Block Copolymer Synthesis by Styrene Polymerization Initiated with Nitroxy-Functionalized Polybutadiene

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Received December 12, 1997
Revised Manuscript Received March 13, 1998

Introduction

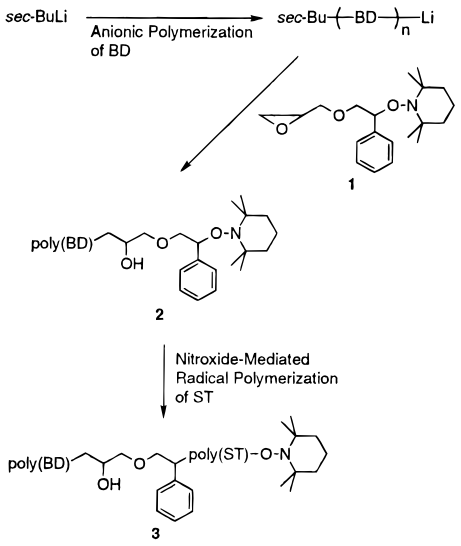
Living polymerization techniques are useful not only to control molecular weights and molecular weight distributions of polymers but also to synthesize block copolymers and end-functionalized polymers.[1] In general, block copolymers are synthesized by ionic or coordination polymerization because of the living nature of the polymer chain end.[2] Typical block copolymers such as polystyrene-*block*-polyisoprene and polystyrene-*block*-polybutadiene arise from anionic polymerization processes.[3] These materials are costly to produce in industry because of the need for highly purified monomers and solvents. Free radical polymerization is the preferred chemistry for polymer manufacturing because it has the lowest cost and is the most versatile. Recent advances in the past decade have led to the development of living free radical polymerization techniques.[4] These techniques have been used to prepare polymers with narrow molecular weight distributions and block copolymers.[4−16]

Recently, it has been reported that radical polymerizations of styrene (ST) initiated by alkoxyamines at elevated temperatures exhibit the characteristics of living polymerizations and that polymers with narrow molecular weight distributions are obtained.[5−16] A nitroxy free radical such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) combines with the propagating radical and produces a labile bond that is reversibly broken at high temperature. Initiators for such systems may be formed *in situ*[5a,i,16] or compounds bearing the TEMPO−phenethyl bond may be employed.[5d,6,7,9]

Nitroxide-mediated radical polymerizations have been also used to prepare polymers and polymer segments for block copolymers.[5i,j,7c,9d,10a,11b,e,f,12−14] Although block copolymer syntheses were attempted using poly(ST)s bearing the TEMPO group as macroinitiators, the degree of reinitiation has been reported to be <60% for acrylate polymerization and <40% for methacrylate polymerization at 125 °C.[12] As a result, block copolymers with narrow molecular weight distributions are not obtained. Effective block copolymer syntheses are limited to polymerizations of ST and substituted styrenes.[5j,7c,9d,11b,e] ST−butyl acrylate, ST−methyl methacrylate, and ST−isoprene block copolymers have effectively been synthesized by sequential normal/living radical polymerization using a nitroxy-functionalized azoinitiator.[7d] The ST−isoprene block copolymer obtained by the method formed a clear film with microphase-separated polymer morphology. However, the molecular weight distribution of the polymer was not well controlled by the process because one block was prepared by a normal free radical polymerization process. A dimethylsiloxane−ST block copolymer was synthesized by nitroxide-mediated ST polymerization with a poly(dimethylsiloxane) macroazoinitiator.[11f] A well-defined poly(tetrahydrofuran)-*block*-poly(ST) was synthesized with a poly(tetrahydrofuran) macroazoinitiator.[15]

In a previous communication, we reported the synthesis of an epoxy-functionalized alkoxyamine (**1**) and its use as a terminator for anionic polymerizations of butadiene (BD).[17] In this paper, we deal with the synthesis of ST−BD (SB) block copolymers by nitroxide-mediated ST polymerization initiated with a nitroxy-functionalized poly(BD) (**2**) as a macroinitiator. The general approach is shown in Scheme 1. Also, one of the objectives of our research was *in situ* formation of high-impact poly(ST) by radical polymerization of ST with the nitroxy-functionalized poly(BD).

Scheme 1. Synthetic Approach to a BD−ST Block Copolymer



Experimental Section

Materials. BD and cyclohexane were commercially available and were purified according to procedures described in the literature.[18] *sec*-Butyllithium in cyclohexane solution was used as received. Commercial ST was purified by distillation under reduced pressure before use. Commercially available camphorsulfonic acid (CSA) was used without further purification. 2,2,6,6-Tetramethyl-1-(2-glycidyloxy-1-phenylethoxy)piperidine (**1**) was synthesized by reacting 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)piperidine with epichlorohydrin in the presence of aqueous NaOH and Bu_4NHSO_4 and was purified by recrystallization from methanol (mp = 35−36 °C).[17]

Anionic Polymerization of BD. Anionic polymerizations of BD in cyclohexane (5−10 vol % solution) were carried out for 24 h at room temperature in all-glass, sealed reactors with break-seals by standard high vacuum techniques.[18] Small portions of the polymerization mixtures were then collected and quenched with methanol to obtain materials for the

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S0024-9297(97)01815-9 CCC: $15.00
Published on Web 05/06/1998

Table 1. Results of Anionic Polymerizations of BD

[BD]/[*s*-BuLi] (molar ratio)	[**1**]/[*s*-BuLi] (molar ratio)	M_n (calcd)[a]	M_n (GPC)[b]	M_w (GPC)[b]	M_w/M_n (GPC)[b]	functionality[c]
60	0	3300	3450	3550	1.03	—
60	1.2	3630	3840	3930	1.02	0.95

[a] Calculated based on the molar ratio of BD to *s*-BuLi and the chain end group. [b] Determined using standard poly(BD) for the calibration. [c] Determined based on the quantification of the chain end by ^{1}H NMR spectroscopy.

Table 2. Bulk Polymerization of ST at 120 °C[a]

2 (g)	CSA (g)	time (h)	conversion (%)	M_n (GPC)[b]	M_w/M_n (GPC)[b]
none	none	20	89	249 000	2.16
0.28	none	20	65	17 400	1.22
0.28	0.0080	10	93	27 800	1.39

[a] ST: 1.4 g. [b] Determined using standard poly(ST) for the calibration.

molecular weight and molecular weight distribution measurements. The remaining portions of the polymerization mixtures were treated with a solution of excess **1** (1.2-fold) in cyclohexane, and the reaction mixtures were allowed to stir for 24 h at room temperature. The polymerization mixtures were then poured into methanol to precipitate the polymers. The polymers were collected by decantation, reprecipitated from hexane solution into methanol, and dried under reduced pressure. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis, and the results are shown in Table 1.

Radical Polymerization of ST. Bulk radical polymerizations of ST initiated with the nitroxy-functionalized poly(BD) as a macroinitiator or initiated thermally were carried out at 120 °C, with reaction mixtures sealed under high vacuum in glass tubing. After polymerization for 20 h, the mixtures were poured into methanol to precipitate the polymers. The resulting polymers were purified by reprecipitation from a chloroform solution into methanol and were dried under reduced pressure. The conversion of ST was determined gravimetrically. The molecular weights of the polymers were determined by GPC analysis and the results are shown in Table 2. The nitroxy-functionalized poly(BD)-initiated bulk polymerization of ST in the presence of CSA was carried out at 120 °C for 10 h by a similar method.

Degradation Procedure. The degradation of the poly(BD) segments in the SB block copolymers was carried out according to a method described in the literature.[19]

NMR Measurement. The ^{1}H NMR spectra were recorded with a Varian Gemini-200 NMR spectrometer (200 MHz) using deuteriochloroform as solvent and tetramethylsilane as internal standard.

Gel Permeation Chromatography (GPC). Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) of polymers were measured by GPC analysis at 35 °C, using tetrahydrofuran as the eluent. GPC was performed with a Waters system equipped with a Waters 510 HPLC pump, Waters Styragel columns (HR-5E, HR-4E, and HR-1 connected in this order), and a Waters 410 differential refractometer. Calibration curves were prepared with standard poly(ST) samples or standard poly(BD) samples.

Transmission Electron Microscopy (TEM). Transmission electron micrographs of the block copolymer films were examined with a Hitachi H-600 TEM at 100 kV.

Results and Discussion

Anionic polymerization of BD was carried out under the conditions shown in Table 1. A portion of the polymerization mixture was quenched with methanol to obtain material that could provide information about the polymer. The unfunctionalized poly(BD) thus obtained had an M_n of 3450 and a narrow molecular weight distribution (M_w/M_n = 1.03). Its M_n value was

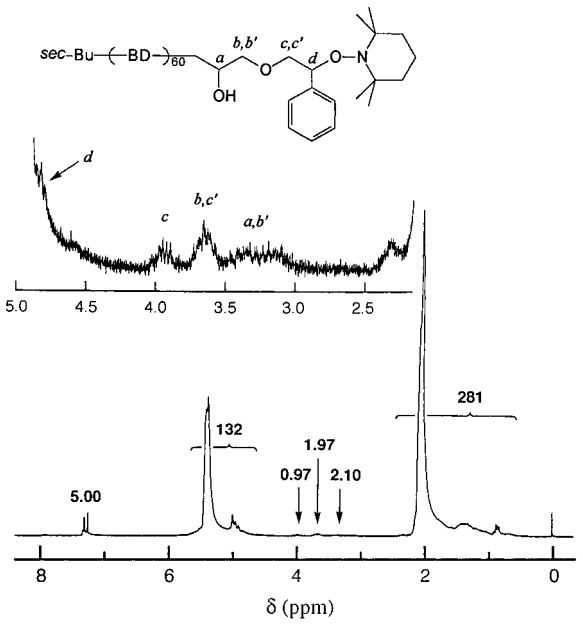


Figure 1. The ^{1}H NMR spectrum of the nitroxy-functionalized poly(BD) terminated with **1**. The numbers in the spectrum indicate intensities of respective resonances.

in agreement with the value expected (3300) based on the 60:1 molar ratio of BD to *sec*-butyllithium employed. The living poly(BD) anions present in the remainder of the sample were terminated by reaction with **1** to obtain the nitroxy-functionalized poly(BD), **2**. This material had a narrow molecular weight distribution (M_w/M_n = 1.02) and an M_n of 3840, which agreed well with that expected for the functionalized polymer (3630).

The ^{1}H NMR spectrum (Figure 1) of the nitroxy-functionalized poly(BD) contained resonances in the δ = 3.0−4.0 ppm range that are assignable to the protons of the methylene and methine groups next to oxygen atoms in the functionalized ends. By comparing the relative intensities of these resonances to those at δ = 4.3−6.0 ppm, which are due to the olefinic protons in the BD units, it was estimated that there were 62 BD units per nitroxy end group in the polymer. Because the degrees of polymerization (DP) of the parent and functionalized polymers, determined by GPC measurements, were 63 and 64, respectively, it may be concluded that a high proportion (> 95%) of the poly(butadienyl)-lithium chains was functionalized by reaction with **1**.

The polymers were also analyzed by thin-layer chromatography CTLC) with SiO_2-coated plates and toluene as the eluent. The unfunctionalized poly(BD) was observed as a spot (R_f) with a retention factor of > 0.9, as shown in Figure 2. However, the nitroxy-functionalized poly(BD) migrated as a spot with an R_f of <0.25. The hydroxy groups present on the functionalized polymer are likely responsible for its enhanced retention by the plate. No spot with an R_f > 0.9 was observed for the nitroxy-functionalized poly(BD). These results also indicate that the functionalization reaction took place to a large extent.

The phenethylalkoxyamine functionalized poly(BD) was then used as a macroinitiator for nitroxide-mediated ST polymerization to make a SB block copolymer. The radical polymerization of ST (1.4 g) initiated with the nitroxy-functionalized poly(BD) (**2**; 0.28 g; [ST]/[**2**] = 1.7 × 10^2) was carried out in bulk at 120 °C. The conversion of ST reached 65% after 20 h. The results

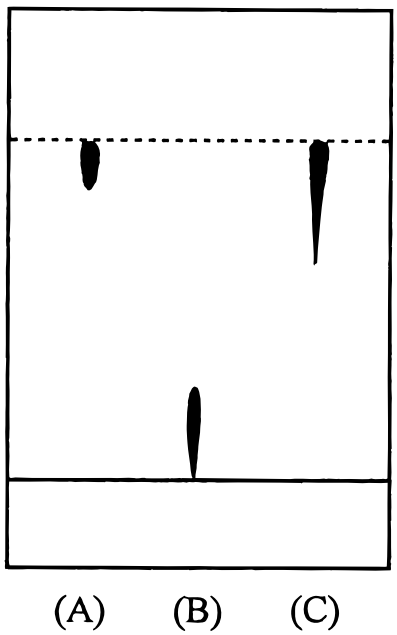


Figure 2. (A) Thin-layer chromatographs of the unfunctionalized poly(BD); (B), the nitroxy-functionalized poly(BD); and (C) the SB block copolymer.

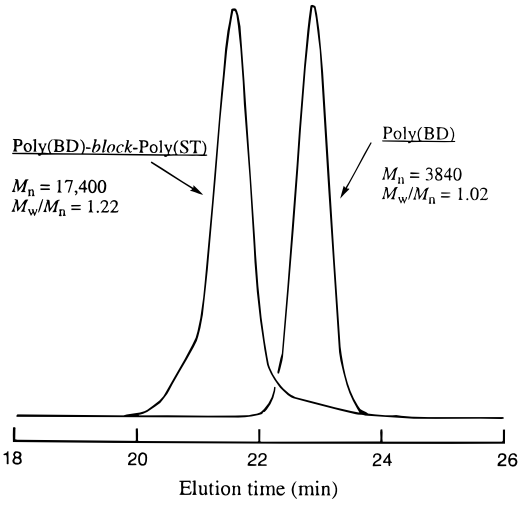


Figure 3. The GPC elution curves of the nitroxy-functionalized poly(BD) and the SB block copolymer.

of TLC analysis of the block copolymer are also shown in Figure 2, where the SB block copolymer is observed as a spot with an R_f of >0.6, and there is no evidence for any material present in the sample with an R_f < 0.25. Thus, none of the functionalized poly(BD) macroinitiator appears to remain in the sample. This result indicates that blocking occurred; however, it should be pointed out that TLC is only qualitative. The rather high R_f observed for the block copolymer compared with that of the poly(BD) macroinitiator is probably due to the ability of the poly(ST) block segments (83 wt %) to enhance the affinity of the solvent for the polymer, thus raising its R_f. In addition, the hydroxy groups are now located at the block junction compared with the chain end location in the functionalized polymer.

Figure 3 shows GPC elution curves of the nitroxy-functionalized poly(BD) and the resulting block copolymer. The M_n of the block copolymer determined by GPC [17 400, calibrated with poly(ST) standard] is in agreement with the calculated value (15 000) based on the

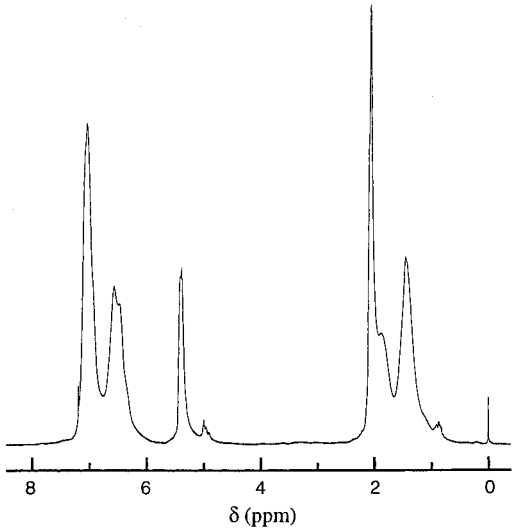
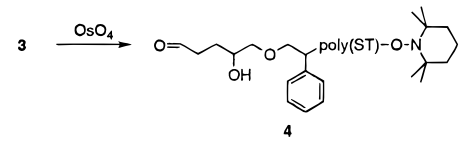


Figure 4. The ^{1}H NMR spectrum of the SB block copolymer.

Scheme 2. Digestion of the BD−ST Block Copolymer by OsO_4



initial molar ratio of ST to the poly(BD) macroinitiator and the conversion. The molecular weight distribution of the block copolymer was relatively narrow (M_w/M_n = 1.22). The thermal polymerization of ST at 120 °C for 20 h gave a poly(ST) with M_n = 249 000 and M_w/M_n = 2.16. These results indicate that the polymerization initiated with the nitroxy-functionalized poly(BD) occurred by TEMPO-mediated polymerization. The GPC chromatograph of the block copolymer shows a small amount of material (<5 area %) eluting between 22 and 24 min. This result indicates that most of the poly(BD) macroinitiator was converted to block copolymer. The small shoulder on the high molecular weight side of the GPC curve indicates some contamination of the block polymer by high molecular weight polystyrene that is probably formed by autoinitiation of styrene polymerization.

Figure 4 shows the ^{1}H NMR spectrum of the SB block copolymer. The spectrum exhibits resonances derived from poly(BD) and poly(ST) segments. The content of the poly(ST) segments was estimated by comparison of the resonances at 4.5−5.8 ppm with those at 5.8−7.8 ppm. The block copolymer was shown to contain 1.83 ST units per BD unit. If it is assumed that blocking was 100% efficient and that the molecular weight of the macroinitiator was 3630 (DP = 60), a M_n of 15 100 can be calculated for the copolymer for the ST/BD ratio. This result agrees reasonably well with that found by GPC analysis (17 400). Furthermore, the calculated M_n of the poly(ST) segments should be 11 400.

To confirm the SB block copolymer formation, the SB block copolymer was digested with OsO_4 to degrade the poly(BD) segments and to obtain BD-free poly(ST), **4**. This reaction is illustrated in Scheme 2, but it must be noted that the nature of the end groups in the poly(ST) formed by this process may not be those shown. Figure 5 shows GPC elution curves of the block copolymer and the resulting poly(ST). The molecular weight distribution curve of **4** was monomodal and corresponded to a

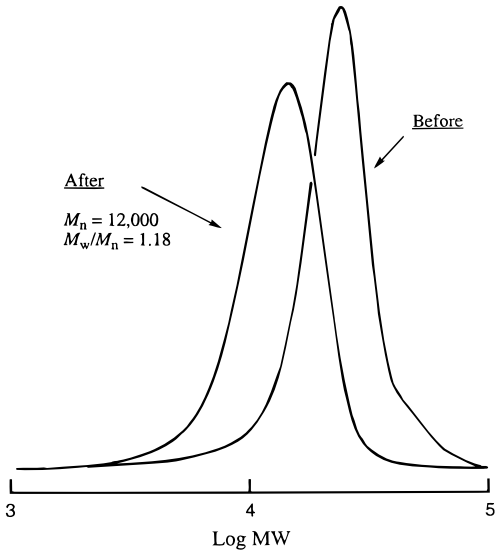


Figure 5. The GPC elution curves of the SB block copolymer and the BD-free poly(ST) after digestion.

poly(ST) with M_n = 12 000 and M_w/M_n = 1.18. This result is in good agreement with the value expected for the poly(ST)-block segments of the block copolymer based on the molecular weights of the nitroxy-functionalized poly(BD) and the SB block copolymer and also on the basis of the NMR analysis already discussed. These results demonstrate that the SB block copolymer is effectively produced by nitroxide-mediated ST polymerization initiated with the nitroxy-functionalized poly(BD).

It has been reported that the addition of strong organic acids such as CSA suppresses thermal initiation of styrene polymerization[20] while enhancing the rate and polymer molecular weight during nitroxide-mediated ST polymerization.[5c,h] Therefore, nitroxy-functionalized poly(BD)-initiated, nitroxide-mediated ST polymerization was attempted in the presence of CSA. The results of the polymerization are shown in Table 2 together with those obtained in the absence of CSA. The polymer yield, polymerization rate, and the molecular weight of the polymer are increased somewhat by the presence of CSA.

The presence of elastomeric poly(BD) domains in blends of poly(ST) and poly(BD) imparts impact resistance to the blends.[21,22] These high-impact poly(ST)s (HIPS) are very important materials in commerce, with >100 million tons/year being produced globally. Unfortunately, the poly(BD) domains are large enough to scatter visible light, thus causing the blends to be opaque and restricting their use for nontransparent applications. For applications requiring high clarity, poly(ST) is blended with SB block copolymers.[23,24] However, these transparent impact poly(ST)−poly(BD) blends (TIPS) are rather costly to produce because of the high cost of the SB block copolymers (manufactured by anionic polymerization). It is our goal to prepare TIPS in a single step by free radically polymerizing ST in the presence of a nitroxy-functionalized poly(BD), resulting in the formation of SB block copolymers dispersed in a poly(ST) matrix. This procedure would simplify the preparation of such blends and could significantly lower their manufacturing cost.

This possibility was investigated by thermally polymerizing ST containing 5% (w/w) nitroxy-functionalized poly(BD) (M_w = 50 000). As a control, a solution of the same poly(BD) without the nitroxy terminal group in ST was polymerized under identical conditions. Solution cast films obtained from the two polymers were analyzed by TEM. Figure 6 shows a comparison of the morphologies. The TEMs clearly show microphase separation (<0.1 μm) with the nitroxy-functionalized rubber, whereas the unfunctionalized rubber leads to very broad rubber particle size distribution. Furthermore, the film obtained with the nitroxy-functionalized poly(BD) was transparent and flexible, whereas the film resulting from the unfunctionalized poly(BD) was opaque and very brittle. These results indicate that it may indeed be possible to prepare TIPS by conventional poly(ST) processes, provided that nitroxy-functionalized poly(BD) is used. Studies on the impact resistance of TIPS samples prepared in this way are currently underway.

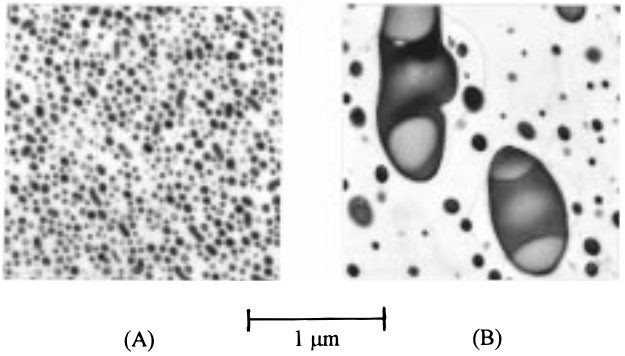


Figure 6. Transmission electron micrographs of polymers obtained by thermal polymerizations of (A) ST containing 5% (w/w) the nitroxy-functionalized poly(BD) and of (B) ST containing 5% (w/w) the unfunctionalized poly(BD).

Conclusions

Nitroxy-functionalized poly(BD) can be prepared by terminating poly(butadienyl)lithium with an epoxy-functionalized alkoxyamine and used to initiate nitroxide-mediated thermal polymerization of ST. Block copolymers containing poly(ST) and poly(BD) segments with nearly monodisperse segment block lengths can be prepared by such polymerizations. TIPS samples prepared by thermally polymerizing solutions of the nitroxy-functionalized poly(BD) in ST contain small poly(BD) domains and are transparent to visible light.

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MA9718154