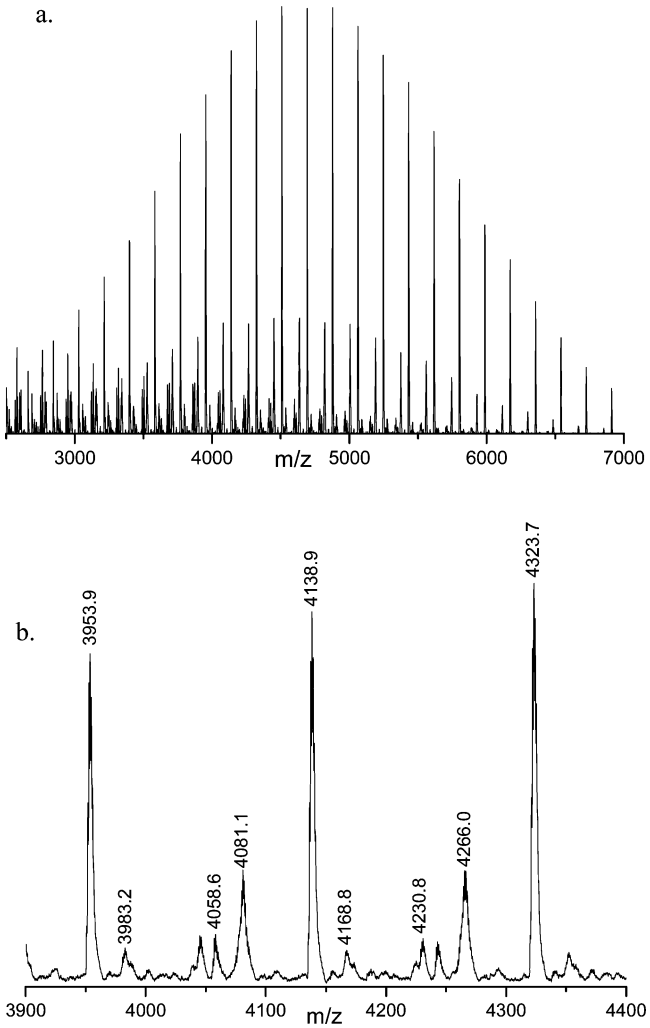


Figure 6. (a) MALDI-TOF spectrum of P(2-EHA) using TTC2. (b) Magnification of a region in the MALDI-TOF spectrum.

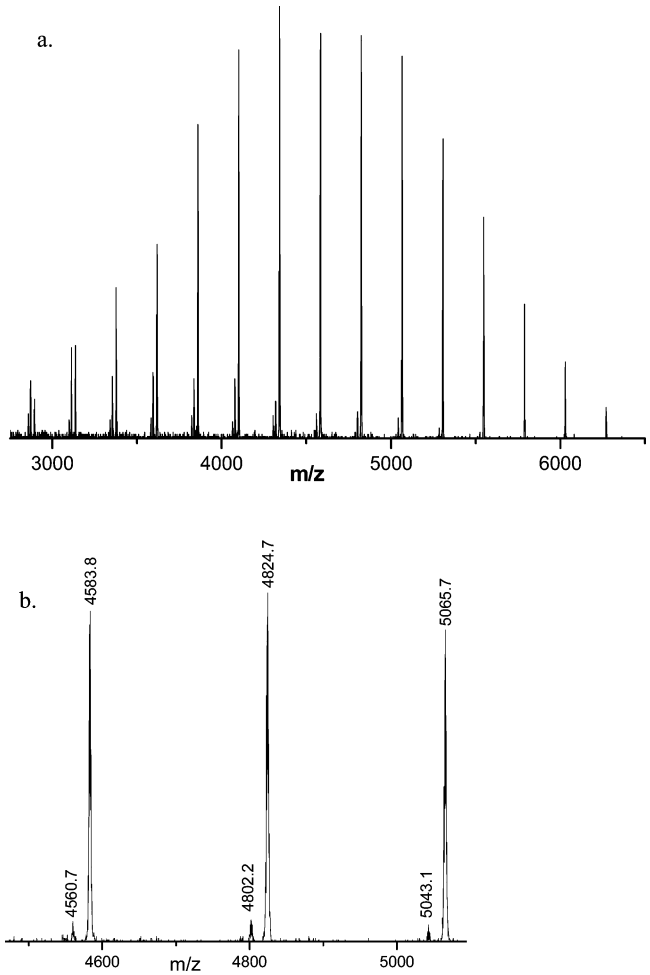


Figure 7. (a) MALDI-TOF spectrum of PLA using TTC3. (b) Magnification of a region in the MALDI-TOF spectrum.

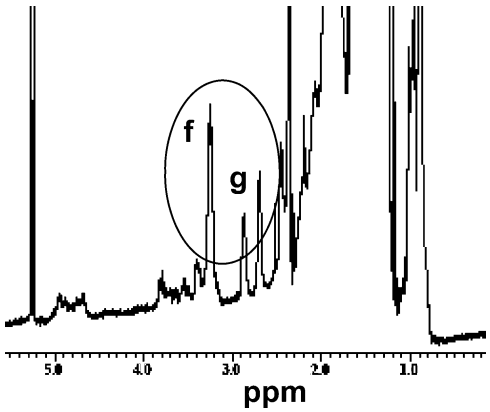


Figure 8. ^{1}H NMR of PS (M_n = 2741) synthesized using the epoxy-functional RAFT agent TTC2. The presence of epoxy ring after polymerization is confirmed by the presence of peaks at 2.6−2.9 and 3.2 ppm (circled) corresponding to "g" and "f" protons, respectively, as shown in Figure 1.

peaks. The peak at *m*/*z* 4138 can be assigned to the mass of the molecular ion plus 2 sodium atoms minus the hydrogen for a molecule containing 20 repeating units of 2-EHA ($m/z = M_w$ of $C_{12}H_{25}SC(=S)S-(2\text{-EHA})_n-C(Me_2)COOCH_2-$epoxy + 46 − 1, $n = 20$). Similarly, the peak at *m*/*z* 4081 can be assigned to the mass of the molecular ion minus glycidyl ether plus two sodium atoms minus the hydrogen ($m/z = M_w$ of $C_{12}H_{25}SC(=S)S-(2\text{-EHA})_n-C(Me_2)COOCH_2-$epoxy + 46 − 57, $n = 20$). The peak at *m*/*z* 4058 can be assigned to the mass of the molecular ion minus glycidyl ether plus one sodium atom ($m/z = M_w$ of $C_{12}H_{25}SC(=S)S-(2\text{-EHA})_n-C(Me_2)COOCH_2-$epoxy + 23 − 57, $n = 20$). Finally, the peak at *m*/*z* 3983 can be assigned to the mass of the molecular ion minus the $C_{11}H_{23}$ tail of the RAFT agent plus two sodium atoms ($m/z = M_w$ of CH_2-$SC(=S)S-(2\text{-EHA})_n-C(Me_2)COOCH_2-$epoxy + 46, $n = 20$). Figure 7 a,b shows the MALDI spectrum of poly(lauryl acrylate) (PLA, $M_n = 5620$) synthesized with TTC3. Two series of peaks are visible in the spectrum for PLA. The peak at *m*/*z* 4583 can be assigned to the mass of the molecular ion plus two sodium atoms minus hydrogen for a molecule containing 17 repeating units of LA ($m/z = M_w$ of $C_{12}H_{25}SC(=S)S-(LA)_n-C(Me_2)$-$COOCH_2C-$oxetane$-CH_2CH_3$ + 46 − 1, $n = 17$). The peak at *m*/*z* 4560 can be assigned to the mass of the molecular ion plus one sodium atom ($m/z = M_w$ of $C_{12}H_{25}SC(=S)S-(LA)_n-C(Me_2)COOCH_2C-$oxetane$-CH_2CH_3$ + 23, $n = 17$). Polymerization reactions controlled using TTC3 do not show any significant fragmented ions in MALDI spectrum unlike the polymers made using TTC2.

Figure 8 shows the ^{1}H NMR of polystyrene synthesized (M_n = 2741) using TTC2. The presence of the epoxy ring after polymerization is confirmed by the presence of peaks at 2.6−2.9 and 3.2 ppm (circled) corresponding to "g" and "f" protons, respectively, as shown in Figure 1.

The presence of the oxetane group after the polymerization of monomers using TTC3 was confirmed using FTIR spectros-

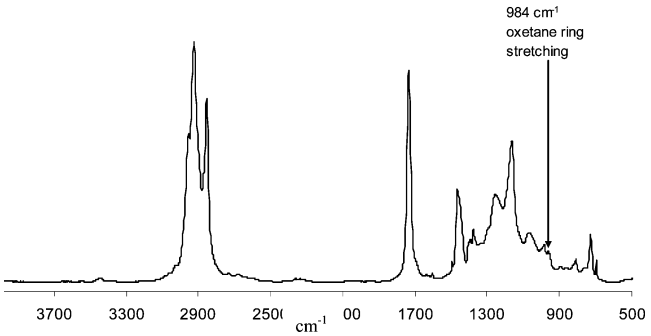


Figure 9. FTIR spectrum of PLA synthesized using the oxetane-functional RAFT agent TTC3.

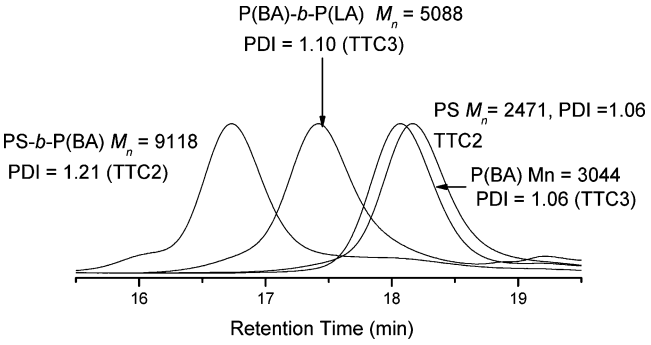


Figure 10. GPC traces of homo and block copolymers synthesized using TTC2 and TTC3.

Table 2. Block Copolymers Synthesized Using TTC2 and TTC3

M_1	TTC 2 or 3 (mg)	M_n	M_w/M_n	M_2	M_n	M_w/M_n
STY	2 (81.3)	2741	1.08	BA	9118	1.21
BA	2 (60.5)	3345	1.06	2-EHA	4378	1.14
BA	2 (60.5)	3287	1.06	LA	5688	1.09
BA	3 (68.0)	3044	1.06	2-EHA	4364	1.13
BA	3 (68.0)	3044	1.06	LA	5088	1.10

copy. The IR spectrum of PLA (Figure 9) controlled with TTC3 shows the characteristic peak at 984 cm^{-1}, which is due to C−O−C antisymmetric stretching in the oxetane ring.[29] The acrylate and methacrylate monomers with pendant oxetane ring have been previously polymerized by free-radical polymerization, and it has been shown that the oxetane ring does not participate in the free-radical polymerization.[29,31,32] Block copolymers via sequential addition using TTC2 and TTC3 were also synthesized. After the first block was polymerized, any residual unreacted monomer was removed by evaporation and was followed by chain extension with the second monomer. Most block polymers had narrow polydispersity indices, and the experimental molecular weights were close to the theoretical values. This indicates that the homopolymerization of the epoxy and the oxetane rings did not occur during the controlled radical polymerizations. Table 2 shows several block copolymers synthesized using TTC2 and TTC3. GPC traces of homo and block copolymers using TTC2 and TTC3 are shown in Figure 10. It can be seen from the GPC curves that the sequential addition of monomers to synthesize block copolymers can be successfully carried out using the novel epoxy and oxetane-functional RAFT agents. The block copolymer polystyrene (PS)-*b*-poly(butyl acrylate) (PBA) synthesized using TTC2 shows a high molecular weight shoulder, which could be due to chain termination reactions by combination. Similarly, the low molecular weight tail observed for block copolymers using both RAFT agents could be due to the residual macroRAFT agent, which did not initiate the polymerization of the second block.

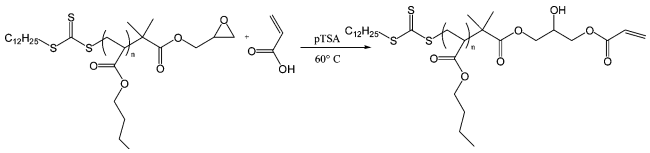


Figure 11. Reaction of epoxy-functional PBA with acrylic acid to form the acrylate-functional PBA macromer.

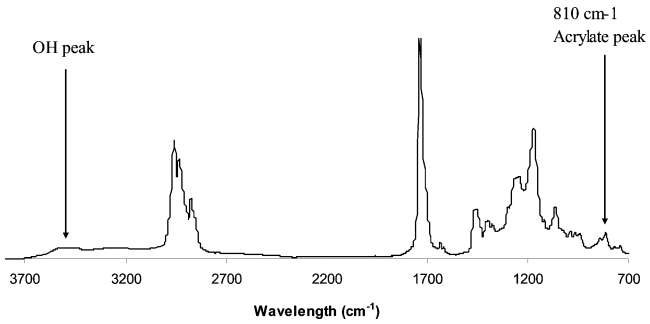


Figure 12. FTIR of acrylate-functional PBA.

Since the polymers synthesized using these new RAFT agents are functionalized with reactive end groups, these end groups can be used in a variety of ways. For example, the functional polymers can be easily coupled with functional oligomers containing complementary functional groups. Epoxy-functional polymers can be coupled with amine-, carboxylic acid-, and alcohol-functional polymers. Similarly, oxetane-functional polymers can be reacted with carboxylic acid-functional or alcohol-functional oligomers. Either the epoxy or the oxetane-functional groups can be homopolymerized by cationic ring-opening polymerization or can be cationically UV cured using appropriate photoinitiators.

As an example of the use of the epoxy-functional group, a low molecular weight epoxy-functional PBA (M_n = 1866) was reacted with acrylic acid using *p*-toluenesulfonic acid as a catalyst to form the acrylate-functional PBA (Figure 11). The reaction was monitored by the disappearance of the epoxy peak at 910 cm^{-1} and the appearance of the acrylate peak at 810 cm^{-1} (Figure 12). This approach represents a facile method for synthesizing an oligomer or polymer having an acrylate-functional end group. Acrylate-functional polymers made with RAFT and "click" chemistry have been previously reported, and they can be used for the synthesis of hyperbranched polymers.[33]

Similarly, the oxetane-functional RAFT agent TTC3 was copolymerized with EHMO using boron trifluoride etherate as the initiator. The disappearance of the oxetane peak was monitored using ^1H NMR. The resulting trithiocarbonylthio macromer was then used for controlled free-radical polymerization (CRP) of butyl acrylate (BA) (Figure 13).

Polymerization of BA using the macromer was confirmed by GPC anaylsis. Figure 14 shows the difference in the molecular weight before and after the polymerization of BA, indicating the formation of a graft copolymer

One of the main difficulties in synthesizing amphiphilic block copolymers with highly hydrophilic and hydrophobic blocks is conducting the polymerization of both blocks in a common solvent, and hence, to overcome it most times, a mixture of solvents or the emulsion polymerization technique has to be used.[34] On the other hand, the coupling of hydrophobic and hydrophilic blocks prepared separately is a relatively easy way to synthesize truly amphiphilic block copolymers. Currently, we are working on the synthesis of amphiphilic block copolymers by coupling reactions using these functional RAFT agents. Most polymers have narrow polydispersity indices and can be synthesized within a few hours. These polymers have potential

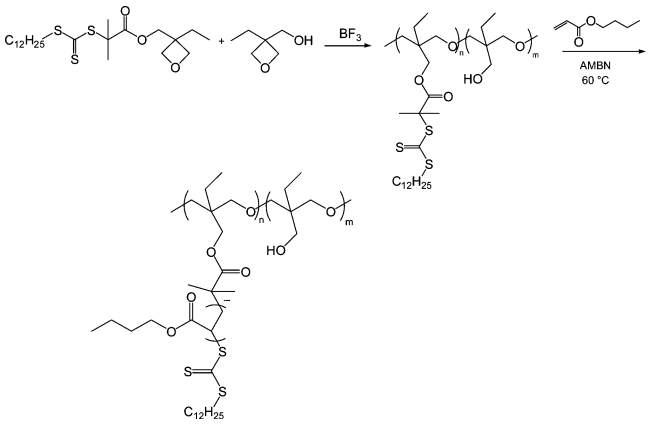


Figure 13. Copolymerization of TTC3 and EHMO followed by controlled free-radical polymerization of BA to form the graft copolymer.

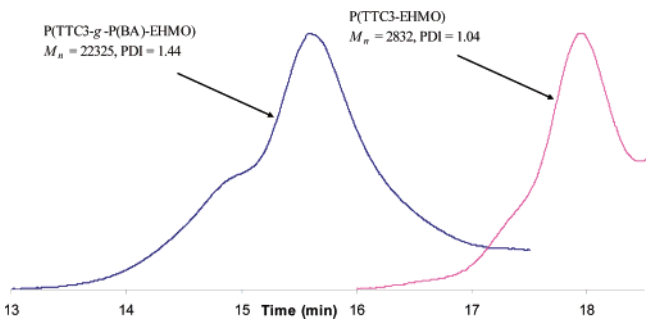


Figure 14. GPC traces of the copolymerization of P(TTC3−EHMO) and P(TTC3-*g*-PBA-EHMO).

applications as dispersing agents, drug delivery systems, adhesives, etc.[13]

Conclusion

We have synthesized novel epoxy- and oxetane-functional trithiocarbonate RAFT agents. The RAFT agents were characterized by NMR and FTIR techniques. Several homo and block copolymers were synthesized using acrylate monomers and styrene. Polymers were characterized using GPC and MALDI-TOF. All polymers have narrow polydispersity indices. The epoxy-functional polymer was modified with acrylic acid to form an acrylate-functional polymer, whereas the oxetane-functional RAFT agent was copolymerized with EHMO followed by polymerization with butyl acrylate to form a graft copolymer. The functional polymers can also be coupled with different functional polymers to synthesize block copolymers.

Experimental Section

Materials. Chain transfer agent (CTA) S-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (TTC1) was synthesized and purified according to literature procedure.[6] Toluene, hexane, ethyl acetate (EA), isopropanol (IPA), dichloromethane (DCM), epichlorohydrin (EPI), sodium hydroxide (NaOH), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopydridine (DMAP), butyl acrylate (BA), butyl methacrylate (BMA), styrene (STY), and 2-ethylhexyl acrylate (2-EHA) were purchased from Aldrich. Lauryl acrylate (LA) was received from Sartomer. Glycidol (GLY) was received from Dixie Chemicals. UVR 6000, monofunctional reactive oxetane diluent (3-ethyl-3-hydroxymethyl oxetane) (EHMO), was received from Dow Chemical Company. 2,2′-azobis(2-methylbutyronitrile) (AMBN, VAZO 67) was received from Dupont Chemicals. All materials were used as received without further purification.

Instrumentation and Measurements. The CTAs were characterized using nuclear magnetic spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR). Polymers were characterized using gel permeation chromatography (GPC), matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry, and NMR. ^{1}H and ^{13}C NMR measurements were done at 23 °C using JEOL-ECA (400 MHz) NMR spectrometer with an autosampler accessory. All measurements were made using $CDCl_3$ as the solvent. The data were processed using Delta software package. Molecular weight was determined using a Waters 2410 GPC equipped with a refractive index detector. A 1% sample solution in THF using a flow rate of 1 mL/min was used. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex II spectrometer equipped with a 1.85 m linear flight tube and a Smart beam laser. All mass spectra were obtained in positive ion and linear mode. Dithranol (20 mg/mL in THF) was used as a matrix, silver trifluoroacetate and sodium iodide (NaI) (2 mg/mL) were used as the cationizing agents, and polymer samples were dissolved in THF (2 mg/mL). A 100 μL portion of the matrix, 20 μL of the dopant, and 20 μL of the polymer were mixed together, and a 3 μL sample solution was spotted on the target plate. All data were processed using Flex analysis and PolyTools software package. FTIR measurements were made using a Nicolet Magna-850 FTIR spectrometer. Samples were coated on a potassium bromide salt pellet, and spectra acquisitions were based on 16 scans with a data spacing of 1.98 cm^{-1}. The FTIR was set for autogain to monitor spectral ranges of 4000−500 cm^{-1}.

Synthesis of Epoxy-Functional RAFT Agent (TTC2) Using Epichlorohydrin. In a 250 mL round-bottom flask equipped with a thermometer and magnetic stir bar was taken 3.0 g (8.24 mmol) of TTC1, 50 mL (0.65 mol) of IPA, and 0.327 g (8.17 mmol) of NaOH. The mixture was stirred for 30 min at 65 °C to dissolve the TTC1 and NaOH. EPI (7.06 g, 76.30 mmol) was then added dropwise using a syringe. The temperature was maintained at 65 °C, and the reaction was allowed to stir overnight. The resulting solution was filtered to remove the sodium chloride formed during the reaction. IPA and excess EPI were removed in vacuo, and the product was dissolved in hexane and then washed with water. Hexane was removed in vacuo, and the crude product was eluted through a silica gel column using hexanes/ethyl acetate (98:2 v/v) to yield the pure CTA TTC2 as a yellow-brown oil. The yield was 2.28 g (66%). The product was confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz, $CdCl_3$ 23 °C, δ): 0.87, 1.2−1.5, 1.7, 2.6−2.83, 3.2, 3.25, and 3.9−4.4. ^{13}C NMR (400 MHz $CdCl_3$, δ): 14.2, 22.8, 25.4, 27.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 32.0, 37.1, 44.8, 49.2, 55.9, 66.4, 172.9, and 221.6

Synthesis of Epoxy-Functional RAFT Agent (TTC2) Using Glycidol. In a 250 mL round-bottom flask equipped with magnetic stir bar was taken 1.0 g (2.74 mmol) of TTC1, 0.567 g (2.74 mmol) of DCC, 0.07 g (0.57 mmol) of DMAP, and 100 mL of DCM. The reaction was stirred at room temperature for 30 min before adding 0.40 g (5.48 mmol) of GLY. The reaction was stirred for 72 h at room temperature. The solution was then filtered, and DCM was removed in vacuo. The product was dissolved in hexane and filtered. The filtrate was washed with water, and hexane was removed in vacuo. The resulting crude product was eluted through a silica gel column using hexanes/ethyl acetate (95:5 v/v) to yield the pure chain transfer agent TTC2 as a yellow-brown oil. The yield was 0.5 g (43.5%). NMR and FTIR characterization revealed the same composition as TTC2 synthesized using epichlorhydrin.

Synthesis of Epoxy-Functional RAFT Agent (TTC3) Using 3-Ethyl-3-hydroxymethyl Oxetane. In a 250 mL round-bottom flask equipped with magnetic stir bar was taken 1.0 g (2.74 mmol) of TTC1, 0.637 g (5.48 mmol) of EHMO, 0.355 g (2.74 mmol) of DMAP, and 50 mL of DCM. The reaction was stirred for 30 min at 0 °C, and 0.58 g (2.74 mmol) of DCC dissolved in 5 mL of DCM was slowly added to the mixture. The resulting mixture was warmed to room temperature, and the reaction was stirred for 20 h. The solution was then filtered, and DCM was removed in vacuo. The product was dissolved in hexane and filtered again. Hexane was removed in vacuo, and the resulting crude product was eluted through a silica gel column using hexanes/ethyl acetate (95:5 v/v) to yield the pure chain transfer agent TTC3 as a yellow-brown oil.

The yield was 0.735 g (57%). The product was confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$ 23 °C, δ): 0.87, 1.2−1.5, 1.7, 3.25, 4.2, and 4.4. ^{13}C NMR (400 MHz $CDCl_3$, δ): 8.3, 14.2, 22.8, 25.4, 26.9, 27.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 32.0, 37.1, 42.6, 56.0, 68.0, 78.0, 173.2, and 221.8.

Representative Homopolymerization of Styrene Using TTC2. In an 8 mL glass vial with a magnetic stir bar was taken 0.25 g (2.40 mmol) of styrene, 23.0 mg of TTC2, 0.25 g of toluene, and 4.2 mg (0.021 mmol) of AMBN. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 60 °C for 24 h (M_n = 2457, PDI = 1.08).

Representative Homopolymerization of Butyl Acrylate Using TTC3. In an 8 mL glass vial with a magnetic stir bar was taken 0.50 g (3.90 mmol) of butyl acrylate, 50.86 mg of TTC3, 0.50 g of toluene, and 8.5 mg (0.042 mmol) of AMBN. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 60 °C for 3 h (M_n = 5996, PDI = 1.07).

Representative Block Copolymerization of Styrene and Butyl Acrylate Using TTC2. In an 8 mL glass vial with a magnetic stir bar was taken 0.25 g of polystyrene (PS) synthesized previously (M_n = 2457, PDI = 1.08), 1.0 g of toluene, 17.35 mg (0.089 mmol) of AMBN, and 0.55 g (4.27 mmol) of butyl acrylate. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 60 °C for 12 h (M_n = 9118, PDI = 1.21).

Representative Block Copolymerization of Butyl Acrylate and Lauryl Acrylate Using TTC3. In the first step, to an 8 mL glass vial with a magnetic stir bar was added 0.3 g of butyl acrylate, 0.3 g of toluene, 11.3 mg (0.058 mmol) of AMBN, and 68 mg of TTC3, and the vial was degassed by purging with nitrogen for 2 min. The reaction was carried out at 60 °C in an oil bath for 2 h. The reaction was then stopped and the solvent and any residual monomer were removed under vacuuo. For block copolymerization, to the resulting poly(butyl acrylate) (PBA) (M_n = 3032, PDI = 1.06) was added 0.3 g of toluene, 7.70 mg (0.04 mmol) of AMBN, and 0.3 g (1.2 mmol) of LA. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 60 °C for 12 h (M_n = 5088, PDI = 1.10).

Reaction of Epoxy-Functional PBA with Acrylic Acid. In a 8 mL glass vial with a magnetic stir bar was taken 0.25 g of PBA (M_n = 1860), 0.029 g of acrylic acid, 3 mg of *p*-TSA, and a small quantity of hydroquinone. The reaction was carried out at 60 °C for 8 h and was monitored with an FTIR. After completion of the reaction, the excess acrylic acid was removed under vacuuo. FTIR shows peaks at 810 and 3500 cm^{-1}, which correspond to the carbon−carbon double bond and the hydroxyl, respectively. The epoxy peak at 910 cm^{-1} had completely disappeared, indicating the completion of the reaction.

Copolymerization of TTC3 and EHMO Followed by Graft Polymerization of Butyl Acrylate. In the first step, 0.1 g of TTC3, 0.025 g of EHMO, and 2 drops of $BF_3{\cdot}(C_2H_5)_2O$ were added to 5 mL of DCM taken in a 8 mL vial with a magnetic stirrer. The reaction was stirred for 3 h at room temperature. DCM was removed under vacuuo, and GPC analysis of the TCC3−EHMO gave values of M_n = 2830 and PDI = 1.05. In the second step, 21 mg of the block copolymer synthesized in the first step, 0.5 g of butyl acrylate, 0.5 g of toluene, and 5 mg of AMBN were taken in an 8 mL vial. The reaction was carried out at 60 °C for 3 h. The resulting polymer had M_n = 22 300 and PDI = 1.42.

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