Articles

Synthesis of ABA Triblock Copolymers by a Tandem ROMP−RAFT Strategy

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ABSTRACT: A symmetric, acyclic olefin possessing trithiocarbonate moieties, available in two synthetic steps from commercially available starting materials, is demonstrated to act as a chain transfer agent (CTA) in ring opening metathesis polymerizations (ROMP). The synthetic efficiency of the ruthenium-catalyzed ROMP of 1,5-cyclooctadiene in the presence of this new CTA is investigated as a means of producing telechelic polybutadienes bearing trithiocarbonate endgroups. Telechelic polymers thus synthesized are macromolecular chain transfer agents in the reversible addition fragmentation chain transfer (RAFT) polymerization of styrene and acrylate monomers, enabling the synthesis of ABA-type triblock copolymers of varying compositions possessing monomodal molecular weight distributions.

Introduction

Over the past fifty years, advances in precision polymerization techniques have provided synthetic access to well-defined homopolymers and block copolymers constituted of simple dienes and substituted styrenes, as well as a variety of functionalized monomers.[1] While some of these methodologies offer the ability to produce block copolymers by sequential addition of monomers that polymerize by the same mechanism (*mechanistically compatible monomers*),[2−4] the development of facile methods for the block copolymerization of *mechanistically incompatible monomers* continues to provide an open synthetic frontier which will beget new opportunities in the design and application of functional organic materials. Block copolymerization of mechanistically incompatible monomers typically requires multiple synthetic steps to functionalize the polymer chain ends with initiating sites that facilitate the polymerization of a second monomer by a different polymerization mechanism. Numerous examples of so-called change of mechanism block copolymerizations have been employed in the synthesis of linear and branched block copolymers possessing novel properties.[5−13]

Examples of block copolymer syntheses incorporating mechanistically incompatible monomers employing various free radical polymerization techniques have been reported recently. Known for their remarkable functional group tolerance, “controlled” and “living” free radical polymerizations such as atom transfer radical polymerization (ATRP),[2] nitroxide-mediated free radical polymerization,[3] catalytic chain transfer polymerization,[14] and more recently, reversible addition fragmentation transfer (RAFT) polymerization[15,16] have emerged as standard tools for the synthesis of functional polymeric materials. Recent reports on the synthesis of block copolymers incorporating mechanistically incompatible monomers include combinations of Ziegler−Natta polymerization with nitroxide-mediated living free radical polymerization[17] and ring-opening polymerization (ROP) with RAFT.[7,9] Bielawski et al. exhaustively explored the ruthenium-catalyzed chain transfer ring-opening metathesis polymerization (ROMP−CT) of various cyclic monomers in the presence of chain transfer agents (CTA) containing latent ATRP initiating sites.[18−22] Upon completion of a ROMP−CT of a strained cyclic olefin with a CTA bearing activated halogens, they demonstrated that addition of an ATRP catalyst and a second monomer facilitates the formation of block copolymers. In later work, Bielawski et al. also demonstrated that a difunctional ruthenium catalyst simultaneously mediates the ATRP of methyl methacrylate as well as the ROMP of 1,5-cyclooctadiene (1,5-COD).[23] Newer work by Charvet and Novak shows that tandem ROMP/ATRP reactions can be used to synthesize bottle-brush polymers derived from norbornene-based monomers containing ATRP initiating sites.[24]

Facile methods for the introduction of latent reactive functionalities into polymers as exemplified by the aforementioned cases provide convenient access to block copolymers of mechanistically incompatible monomers. Herein, we report the synthesis of a CTA for ROMP−CT that enables the synthesis of telechelic polymers possessing trithiocarbonate functionalized termini capable of mediating RAFT polymerizations. On this basis, we demonstrate the synthesis of ABA-type triblock copolymers of mechanistically incompatible monomer pairs such as 1,5-cyclooctadiene with styrene and acrylate monomers by a tandem ROMP and RAFT method.

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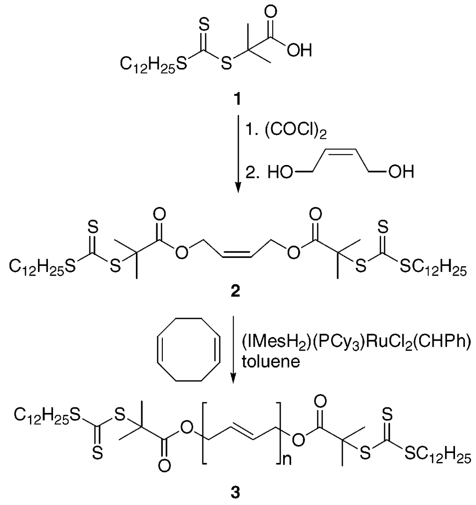
Scheme 1



Results and Discussion

The synthesis of CTA **2** is depicted in Scheme 1. Lai et al. reported a convenient, scalable synthesis of carboxylate functionalized RAFT agent **1** under phase transfer catalysis conditions in one synthetic step from commercially available starting materials.[25] Reaction of **1** with oxalyl chloride at 22 °C until the evolution of gases ceases and subsequent removal of the excess chlorinating agent in vacuo provides the acyl chloride (vide infra). The neat acyl chloride reacts with a substoichiometric amount of *cis*-2-butene-1,4-diol (~97% cis) resulting in vigorous evolution of HCl(g) and formation of a dark yellow-brown oil. Elution of this material through a column of silica gel using hexane/CH_2Cl_2 (v/v 1:1) provides **2** in high yields as a yellow-orange oil at room temperature. (Alternatively, trituration of the reaction mixture with 2-propanol followed by cooling to −20 °C causes **2** to phase separate as a thick oil, which can be recrystallized from hexanes at −20 °C.) ^{1}H and ^{13}C NMR, and elemental analysis confirm the identity and purity of this compound.

Since symmetric acyclic olefins (e.g., 1,4-disubstituted 2-butenes) are well-established chain transfer agents in the ROMP−CT of cyclic monomers to provide telechelic homopolymers,[19] we examined the chain transfer efficiency of **2** in the ruthenium catalyzed ROMP of 1,5-cyclooctadiene(1,5-COD) (Scheme 1). In the presence of first generation Grubbs' olefin metathesis catalyst, $(Cy_3P)_2RuCl_2(CHPh)$, no polymerization activity is observed with [CTA]:[Ru] = 143 and [COD]:[CTA] = 67; only starting materials are recovered from the reaction. The lack of polymerization activity is not surprising given the low functional group tolerance of first generation Grubbs' catalysts toward Lewis basic functionalities such as nitriles and amines.[26] We attribute this complete lack of reactivity to the possible binding or reaction of the trithiocarbonate moieties and the coordinatively unsaturated ruthenium carbene complex. In sharp contrast to this result, second generation Grubbs' olefin metathesis catalyst, $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ ($IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy = cyclohexyl),[27] facilitates the ROMP of 1,5-COD in toluene solution with [CTA]:[Ru] = 285 and [COD]:[CTA] = 42 to furnish a telechelic polybutadiene **3** bearing trithiocarbonate functionalities at its termini. ^{1}H NMR analysis at 500 MHz of a dried aliquot of the reaction mixture permits discrimination between resonances associated with unreacted CTA **2** (δ 4.57(cis) and 4.69(trans) ppm) and the polymer endgroups associated with ROMP−CT to **2** (δ 4.52(cis) and 4.62(trans) ppm) (Figure 1). Integration of these resonances demonstrates that the chain transfer efficiency of **2** is 52% after 8 h, with no variation at longer reaction times (Table 1, Entry B-2). Integration of ^{1}H NMR resonances associated with all of the methylene protons adjacent to sulfur in **2** and **3** relative to the polybutadiene backbone olefinic protons indicates greater than 95% 1,5-COD conversion in this ROMP reaction. The telechelic polymer backbone stereochemistry is 71% trans, suggesting that the ROMP of 1,5-COD proceeds quickly with partial equilibration of the backbone stereochemistry by secondary metathesis toward the equilibrium value of ~80% trans olefins.[28] NMR analysis also reveals that unreacted **2** is substantially isomerized from 97% cis to 48% cis isomer in the reaction, far from the expected equilibrium value of ~15% cis.[29] Conventional SEC analysis of a reaction aliquot versus polystyrene standards shows that the polydispersity of the telechelic polymer is $M_w/M_n = 2.02$, while SEC with light scattering detection provides an absolute measure of M_n that agrees favorably with that determined by ^{1}H NMR endgroup analysis (Table 1). Molecular weights thus determined are in reasonable agreement with that calculated from [COD]:[**2**] and the observed chain transfer efficiency from ^{1}H NMR spectroscopy. Assuming that the extinction coefficients of the trithiocarbonate moieties are not substantially affected by the presence of polybutadiene, integration of the SEC−UV trace obtained with detection at $\lambda = 325$ nm enables a secondary measurement of the chain transfer efficiency as 49%, which corroborates the aforementioned result derived from ^{1}H NMR. Due to the solubility of **2** in 2-propanol, precipitation of the polymer from CH_2Cl_2 into 2-propoanol twice reduces the amount of **2** present to less than 5 mol % as determined by SEC−UV and ^{1}H NMR spectroscopy.

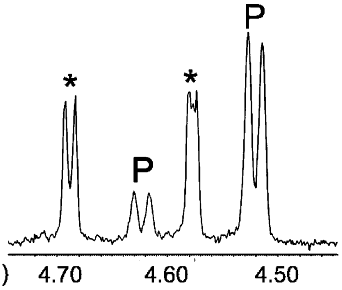


Figure 1. ^{1}H NMR spectrum of a telechelic polybutadiene produced from ROMP of 1,5-COD in the presence of **2** highlighting the allylic resonances adjacent to the ester linkage. Peaks labeled with a "P" and a "*" correspond to cis and trans isomers of the polymeric endgroups and **2**, respectively.

To understand the origin of the low chain transfer efficiency of **2** in the ROMP−CT of 1,5-COD, the effects of different polymerization reaction conditions were examined as summarized in Table 1. The most probable molecular weight distribution ($M_w/M_n \sim 2.0$) is obtained for the resulting polybutadienes under all conditions, and the monomer conversion is consistently greater than 95%. Use of a more polar solvent such as CH_2Cl_2 results in a lower degree of incorporation of **2** into the polybutadiene. Based on runs B-1, B-2, and B-5 in Table 1, one observes that increasing the reaction temperature to 55 °C increases the chain transfer efficiency of **2**,

Table 1. Effects of Reaction Conditions on the Chain Transfer Efficiency of 2 in ROMP−CT of 1,5-COD with $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$

		mol % **2** incorporated		before purification			after purification	
run	reaction conditions[a]	^{1}H NMR	SEC−UV[b]	$M_{n,th}$[c] (kg/mol)	$M_{n,NMR}$[d] (kg/mol)	$M_{n,SEC}$ (M_w/M_n)[e]	$M_{n,SEC}$ (M_w/M_n)[e]	% trans[d]
B-1	0 °C	28.5	27.9	16.8	17.6	15.7 (2.05)	15.8(2.11)	71
B-2	22 °C	51.9	49.1	10.0	10.3	11.9 (2.02)	11.8 (2.06)	79
B-3	CH_2Cl_2	34.9	34	14.4	15.1	14.1 (2.10)	14.8 (2.04)	75
B-4	THF[f]	47.6	46.7	9.1	9.6	10.9 (2.02)	10.8 (2.08)	77
B-5	55 °C	62.9	58.7	8.3	8.9	9.6 (1.90)	10.0 (1.92)	73

[a] Reactions were conducted in toluene, with [COD]:[**2**] ~ 42 and [**2**]:[Ru] ~ 285 at 22 °C for 12 h unless otherwise specified. [b] Determined by SEC in THF at 22 °C with UV detection at $\lambda = 325$ nm. [c] Calculated from [COD]:[**2**] and the mol % **2** incorporated assessed by ^{1}H NMR spectroscopy. [d] Determined by ^{1}H NMR spectroscopy with endgroup analysis assuming that the degree of end-functionalization $F_n = 2.0$ (see Figure 1). [e] $M_{n,SEC}$ (kg/mol) determined by SEC with light scattering detection, and M_w/M_n calculated from conventional SEC versus polystyrene standards. [f] Reaction was conducted in toluene with [THF]:[Ru] = 2920.

Table 2. Triblock Copolymers Derived from RAFT Chain Transfer Agents B-2 and B-5

	triblock copolymer			end block	
polymer	w_B[a]	$M_{n,NMR}$[b]	$M_{n,SEC}$ (M_w/M_n)[c]	$M_{n,NMR}$[b]	$M_{n,SEC}$ (M_w/M_n)
S(B-2)S-1	0.495	23.9	24.6 (1.52)	6.0	6.5 (1.12)[d]
S(B-2)S-2	0.442	26.7	25.7 (1.58)	7.5	7.8 (1.12)[d]
A(B-2)A-1	0.791	14.9	25.1 (1.67)	1.6	3.0 (1.28)[c]
A(B-5)A-3	0.487	20.5	27.7 (1.45)	5.3	7.0 (1.29)[c]

[a] Weight fraction of polybutadiene determined by ^{1}H NMR spectroscopy. [b] Reported in kg/mol as calculated from w_B and $M_{n,SEC}$ for the purified polybutadiene block (Table 1). [c] Determined by SEC in THF at 22 °C versus polystyrene standards and reported in kg/mol. [d] $M_{n,SEC}$ (kg/mol) determined by SEC with light scattering detection, and M_w/M_n calculated from conventional SEC versus polystyrene standards.

suggesting the possibility that the trithiocarbonates reversibly bind to the ruthenium center, thus retarding reaction equilibration by cross metathesis. Addition of tetrahydrofuran as a competitive Lewis basic solvent has a negligible effect on the chain transfer efficiency in these reactions. Surprisingly, THF does not substantially affect the polybutadiene stereochemistry, in sharp contrast to previous reports regarding ROMP−CT of 1,5-COD with *cis*-2-butene-1,4-diol in the presence of THF.[21] The above observations indicate that ROMP of 1,5-COD occurs quickly in high conversion, and secondary metathesis reactions control the polymer backbone stereochemistry and incorporation of CTA **2**. Furthermore, the low chain transfer efficiency of **2** in the context of previous reports on ROMP−CT[27] suggests that the trithiocarbonate moieties poison the ruthenium metathesis catalyst irreversibly. The exact nature of catalyst deactivation is not known; however, the high affinity of ruthenium toward sulfur and the coordinative unsaturation of the 14-electron active metathesis catalyst could result in an irreversible reaction of **2** with ruthenium.

Using purified, trithiocarbonate terminated polybutadienes as macromolecular RAFT chain transfer agents, we synthesized a series of ABA-type triblock copolymers having polybutadiene center blocks (Table 2). Bulk polymerization of styrene under an argon atmosphere at 110 °C using **B-2** yields SBS triblock copolymers (~80% isolated yield based on monomer conversion from ^{1}H NMR spectroscopy) using styrene autoinitiation[29] as the source of free radicals that initiate the RAFT reaction. SEC analyses of these SBS triblock copolymers show that the polymers have decreased elution volumes consistent with increased molecular weights, and the SEC traces are monomodal with lower polydispersities than that of the parent chain transfer agent (Figure 2). To show that the styrene end blocks of these triblock copolymers are monodisperse, the polybutadiene block of each triblock was degraded by cross metathesis with 1-hexene using $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ to yield polystyrene and various small molecules;[31,32] complete degradation of the center diene block was confirmed by ^{1}H NMR spectroscopy. SEC of the polystyrenes thus obtained demonstrates that the end blocks have $M_w/M_n = 1.12$ (Table 2). For each triblock copolymer, the M_n of the PS end blocks determined by SEC agrees within experimental error with that calculated from $M_{n,SEC}$ for the purified parent polybutadiene and integration of quantitative ^{1}H NMR spectra of the block copolymer assuming a triblock architecture. This analysis proves that the polybutadiene starting material is a difunctional telechelic with a high degree of trithiocarbonate end functionalization.

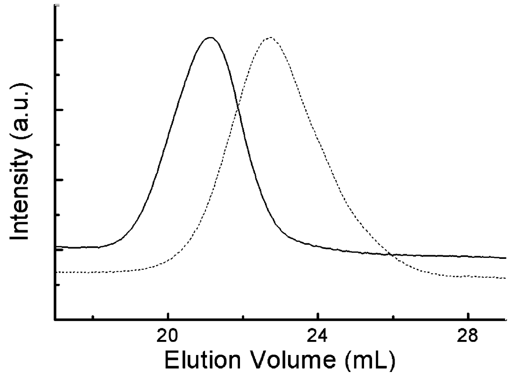


Figure 2. Representative SEC traces of telechelic polybutadiene **B-2** synthesized from ROMP with chain transfer agent **2** (dashed line), and **S(B-2)S-1** triblock copolymer synthesized by RAFT of styrene at 110 °C (solid line).

Polybutadiene RAFT chain transfer (**3**) agents also facilitate the synthesis of triblock copolymers containing polyalkyacrylate blocks. For example, an ABA-triblock copolymer of poly(*tert*-butylacrylate) (P*t*BuA) and polybutadiene was synthesized by solution RAFT polymerization of *tert*-butylacrylate in benzene at 60 °C initiated by AIBN (Table 2). Low monomer conversions were employed in these reactions to prevent cross-linking of the polybutadiene segments. Monomodal triblock copolymers with RAFT agent termini with narrow polydispersities are readily produced and isolated in variable isolated yields (~20−50%) by unoptimized precipitation in methanol. SEC analyses of products of the ruthenium-catalyzed 1-hexene degradations of these triblock copolymers directly demonstrate that the $M_w/M_n \sim 1.3$ for the P^{t}BuA end blocks. (Due to differences in the hydrodynamic volumes of P*t*BuA and the PS standards used for SEC calibration, $M_{n,SEC}$ determined for these materials does not match with those calculated from ^{1}H NMR data in Table 2.) The observed end block polydispersities are consistent with previous observations by Moad et al., which indicate that the polydispersities of polymers produced by RAFT are broader at low monomer conversion and decrease as monomer conversion increases.[16]

Conclusion

We have described a scalable synthesis of triblock copolymers by a ROMP−RAFT polymerization strategy. This method provides block copolymers containing a polydisperse center segment and monodisperse end blocks. The effects of polydispersity on the phase behavior and microphase separated morphologies adopted by these materials are currently being investigated.

Experimental Section

Materials. Standard Schlenk techniques and a Vacuum Atmospheres drybox were used in the handling of all moisture- and air-sensitive compounds under a high purity argon atmosphere. Tetrahydrofuran, toluene, and CH_2Cl_2 were degassed by sparging with argon for 30 min followed by passage through activated alumina to remove protic impurities. Reagent grade solvents were otherwise used without further purification. $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$, ethyl vinyl ether, 1,5-cyclooctadiene, 2-butene-1,4-diol (97% cis), oxalyl chloride, styrene, *tert*-butylacrylate, and 1-hexene were purchased from Aldrich. 1,5-Cyclooctadiene (Aldrich, 99%) was fractionally distilled under argon to remove terminal olefin impurities;[33] the fraction with bp 148−149 °C was dried over di(*n*-butyl-magnesium) and used for polymerization reactions. *Cis*-2-butene-1,4-diol was vacuum distilled under reduced pressure to removed colored impurities. Styrene and *tert*-butylacrylate were purified by stirring with neutral alumina for 1 h to remove the inhibitor followed by removal of solids by filtration through a medium frit. 2,2′-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was recrystallized from MeOH at 4 °C. *S*-1-Dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (**1**) was synthesized according to a literature procedure.[25]

^{1}H NMR spectra were recorded on a Varian Unity Inova 500 spectrometer and were referenced relative to the residual protiated solvent peaks in the samples. ^{13}C NMR spectra were obtained at 125 MHz using the Varian Inova 500 spectrometer. Elemental analysis was performed at Desert Analytics Laboratory (Tucson, AZ).

Size-exclusion chromatography (SEC) analyses were performed on a Waters 717 gel permeation chromatograph equipped with three Polymer Labs mixed-C columns, a Waters 410 differential refractometer, and a Spectroflow 757 UV absorbance detector employing THF as the mobile phase at 22 °C with a flow rate of 1.0 mL/min. A calibration curve, constructed based on 10 polystyrene standard samples with $M_n = 580-377400$ Da, was used to determine polydispersities of the analytes. Absolute molecular weights were determined by room-temperature SEC using three Phenomenx Phenogel columns (pore sizes: 10−6 to 10−3 μm) with THF eluent at 22 °C with a flow rate of 1.0 mL/min employing a Wyatt Optilab DSP differential refractometer and a Wyatt Dawn multiangle light scattering detector. The refractive index increment d*n*/d*c* = 0.1295 cm^3/g for polybutadiene was used to analyze the SEC-LS data.

Synthesis of 2. Under an argon atmosphere, $(COCl)_2$ (12.0 mL, 140 mmol) was added by syringe to **1** (4.77 g, 13.1 mmol) at 22 °C with rapid stirring, causing the vigorous evolution CO_2(g), CO(g), and HCl(g). (**CAUTION**: Poisonous and corrosive gases.) After 4.5 h, the evolution of gases had ceased and the reaction was homogeneous. The excess $(COCl)_2$ was removed in vacuo to yield acyl chloride **3** (vide infra). 2-Butene-1,4-diol (0.500 mL, 6.07 mmol) was added by syringe to the acyl chloride under argon resulting in the vigorous evolution of HCl(g). After 9 h, the reaction was opened to air and stirred with 3.0 mL 2-propanol for 1 h. Removal of the 2-propanol under reduced pressure yielded a yellow-brown oil, which was eluted through a short silica gel column (2 in. × 1.5 in. dia.) using hexanes/CH_2Cl_2 (1:1 v/v) to yield the pure chain transfer agent **2**. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ (ppm) 5.70 (t, 1H, $^3J_{H-H} = 5$ Hz, $=CHCH_2O$), 4.68 (d, 2H, $^3J_{H-H} = 5$ Hz, $=CHCH_2O$), 3.25(t, 2H, $^3J_{H-H} = 7.0$ Hz, $C(S)-SCH_2CH_2R$), 1.67 (s, 6H, $-SC(CH_3)_2C(O)O-$), 1.64 (tt, 2H, $^3J_{H-H} = 7.5$ and 7.0 Hz, $C(S)-SCH_2CH_2R$), 1.2−1.4 (m, 18H, $-SCH_2CH_2(CH_2)_9CH_3$), 0.86 (t, 3H $^3J_{H-H} = 7.5$ Hz, $-S(CH_2)_{11}CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C): δ (ppm) 14.35, 22.91, 25.55, 28.06, 29.18, 29.33, 29.56, 29.67, 29.78, 29.84, 32.13, 37.20, 56.02, 61.75, 113.15, 128.09, 172.94, 221.48. Anal. Calcd. for $C_{38}H_{68}O_4S_6$: C 58.42, H 8.77, S 24.62. Found: C 58.60, H 8.58, S 24.43.

Representative Synthesis and Purification of Telechelic Polybutadiene (B-2). In a glovebox under an argon atmosphere, a 100 mL round-bottom flask equipped with a stirbar was charged with **2** (0.501 g, 0.640 mmol), 1,5-cyclooctadiene (3.077 g, 28.4 mmol), 3.07 g toluene. The polymerization was initiated by the addition of a solution of $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ (0.002 g, 0.002 mmol) in 1.0 mL toluene. After 18 h at 22 °C, the reaction was quenched by the addition of ethyl vinyl ether (1.0 mL, 10 mmol). The resulting solution was precipitated dropwise into stirring 2-propanol (100 mL) at room temperature. The precipitated polymer was redissolved in 5 mL CH_2Cl_2 and reprecipitated into 2-propanol (100 mL). The isolated polymer was freeze-dried in vacuo from benzene to remove any traces of solvent. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ (ppm) 4.9−5.8 (m, $=C(H)CH_2-$ backbone), 4.62 (d, $^3J_{H-H} = 7.5$ Hz, $=CHCH_2O$, cis endgroup), 4.52 (d, $^3J_{H-H} = 7$ Hz, $=CHCH_2O$, trans endgroup), 3.25(t, $^3J_{H-H} = 7.0$ Hz, $C(S)-SCH_2CH_2R$), 1.75−2.20 (m, $=C(H)CH_2-$ backbone), 1.67 (s, $-SC(CH_3)_2C(O)O-$), 1.64 (tt, $^3J_{H-H} = 7.5$ and 7.0 Hz, $C(S)$-SCH_2CH_2R), 1.2−1.4 (m, $-SCH_2CH_2(CH_2)_9CH_3$), 0.86 (t, $^3J_{H-H} = 7.5$ Hz, $-S(CH_2)_{11}CH_3$). SEC (THF, 22 °C): $M_n = 11.8$ kDa (GPC-LS), $M_w/M_n = 2.06$.

Synthesis of Poly(styrene-*b*-butadiene-*b*-styrene) (S(B-2)S-1). Polybutadiene **B-2** (0.330 g, 0.025 mmol) was dissolved in styrene (1.494 g, 14.3 mmol) in a 5 mL pear-shaped flask sealed with a rubber septum. After vigorously sparging the reaction mixture with argon for 30 min, the flask was heated to 110 °C in an oil bath. After 2 h, the reaction was removed from the oil bath and cooled under cold running water for five minutes. The thick solution was diluted with 5 mL CH_2Cl_2 and precipitated into EtOH (125 mL). The isolated polymer was dried in vacuo. (Polymer composition data are listed in Table 2.) SEC (THF, 22 °C): $M_n = 24.6$ kDa, $M_w/M_n = 1.52$.

Representative Procedure for Metathesis Degradation of Triblock Copolymers. S(B-2)S-1 (150 mg) was dissolved in a mixture of benzene (1 mL) and 1-hexene (1 mL, 8.2 mmol) in a 20 mL scintillation vial equipped with stirbar in a glovebox. Solid $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ (0.005 g, 0.006 mmol) was added to the reaction, and it was sealed and stirred at 22 °C. After 12 h, the reaction was treated with ethyl vinyl ether (1.0 mL, 10 mmol) for 1 h, and the volatiles were then removed under reduced pressure. Analysis of the reaction products by ^{1}H NMR demonstrates the complete removal of the polybutadiene block. SEC (THF, 22 °C): $M_n = 6.5$ kDa (GPC-LS), $M_w/M_n = 1.12$.

Synthesis of Poly(*tert*-butylacrylate-*b*-butadiene-*b*-*tert*-butylacrylate) (A(B-2)A-1). Polybutadiene **B-2** (0.231 g, 0.018 mmol) was dissolved in a mixture of benzene (1.52 g), *tert*-butylacrylate (1.533 g, 12 mmol), and AIBN (0.0015 g, 0.009 mmol) in a 5 mL pear-shaped flask sealed with a rubber septum. After degassing the reaction mixture by sparging argon through the solution for 20 min, the flask was heated in a 60 °C oil bath. After 20 min, the reaction was removed from the oil bath and cooled under cold running water for 5 min. The solution was precipitated into MeOH (100 mL) to yield a gummy polymer, which was isolated and dried in vacuo. SEC (THF, 22 °C): $M_n = 25.1$ kDa, $M_w/M_n = 1.67$.

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Supporting Information Available: ^{1}H NMR spectra and SEC traces of the triblock copolymers (Table 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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