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ROMP-CT/NMP Synthesis of Multiblock Copolymers Containing Linear Poly(ethylene) Segments

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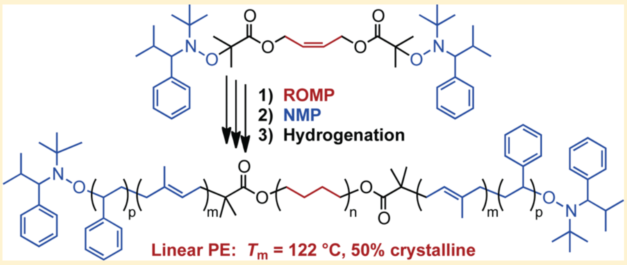
Supporting Information



ABSTRACT: Perfectly regioregular α,ω-telechelic poly(1,4-butadienes) (1,4-PB$_{lin}$ or B) bearing terminal alkoxyamine functionalities are synthesized by chain transfer ring-opening metathesis polymerization (ROMP-CT) of *trans,trans,cis*-1,5,9-cyclododecatriene in the presence of an acyclic olefin chain transfer agent. We demonstrate that these polydisperse, telechelic 1,4-PB$_{lin}$ polymers are macromolecular initiators for nitroxide-mediated polymerizations (NMP) of styrene and isoprene to produce SBS, IBI, and SIBIS block copolymers (S = poly(styrene) and I = poly(4,1-isoprene)). Selected SBS and SIBIS multiblock copolymers were hydrogenated to produce microphase-separated multiblock copolymers containing polydisperse, high-density poly(ethylene) (E_{lin}) segments inaccessible by other polymerization techniques.

INTRODUCTION

Widely used thermoplastic elastomers (TPEs) exhibit tunable properties that depend sensitively on their constituent monomers, molecular compositions, and chain architectures. Typically derived from the sequential anionic polymerization of styrenic and diene monomers, block copolymer TPEs contain glassy and elastomeric homopolymer segments that microphase separate into nanoscale morphologies that nonlinearly combine the properties of the two constitutent homopolymers.[1,2] Numerous studies of the morphological and mechanical properties of glassy−rubbery multiblock copolymers have furnished insights into design criteria for new high-strength plastics and elastomers.[1,3] Some of the most well-known thermoplastic elastomers are based on an ABA triblock architecture comprised of an elastomeric B segment flanked by glassy A end blocks, which microphase separate into spheres or cylinders of A that physically cross-link the rubbery B blocks. By virtue of this morphology, entanglements in the B segments are trapped in a molecular "block and tackle" arrangement that prevents chain pull out and accommodates substantial mechanical deformation.[4−8] Recent studies have focused on the mechanical properties of multiblock copolymers containing combinations of glassy, rubbery, and semicrystalline polymer segments.[9−13] Bates and coworkers recently demonstrated that glassy−rubbery−semicrystalline pentablock copolymers containing poly(ethylene-*co*-butylene) (PEB) segments derived from hydrogenation of anionic poly(1,4-butadiene) (≥6 mol % 1,2-vinyl content) exhibit unusual mechanical strength and elasticity, depending on the relative amounts of each component and the crystallinity of the PEB block.[8,9] Trends in their data suggest that increasing the crystallinity of the PEB segments and incorporation of a rubbery block should increase the observed ultimate tensile strength. However, such high crystallinity materials are unavailable from hydrogenation of anionic poly(1,4-butadiene) due to the presence of unavoidable 1,2-regiodefects, which result in a linear low-density PEB (25 ethyl branches per 1000 backbone carbon atoms) with limited crystallinity.[14]

The incorporation of high-density poly(ethylene) (E_{lin}) segments into block copolymers represents a substantial synthetic challenge with potentially important practical and fundamental implications. E_{lin} exhibits a high melting temperature (T_m = 125−145 °C), good solvent resistance, and a strong propensity to crystallize.[11] Therefore, judicious design of block copolymers containing E_{lin} segments may yield materials with the aforementioned desirable attributes coupled with improved mechanical strengths and reversible elasticities.[8,9] E_{lin}-containing block copolymers also offer opportunities to study polymer crystal nucleation and growth from both single-phase and microphase separated polymer melts. In spite of the ubiquity of high-density poly(ethylene)[15] and substantial advances in "living" metal-catalyzed coordination−insertion polymerization of olefins,[16,17] syntheses of well-defined block copolymers containing E_{lin} segments derived directly from ethylene remain obscure.[18,19] In order to access these potentially useful materials, the groups of Register,[11,14,20] Hillmyer,[21,22] Emrick,[23] and Meijer[24] have reported alternative syntheses of block copolymers containing E_{lin} segments by metal-catalyzed ring-opening metathesis polymerization (ROMP) of cyclic olefin monomers and subsequent catalytic hydrogenations. Nevertheless, these synthetic routes suffer from the stoichiometric use of expensive organometallic

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reagents, produce poorly defined mixtures of block copolymers and homopolymers, or are limited in their ability to produce sought after glass—rubbery—semicrystalline copolymers.

ROMP in the presence of symmetric acyclic olefin chain transfer agents (ROMP-CT) enables convenient syntheses of α,ω-telechelic polymers bearing well-defined chain end functionalities for chain extension block copolymerizations.[25] Recent reports have demonstrated the successful combination of ROMP-CT with atom transfer radical polymerization (ATRP),[26] reversible addition—fragmentation chain transfer (RAFT) polymerization,[27] ring-opening polymerizations,[22] and anionic polymerizations.[21] Herein, we report the efficient synthesis of a symmetric acyclic olefin chain transfer agent and demonstrate its utility in ROMP-CT of *trans,trans,cis*-1,5,9-cyclododecatriene to produce perfectly regioregular α,ω-telechelic poly(1,4-butadiene) (1,4-PB$_{\text{lin}}$ or B) bearing alkoxyamine termini. We subsequently demonstrate that these polymers are macroinitiators for nitroxide-mediated polymerizations (NMP) of styrene and diene monomers to yield unimodal SBS, IBI, and SIBIS multiblock copolymers (S = poly(styrene); I = poly(4,1-isoprene)). Subsequent hydrogenation of these materials yields heretofore unknown glassy—rubbery—semicrystalline multiblock copolymers containing high crystallinity E$_{\text{lin}}$ segments not available from other synthetic approaches.

EXPERIMENTAL SECTION

Materials. All reactions were performed under a N_2 atmosphere using standard Schlenk techniques. Anhydrous toluene was obtained by passage through a column of activated alumina under N_2. All other reagents were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received, unless otherwise noted. *trans,trans,cis*-1,5,9-Cyclododecatriene (CDT) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) were vacuum-distilled before use in order to remove colored impurities. Styrene and isoprene monomers were stirred over Brockmann Type I basic alumina for 1 h and gravity filtered to remove inhibitors immediately prior to use. 1,2-Bis(bromoisobutyryloxy)-2-butene (**1**)[28] and 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO)[29] were synthesized according to literature procedures.

^{1}H NMR spectra were recorded on Varian Inova 500, Bruker AC+ 300, and Varian MercuryPlus 300 spectrometers using $CDCl_3$ or $C_2D_2Cl_4$ (Cambridge Isotopes Laboratories, Andover, MA) and were referenced to the residual protiated solvent resonances. ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer at 125 MHz equipped with a variable temperature probe. ESI-MS was recorded on a Waters LCT spectrometer using CH_3CN as the solvent.

Size-exclusion chromatography (SEC) analyses employed a Viscotek GPCMax System with two Polymer Laboratories Resipore columns (250 mm × 4.6 mm) and a differential refractive index detector, using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 40 °C. Molecular weights ($M_{\text{n,SEC}}$) and polydispersity indices (M_w/M_n) of poly(styrene) homopolymers were determined using a conventional poly(styrene) calibration curve constructed using 10 narrow molecular weight distribution poly(styrene) standards with M_n = 580—377 400 g/mol (Polymer Laboratories, Amherst, MA). 1,4-PB$_{\text{lin}}$ molecular weights ($M_{\text{n,SEC}}$) and M_w/M_n were determined using an equivalent calibration curve constructed by Mark—Houwink conversion of the aforementioned poly(styrene) calibration curve.[27] Block copolymer compositions and overall molecular weights ($M_{\text{n,NMR}}$) were calculated from quantitative ^{1}H NMR spectroscopy and the $M_{\text{n,SEC}}$ values of the 1,4-PB$_{\text{lin}}$ segments. Polydispersity indices (M_w/M_n) for all block copolymer samples are reported against poly(styrene) standards.

Thermal Analyses. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q100 modulated differential scanning calorimeter under a N_2 atmosphere. Using a temperature ramp rate of 10 °C/min between −50 and 200 °C with a 3 min isothermal condition at each temperature limit, glass transition temperatures (T_g) were determined by the midpoint method, and peak melting temperatures ($T_{\text{m,peak}}$) were measured using the second and third heating curves. The crystalline weight fraction in the poly(ethylene) blocks was calculated as $\chi_c = \Delta H_{\text{meas}}/(\Delta H_{\text{fus,E}} f_E)$, where ΔH_{meas} is the measured enthalpy of melting of the E blocks, $\Delta H_{\text{fus,E}}$ = 277 J/g is the theoretical enthalpy of fusion for 100% crystalline high-density poly(ethylene), and f_E is the weight fraction of poly(ethylene) in the sample.[30]

Small-Angle X-ray Scattering (SAXS). Synchrotron small-angle X-ray scattering measurements were performed at the 5IDD beamline of the DuPont—Northwestern—Dow Collaborative Access Team Synchrotron Research Center at the Advanced Photon Source (Argonne, IL). Experiments employed a beam energy of 16 keV (λ = 0.7293 Å^{-1}) and a 3.068 m sample-to-detector distance that was calibrated using silver behenate (d = 58.38 Å). Two-dimensional SAXS patterns were recorded on a MAR-CCD detector (133 mm diameter active circular area) with 1024 × 1024 pixel resolution. Samples were heated in a Linkam DSC and equilibrated for 5 min prior to data collection.

Synthesis of Chain Transfer Agent (2). 1,2-Bis(bromoisobutyryloxy)-2-butene (**1**) (3.00 g, 7.77 mmol), TIPNO (3.86 g, 17.5 mmol), PMDETA (80.0 μL, 0.380 mmol), and *N,N*-dimethylformamide (DMF) (45.0 mL) were combined and degassed by three freeze—thaw cycles in a 100 mL Schlenk flask. This solution was transferred via cannula onto a solid mixture of Cu(0) (1.50 g, 23.6 mmol) and Cu(I)Br (56.0 mg, 0.390 mmol) and vigorously stirred for 20 h, during which time the initially dark green reaction mixture turned blue-green in color. The reaction mixture was subsequently exposed to air and passed through a plug of neutral alumina (50 mm × 60 mm diameter) using ethyl acetate as an eluent to remove Cu salts. Concentration of the resulting organic solution yielded a pale orange oil, which was purified by silica gel chromatography using CH_2Cl_2 as the eluent to provide a colorless oil. Yield: 3.19 g (61.5%). ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C, all stereoisomers): δ (ppm) 7.56—7.17 (m, 10H, Ph), 5.76 (m, 2H, $=CHCH_2O$), 4.73 (m, 4H, $=CHCH_2O$), 3.68 (d, 2H, J = 11.0 Hz, $NCH[CH(CH_3)_2](Ph)$), 3.42 (d, 2H, J = 10.2 Hz, $NCH[CH(CH_3)_2](Ph)$), 2.39 (m, 2H, $NCH[CH(CH_3)_2](Ph)$), 1.82 (m, 2H, $NCH[CH(CH_3)_2](Ph)$), 1.62 (s, 6H, $—OC(CH_3)_2CO$), 1.59 (s, 6H, $—OC(CH_3)_2CO$), 1.55 (s, 6H, $—OC(CH_3)_2CO$), 1.48 (s, 6H, $—OC(CH_3)_2CO$), 1.23 (d, 6H, J = 6.5 Hz, $NCH[CH(CH_3)_2](Ph)$), 1.15 (d, 6H, J = 6.1 Hz, $NCH[CH(CH_3)_2](Ph)$), 0.92 (s, 18H, $(CH_3)_3N$), 0.80 (s, 18H, $(CH_3)_3N$), 0.71 (d, 6H, J = 6.3 Hz, $NCH[CH(CH_3)_2](Ph)$), 0.40 (d, 6H, J = 6.7 Hz, $NCH[CH(CH_3)_2](Ph)$). ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C, all stereoisomers): δ (ppm) 175.05, 174.84, 142.05, 131.15, 130.35, 128.24, 127.99, 127.56, 126.71, 126.33, 82.07, 79.86, 74.06, 60.67, 60.52, 60.33, 53.43, 30.95, 30.38, 28.37, 27.44, 26.04, 25.66, 24.54, 22.96, 22.72, 22.64, 22.30, 21.14. ESI-MS Calcd for $C_{40}H_{62}N_2O_6$ $[M + Na]^+$ 689.45. Found: 689.45. (^{1}H and ^{13}C NMR spectra are provided in Supporting Information Figures S1 and S2.)

Representative Synthesis of Telechelic Poly(butadiene) (B-3). A 100 mL round-bottom Schlenk flask was charged with chain transfer agent **2** (0.242 g, 0.363 mmol), CDT (1.80 g, 11.1 mmol), and 4.5 mL of toluene. Oxygen was removed from this mixture by four freeze—thaw degassing cycles. The mixture was frozen in liquid N_2, and $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ (3.00 mg, 0.00353 mmol) was added to the flask under a flush of N_2, after which the flask was placed under N_2 by performing three evacuate—refill cycles. The mixture was then thawed and vigorously stirred at 22 °C. After 30 h, the reaction was exposed to air and precipitated dropwise into rapidly stirred EtOH (250 mL) at 22 °C. The resulting polymer was freeze-dried *in vacuo* from

C_6H_6 at 22 °C. $M_{n,SEC}$ = 8.8 kg/mol, M_w/M_n = 2.03 (against PB standard calibration curve).

Representative Synthesis of Poly(styrene-*b*-butadiene-*b*-styrene) (SBS-3). Poly(1,4-butadiene) **B-3** (0.400 g, 0.0457 mmol) was dissolved in styrene (1.25 mL, 10.9 mmol) in a 100 mL flask equipped with a stirbar, and the mixture was degassed by three freeze—evacuate—thaw cycles and placed under N_2. This reaction was heated at 120 °C for 3 h, after which it was cooled in an ice bath for 10 min. The polymerization reaction mixture was diluted with CH_2Cl_2 (5 mL) and precipitated dropwise into stirring EtOH (250 mL). The resulting polymer was freeze-dried *in vacuo* from C_6H_6 at 22 °C. $M_{n,\ NMR}$ = 20.9 kg/mol (58.1 mol % PB from quantitative ^{1}H NMR spectroscopy), M_w/M_n = 1.76 (against PS standards).

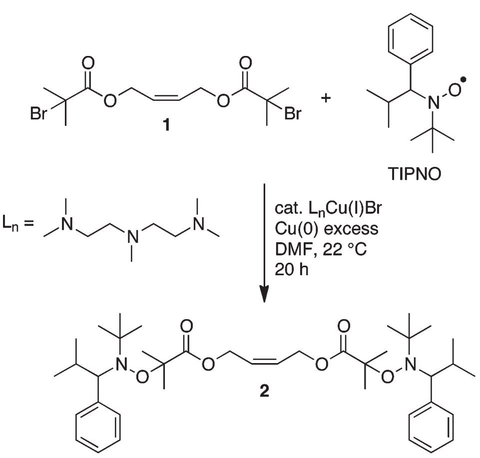
Metathesis degradation[27] of **SBS-3** demonstrates that $M_{n,SEC}$-(S block) = 6.1 kg/mol, M_w/M_n = 1.17 (against PS standards).

Representative Synthesis of Poly(isoprene-*b*-butadiene-*b*-isoprene) (IBI-3). Poly(1,4-butadiene) **B-3** (0.400 g, 0.0457 mmol) was dissolved in isoprene (6.50 mL, 65.0 mmol) in a 100 mL pressure tube and subjected to three freeze—evacuate—thaw degassing cycles. The flask was sealed under N_2 (1 bar) and heated for 48 h at 125 °C. The reaction flask was subsequently cooled in an ice bath for 10 min, exposed to air, and diluted with CH_2Cl_2 (5 mL). The solution was precipitated dropwise into EtOH (200 mL) at 22 °C to yield a pale yellow, sticky solid that was freeze-dried *in vacuo* from C_6H_6. $M_{n,NMR}$ = 14.8 kg/mol (64.5 mol % PB from quantitative ^{1}H NMR spectroscopy), M_w/M_n = 1.65 (against PS standards).

Representative Synthesis of Poly(styrene-*b*-isoprene-*b*-butadiene-*b*-isoprene-*b*-styrene) (SIBIS-2). **IBI-3** (0.250 g, 0.0169 mmol) was dissolved in styrene (1.45 mL, 12.7 mmol) with exogenous TIPNO (3.70 mg, 0.0169 mmol) in a 25 mL Schlenk tube. After degassing this viscous mixture by four freeze—thaw cycles, the flask was heated under N_2 to 120 °C for 9 h. The reaction mixture was then cooled in an ice bath for 10 min, exposed to air, and diluted with CH_2Cl_2 (2 mL). Dropwise precipitation of this mixture into EtOH (250 mL), isolation by filtration, and freeze-drying of the solids in vacuo from C_6H_6 yielded a mixture of the desired **SIBIS-2** and low molecular weight poly(styrene) (from SEC analysis). In order to remove this homopolymer impurity, the material was redissolved in CH_2Cl_2 (2 mL) precipitated into cold acetone (150 mL). The resulting white solid was freeze-dried *in vacuo* from C_6H_6. $M_{n,NMR}$ = 19.4 kg/mol (54.9 mol % PB, 30.2 mol % PI, and 14.9 mol % PS from quantitative ^{1}H NMR spectroscopy), M_w/M_n = 1.55 (against PS standards).

Representative Hydrogenation of SIBIS-1 to hSIBIS-1.[31] **SIBIS-1** (67.3 mg, 0.00248 mmol) was dissolved in xylenes (10.0 mL) in a 50 mL three-necked flask equipped with a stirbar, condenser, and thermometer. After addition of tri-*n*-propylamine (0.350 mL, 1.80 mmol) and *p*-toluenesulfonyl hydrazide (0.340 g, 1.80 mmol), the headspace of the vessel was purged with N_2 for 5 min. This reaction mixture was heated to reflux (130—140 °C) under N_2 for 7.5 h, after which it was exposed to air. Dropwise precipitation of this hot solution into rapidly stirred EtOH (300 mL) followed by allowing this suspension to settle overnight yielded a solid material isolable by vacuum filtration. The resulting solid was washed with EtOH and vacuum-dried to yield white flakes. Isolated yield: 48.9 mg.

Scheme 1. Synthesis of Difunctional Alkoxamine Acyclic Olefin Chain Transfer Agent 2 for ROMP-CT



RESULTS AND DISCUSSION

In order to synthesize regiodefect-free α,ω-telechelic 1,4-PB_{lin} bearing alkoxyamine termini from ROMP-CT as macroinitiators for chain extension block copolymerizations, we examined a variety of conditions for the atom transfer nitoxide radical coupling (ATNRC) of α-bromo diester **1**[28] with TIPNO[29] to synthesize acyclic olefin chain transfer agent **2** (Scheme 1). On the basis of the ATNRC conditions reported by Matyjaszewski et al.,[32] we attempted the synthesis of **2** using catalytic (PMDETA)-Cu(I)Br in toluene at 60 °C. These reaction conditions only slowly convert diester **1** to a mixture of monofunctional and difunctional alkoxyamine products after 20 h. Inspired by the single-electron transfer living radical polymerization (SET-LRP) work of Percec and co-workers[33] and related single-electron-transfer nitroxide radical coupling (SET-NRC),[34,35] we executed the ATNRC of TIPNO and **1** in *N*,*N*-dimethylformamide at 22 °C to obtain high yields of **2** after 20 h (>96% by ^{1}H NMR). We attribute the solvent-dependent rate acceleration to the fast disproportionation of Cu(I) into active Cu(0) and Cu(II) species as described previously.[33] Filtration of the reaction mixture through neutral alumina followed by purification by silica gel chromatography furnished **2** as a viscous, clear oil in moderate yields.

ROMP-CT of CDT in the presence of chain transfer agent **2** catalyzed by Grubbs' second generation olefin metathesis catalyst, $(IMesH_2)(Cy_3P)RuCl_2(CHPh)$ (Grubbs' II), at 22 °C yields α,ω-telechelic 1,4-PB_{lin} bearing alkoxyamine termini (Scheme 2). We utilized CDT as the ROMP-CT monomer due to the previously noted absence of any trace acyclic olefin impurities that could serve as chain transfer agents that diminish the chain end functionality of the resulting α,ω-telechelic polymers.[36] By controlling the [CDT]/[**2**] ratio with [**2**]/[Grubbs' II] = 100:1 to minimize nonfunctional chain ends,[25] polymers with variable molecular weights were synthesized (Table 1). ^{1}H NMR analyses of polymerization reaction aliquots taken at various reaction times indicate complete consumption of **2** after t_{rxn} = 26—30 h, evidenced by the disappearance of the allylic proton resonances of **2** and the appearance of resonances assigned to the polymer end groups (Supporting Information Figure S3). These high chain transfer efficiencies underscore the tolerance of the Grubbs' II catalyst to the TIPNO-based alkoxyamine functionalities, consistent with recent reports.[37,38] This situation starkly contrasts the low chain transfer efficiencies reported previously for ROMP-CT reagents containing trithiocarbonate moieties.[27] Further support for this high level of chain transfer efficiency derives from the close agreement between the 1,4-PB_{lin} molecular weights derived from size-exclusion chromatography (SEC) and ^{1}H NMR end group analyses (Table 1). These reactions proceed to equilibrium yielding most probable molecular weight distributions

Scheme 2. Synthesis of PB_{lin} and Subsequent Chain Extension to Form SBS, IBI, and SIBIS Block Copolymers

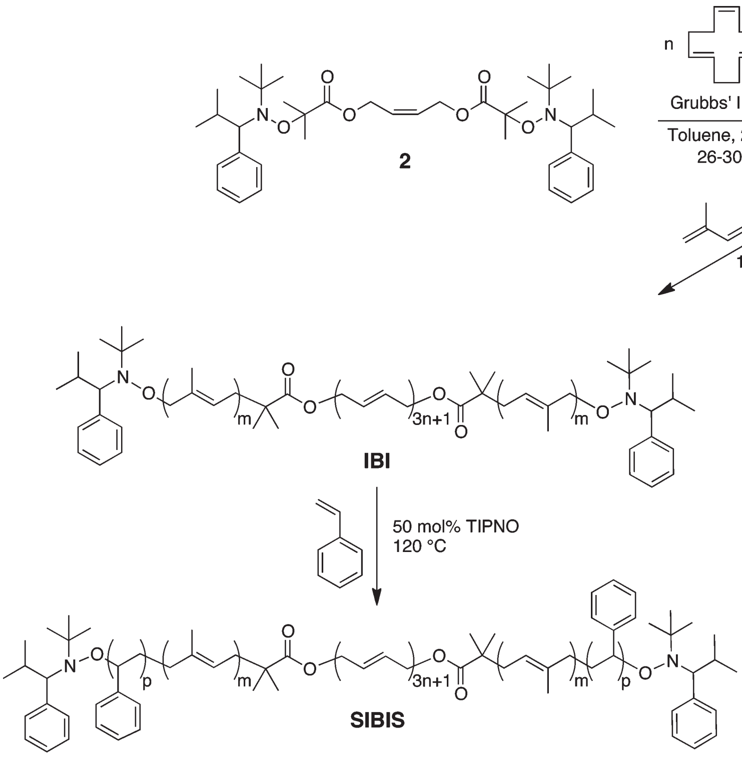


Table 1. Molecular Parameters of Alkoxyamine-Terminated Telechelic 1,4-PB_{lin} Derived from ROMP-CT of 1,5,9-Cyclododecatriene with 2

sample	$M_{n,NMR}$ (kg/mol)[a]	$M_{n,SEC}$ (kg/mol)[b]	M_w/M_n[b]
B-1	6.1	6.5	1.74
B-2	8.0	8.7	2.01
B-3	7.7	8.8	2.03
B-4	11.4	13.0	2.11
B-5	8.7	10.0	1.91

[a] Calculated from quantitative ^{1}H NMR end group analysis in $CDCl_3$ using the allylic ester protons (δ 4.50−4.63 ppm) and the backbone vinylic protons (δ 5.30−5.50 ppm). [b] Determined by SEC in THF at 40 °C versus poly(styrene) standards using Mark−Houwink correction.

Table 2. SBS Triblock Copolymers Synthesized from α,ω-Telechelic 1,4-PB_{lin} Macroinitiators by Nitroxide-Mediated Polymerizations

	triblock copolymer		S block	
entry[a]	w_B[b]	$M_{n,total}$ (PDI)[c]	NMR $M_{n,S}$[c]	SEC $M_{n,S}$ (PDI)[d]
SBS-1 (B-1)	0.40	16.1 (1.54)	4.8	4.4 (1.16)
SBS-2 (B-2)	0.28	30.5 (1.64)	10.9	10.4 (1.19)
SBS-3 (B-3)	0.42	20.9 (1.76)	6.1	6.1 (1.17)
SBS-4 (B-4)	0.42	30.8 (1.81)	8.9	9.9 (1.21)
SBS-5 (B-5)	0.50	20.0 (1.80)	5.0	5.2 (1.17)

[a] SBS synthesized by NMP of styrene at 120 °C from parent 1,4-PB_{lin} macroinitiator noted in parentheses. [b] Weight fraction of 1,4-PB_{lin} determined by quantitative ^{1}H NMR spectroscopy. [c] $M_{n,total}$ (kg/mol) and S block NMR M_n (kg/mol) determined from quantitative ^{1}H NMR spectroscopy and $M_{n,SEC}$ for the initial 1,4-PB_{lin} sample given in Table 1; PDI = M_w/M_n from SEC versus poly(styrene) standards. [d] $M_{n,S}$ (kg/mol) and M_w/M_n of the S block determined after triblock cross-metathesis degradation and SEC analysis versus poly(styrene) standards.

with M_w/M_n ~ 1.7−2.0 (from SEC), while ^{1}H NMR shows the expected ~80% *trans*-olefin microstructure.

By initiating NMP of styrene from both ends of the telechelic 1,4-PB_{lin} macroinitiators, we bidirectionally synthesized a series of poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymers having overall molecular weights ranging from $M_{n,total}$ = 16.1−30.8 kg/mol (Table 2). SEC analyses indicate the formation of higher molecular weight polymer by virtue of the slightly decreased elution volume of the SBS triblock compared to that of the parent 1,4-PB_{lin} and the decreased M_w/M_n for each of the triblocks upon appending monodisperse poly(styrene) blocks (Figure 1). In order to unambiguously demonstrate the bidirectional initiation of styrene from *both* alkoxyamine termini of the 1,4-PB_{lin} macroinitiator and to assess the level of control in the NMP of styrene, we used the previously reported olefin cross-metathesis to degrade the center poly(butadiene) block and to isolate the poly(styrene) end blocks.[27] Close agreement between the $M_{n,S}$ of the poly(styrene) end blocks derived from SEC and those calculated from quantitative ^{1}H NMR spectroscopy based on the molecular weight of the difunctional 1,4-PB_{lin} macroinitiator confirm their high degree of alkoxyamine chain-end functionality. Additionally, SEC analyses of the poly(styrene) end blocks show that NMP from these difuntional macroinitiators proceeds with good control evidenced by their relatively low polydispersities (M_w/M_n ≤ 1.21). These results compare favorably to SBS triblocks synthesized by ROMP-ATRP[26] and

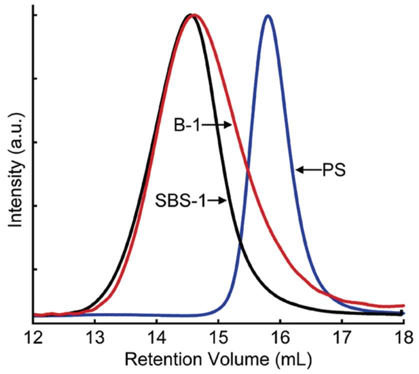


Figure 1. Representative SEC traces of **B-1** (M_n = 6.5 kg/mol, M_w/M_n = 1.74) derived from ROMP-CT, **SBS-1** (M_n = 16.0 kg/mol, M_w/M_n = 1.54), and poly(styrene) end block (PS, M_n = 4.4 kg/mol, M_w/M_n = 1.16) derived from olefin cross-metathesis degradation of **SBS-1**.

Table 3. IBI Triblock Copolymers Derived from Telechelic 1,4-PB$_{lin}$ Macroinitiators

sample[a]	w_B[b]	$M_{n,total}$ (PDI)[c]	I block $M_{n,NMR}$[c]
IBI-1 (B-2)	0.79	10.9 (1.81)	1.1
IBI-2 (B-2)	0.46	18.9 (1.76)	5.1
IBI-3 (B-3)	0.59	14.8 (1.65)	3.0
IBI-4 (B-4)	0.71	18.3 (1.88)	2.7

[a] IBI triblocks synthesized from NMP of isoprene at 125 °C initiated by 1,4-PB$_{lin}$ noted in parentheses. [b] Weight fraction of 1,4-PB$_{lin}$ determined by quantitative ^{1}H NMR spectroscopy. [c] $M_{n,total}$ (kg/mol) and I block $M_{n,NMR}$ (kg/mol) determined from quantitative ^{1}H NMR spectroscopy and $M_{n,SEC}$ of the parent 1,4-PB$_{lin}$ sample given in Table 1; PDI = M_w/M_n from SEC versus poly(styrene) standards.

Table 4. SIBIS Pentablock Copolymers Synthesized by Sequential NMP of Isoprene and Styrene from 1,4-PB$_{lin}$ Macroinitiators

sample[a]	$M_{n,total}$ (PDI)[b]	w_B[c]	w_I[c]	S block $M_{n,S}$[b]
SIBIS-1 (IBI-2)	27.1 (1.69)	0.32	0.38	4.1
SIBIS-2 (IBI-3)	19.4 (1.55)	0.45	0.31	2.3
SIBIS-3 (IBI-4)	22.8 (1.70)	0.57	0.24	2.2

[a] SIBIS polymers synthesized by chain extension of the parent IBI triblock noted in parentheses with styrene at 120 °C in the presence of 50 mol % TIPNO free radical. [b] $M_{n,total}$ (kg/mol) and $M_{n,S}$ (kg/mol) calculated from quantitative ^{1}H NMR spectroscopy using $M_{n,total}$(IBI) from Table 3; PDI = M_w/M_n determined by SEC in THF at 40 °C versus poly(styrene) standards. [c] Weight fraction of 1,4-PB$_{lin}$ (w_B) and poly(isoprene) (w_I) determined by quantitative ^{1}H NMR spectroscopy.

ROMP-RAFT;[27] however, copolymers from ROMP-NMP do not contain metallic or malodorous residues.

To demonstrate the extended monomer scope of the tandem ROMP-NMP strategy beyond that of reported ROMP-ATRP[26] and ROMP-RAFT[27] protocols, we initiated the controlled free radical polymerization of isoprene from the 1,4-PB$_{lin}$ NMP macroinitiators to produce a series of poly(isoprene-*b*-butadiene-*b*-isoprene) (IBI) triblock copolymers (Table 3). **B-2** initiates controlled NMP of isoprene at 125 °C, consistent with the reported NMP of isoprene using TIPNO-based alkoxyamines.[39] The resulting **IBI-2** triblock copolymer is unimodal and exhibits a narrower M_w/M_n compared to that of the parent **B-2**, indicating a controlled isoprene NMP chain extension reaction. ^{1}H NMR spectra of the IBI polymers indicate that the dominant regiochemistry of isoprene monomer enchainment is a combination of *cis* and *trans* 4,1-insertions, with low levels of 1,2- and 3,4-insertions as expected (data not shown).

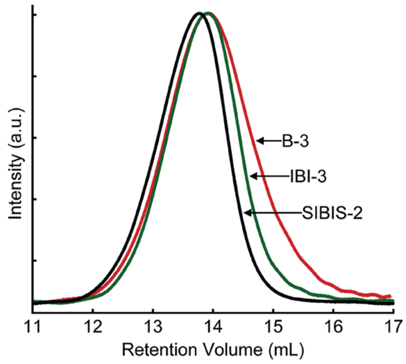


Figure 2. Representative SEC traces of **B-3** (M_n = 8.8 kg/mol, M_w/M_n = 2.03), **IBI-3** (M_n= 14.8 kg/mol, M_w/M_n = 1.65), and **SIBIS-2** (M_n = 19.4 kg/mol, M_w/M_n = 1.55) synthesized by chain extension NMP of styrene from **IBI-3**.

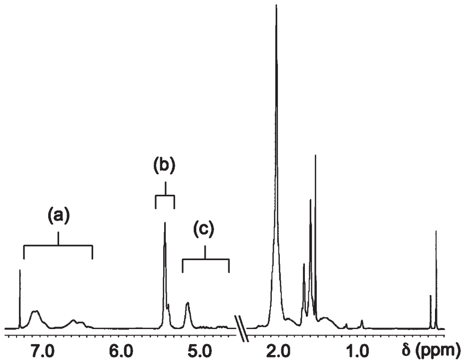
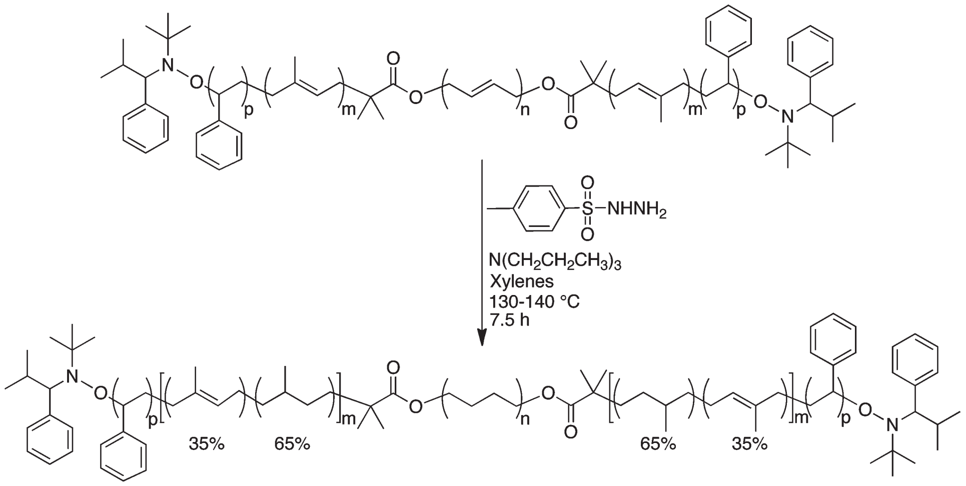


Figure 3. ^{1}H NMR spectrum of **SIBIS-1**, illustrating diagnostic resonances of the aryl protons of poly(styrene) (a, $C_6H_5{-}CH{-}$), vinylic protons of poly(butadiene) (b, $-CH_2-CH{=}CH-CH_2$), and vinylic protons of poly(isoprene) (c, $-CH_2-C(CH_3){=}CH-CH_2$) that were used to calculate block copolymer compositions.

We chain extended the aforementioned IBI triblock copolymers with styrene by sequential NMP at 120 °C (Table 4). Initial attempts to produce poly(styrene-*b*-isoprene-*b*-butadiene-*b*-isoprene-*b*-styrene) (SIBIS) pentablock copolymers resulted in the formation of multimodal materials according to SEC analyses, likely a result of slow initialization of the allylic IBI alkoxyamine chain ends coupled with fast NMP of styrene. This situation is analogous to the previously reported problem in NMP syntheses of styrene–acrylate block copolymers studied by Benoit et al., in which successful syntheses require specific sequences of monomer additions to the alkoxyamine chain end.[29] In order to avert this problem, we conducted NMP of styrene using the IBI macroinitiators in the presence of 50 mol % TIPNO per chain end to suppress uneven styrene initialization. While this protocol furnishes SIBIS pentablock copolymers, we noted the formation of small amounts of low molecular weight poly(styrene) homopolymer due to styrene autoinitiation at 120 °C. These low molecular weight impurities were removed by precipitation of

Scheme 3. Hydrogenation of SIBIS Block Copolymers to Yield hSIBIS Containing a Regiodefect-Free Linear Poly(ethylene) Block



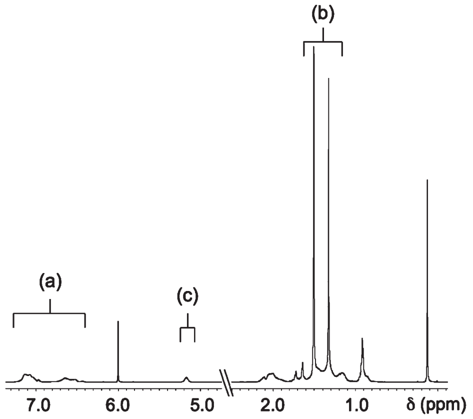


Figure 4. ^1H NMR spectrum of saturated **hSIBIS-1** with resonances associated with poly(styrene) (a, C_6H_5−CH−) and poly(ethylene) and poly(ethylene-*alt*-propylene) (b, $-CH_2CH_2-$ and $-CH_2CH_2CH(CH_3)-$), resulting from complete hydrogenation of 1,4-PB$_{lin}$ and partial hydrogenation of the I block, respectively. Resonances corresponding to unhydrogenated poly(isoprene) are also observed (c, $-CH_2-C(CH_3)=CH-CH_2-$).

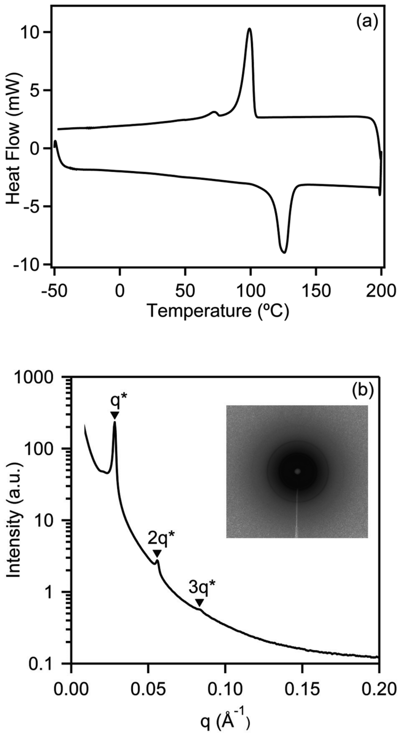


Figure 5. (a) DSC heating and cooling curves (exothermic up; ramp rate = 10 °C/min) for **hSBS-5** demonstrating a peak melting temperature T_m = 126 °C (53 wt % crystallinity in the E$_{lin}$ block) characteristic of a E$_{lin}$ segment and a glass transition temperature T_g ∼ 74 °C associated with the poly(styrene) blocks and (b) synchrotron SAXS of the **hSBS-5** at 190 °C exhibiting a lamellar morphology with characteristic (001), (002), and (003) reflections with q^* = 0.0277 Å^{-1} (d = 22.7 nm).

the pentablock copolymer into cold acetone. The resulting SIBIS copolymers exhibit unimodal SEC traces and polydispersity indices even lower than those of the parent IBI copolymer (Figure 2), the compositions of which were determined using the unique resonances identified in the ^1H NMR spectrum shown in Figure 3.

In order to realize our ultimate goal of synthesizing multiblock copolymers containing high crystallinity E$_{lin}$ segments, we saturated the polydiene blocks of **SIBIS-1** and **SBS-5** multiblock copolymers using the diimide hydrogenation protocol previously reported by Hahn (Scheme 3).[31] ^1H NMR analysis of the hydrogenation product **hSIBIS-1** at 90 °C in $C_2D_2Cl_4$ (Figure 4) established the near complete hydrogenation of the 1,4-PB$_{lin}$ segments evidenced by the disappearance of the vinylic proton resonance (δ 5.30−5.50 ppm) and the appearance of a single, new resonance associated with the methylene units of E$_{lin}$ (δ 1.33 ppm). Using the unreactive S block as an internal standard, in-depth ^1H NMR analysis also shows that the relative integrations of the vinylic resonances associated with the I block change upon hydrogenation of **SIBIS-1**, indicating saturation of ∼65 mol % of the isoprene units. This level of I block hydrogenation is consistent with results of diimide hydrogenations of

SIS triblocks.[31] Extraction of the **hSBS-5** triblock with $CDCl_3$ at 22 °C did not yield any poly(styrene) homopolymer, supporting the notion that diimide hydrogenation causes minimal chain scission. Differential scanning calorimetry studies reveal only one clear thermal transition in **hSIBIS-1** over a temperature range of −50 to 200 °C: a strong melting endotherm at $T_{m,peak}$ = 122 °C (50 wt % crystallinity in the E_{lin} block) assigned to the E_{lin} segment. **hSBS-5** instead exhibits two thermal transitions $T_g \sim$ 74 °C and $T_{m,peak}$ = 126 °C with 53 wt % crystallinity in the E_{lin} segment. These melting temperatures and crystallinities are consistent with previous reports of block copolymers containing E_{lin} segments.[11,14,20−24]

Preliminary small-angle X-ray scattering (SAXS) studies of the hydrogenated **hSBS-5** and **hSIBIS-1** demonstrate that these block copolymers containing polydisperse, high crystallinity E_{lin} segments ($M_w/M_n \sim 2.0$) microphase separate into well-ordered structures. Two-dimensional synchrotron SAXS patterns associated with **hSBS-5** between 130 and 270 °C and attendant azimuthal integrations of these patterns (Figure 5b) display three well-defined scattering maxima characteristic of a lamellar structure with a principal domain spacing d = 22.7 nm. The well-defined scattering observed here is quite different from the broad scattering patterns noted by Switek et al. for $CE_{lin}C$ triblock copolymers (C = poly(cyclohexylethylene)) derived from a macromolecular ROMP-CT process.[21] This difference may arise from homopolymer contaminants present in the latter samples, as opposed to the higher purity triblock copolymer samples from ROMP-NMP. Upon cooling this sample to room temperature, the microphase-separated morphology of **hSBS-5** is disrupted by E_{lin} crystallization and only a single broad SAXS peak is observed, which we attribute to the intercrystal spacing in the E_{lin} block.[14] We observed only correlation hole scattering for **hSIBIS-1** in the melt-phase above 130 °C, whereas poly(ethylene) crystallization below 130 °C drives a crystallization induced segregation again to yield a broad SAXS scattering corresponding to the E_{lin} intercrystal spacing.

■ CONCLUSION

We have described an efficient synthesis of a chain transfer agent that facilitates the synthesis of α,ω-PB_{lin} bearing alkoxyamine chain-end functionalities from ROMP-CT. From these α,ω-telechelic 1,4-PB_{lin} macroinitiators, nitroxide-mediated polymerizations of styrene and isoprene were initiated to produce SBS, IBI, and SIBIS copolymers, in which a polydisperse, perfectly regioregular 1,4-PB_{lin} center block is flanked by monodisperse I and S blocks. A subset of these unsaturated precursors was then hydrogenated to yield multiblock copolymers containing linear, high-density poly(ethylene) (E_{lin}) segments with high melting temperatures and crystallinities. Preliminary studies of these hydrogenated materials demonstrate that they microphase separate, in spite of the broad polydispersity of the E_{lin} internal segment ($M_w/M_n \sim 2.0$). Further studies of the mechanical properties and crystallization behavior of these unique multiblock copolymers will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^1H and ^{13}C NMR spectra of **2**, ^1H NMR spectra of **B-1** (allylic region), and DSC and SAXS data for **hSIBIS-1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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