Synthesis of Nitroxide-Functionalized Polybutadiene Using Halogen-Containing Benzyloxyamine as Terminators for Anionic Polymerization

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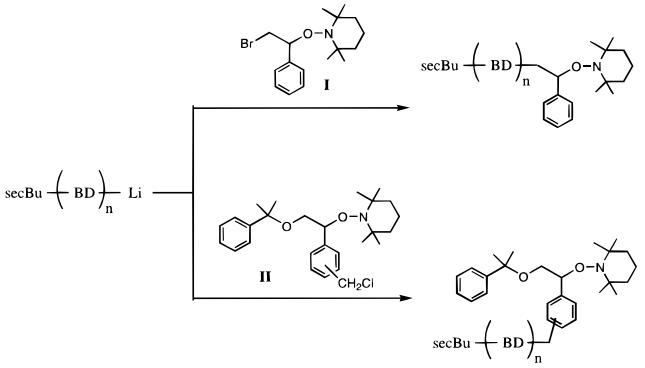
ABSTRACT: Synthesis of benzyloxyamine end-functionalized polybutadiene was investigated using halogen-containing benzyloxyamines as terminators for anionic polymerization of butadiene (BD). The two terminators studied were 2,2,6,6-tetramethyl-1-(2-bromo-1-phenylethoxy)piperidine (**1**), synthesized by allowing styrene to react with 1-oxo-2,2,6,6-tetramethylpiperidinium bromide, and 2,2,6,6-tetramethyl-1-(2-cumyloxy-1-(chloromethylphenyl)ethoxy)piperidine (**2**), synthesized by allowing chloromethylstyrene to react with dicumyl peroxide in the presence of TEMPO. Termination studies of poly(butadienyl)lithiums using **1** and **2** were carried out in heptane/tetrahydrofuran mixtures. Nearly quantitative yields of benzyloxyamine end-functionalized polybutadienes were obtained when the termination reactions were carried out at −78 °C. However, yields were much lower when terminations were carried out at ambient temperature.

Introduction

Since 1987 when Rizzardo first reported that alkoxyamines can initiate nitroxide-mediated radical polymerization (NMRP),[1] there have appeared over 100 papers describing various examples. Another popular controlled radical polymerization technique is atom transfer radical polymerization (ATRP). We favor the NMRP method over ATRP because the resulting polymer is not contaminated with metals that can cause subsequent discoloration and polymer stability problems. NMRP of styrene has been under especially intense investigation since 1993 following a paper by Georges et al. showing the effects of 2,2,6,6-tetramethylpiperdinyloxy (TEMPO) mediation on styrene polymerization.[2] Initially, NMRP research focused on understanding the mechanism[3] and ways to accelerate the polymerization rate.[4] More recently, efforts have moved toward the preparation of random,[5] block,[6] and graft[7] copolymers and the preparation of functionalized polymers.[8] We believe that the most commercially valuable utility for this technology is its use to make block copolymers. However, a key problem that limits the utility of NMRP for the preparation of block copolymers is that it only works well for styrenic monomers. Therefore, the nonstyrenic block is generally prepared using another chemistry in such a way that it is end-functionalized with a nitroxide. The nitroxy functional block then becomes the macroinitiator for NMRP of styrene.

The block copolymers of highest use commercially are the styrene−butadiene (S−B) block rubbers. Several hundred thousand tons per year of these materials is produced globally. The chemistry currently utilized to manufacture these materials is anionic polymerization. Our research is focused upon developing ways to manufacture S−B block rubbers using NMRP-mediated polymerization.

Scheme 1. Preparation of Benzyloxyamine Terminated Polybutadiene



A previous paper described the synthesis, characterization, and use of an epoxy functional benzyloxyamine to terminate polybutadienyllithium (PBD-Li), resulting in the placement of a labile nitroxide functional group on one end of PBD.[9] The benzyloxyamine functional PBD was subsequently used as a macroinitiator for styrene polymerization, resulting in the formation of S−B block copolymer.[10] The synthesis of the epoxy functional benzyloxyamine involved several steps and was not trivial. Our efforts then shifted toward the development of a more economically viable PBD-Li terminating agent, i.e., synthesized in high yield in one step.

In this paper, we report the synthesis of benzyloxyamine-functionalized PBD using halogen-containing benzyloxyamines as terminators. The general approach is shown in Scheme 1.

Experimental Section

Materials. Butadiene (BD), heptane, and tetrahydrofuran (THF) were commercially available and purified according to

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procedures described in the literature.[11] *sec*-Butyllithium in cyclohexane solution was used as received. Chloromethylstyrene (CMST) was available from Aldrich as meta and para mixtures. Styrene and CMST were purified by distillation under reduced pressure before use. The other reagents were used without further purification.

2,2,6,6-Tetramethyl-1-(2-bromo-1-phenylethoxy)piperidine (1). Synthesis of **1** was achieved by allowing styrene to react with 1-oxo-2,2,6,6-tetramethylpiperidinium bromide as follows.[12] Bromine (0.27 mL, 0.84 g) was added slowly to a CCl_4 solution of TEMPO (1.6 g) to make 1-oxo-2,2,6,6-tetramethylpiperidinium bromide. The brown solid formed almost instantaneously. Freshly distilled styrene (6 mL) was added to the reaction mixture, and then the solution was stirred under nitrogen at 50 °C for 30 min. The brown solid gradually disappeared as its adduct with styrene formed. The solvent and the excess styrene were removed by evaporation. The residue was washed with water and taken up in hexane. The hexane extract was dried over $MgSO_4$, and the hexane removed by evaporation to obtain the crude product. The product was purified by silica gel column chromatography using benzene as the eluent and by recrystallization from methanol. The yield of **1** was 1.5 g (44% based on TEMPO): mp = 49.3−50.3 °C. Anal. Calcd for $C_{17}H_{26}NOBr$: C, 60.00; H, 7.70; N, 4.12; Br, 23.48. Found: C, 60.08; H, 7.73; N, 4.26; Br, 24.50. ^{1}H NMR ($CDCl_3$): δ = 0.5−2.0 (complex, 18H, CH_2 and CH_3 of TEMPO group), 3.65 (dd, 1H, J = 8.3 and 9.8 Hz, BrC*H*H), 3.97 (dd, 1H, J = 3.0 and 9.8 Hz, BrCH*H*), 4.95 (dd, 1H, J = 3.0 and 8.3 Hz, CH−ON), 7.0−7.5 (s, 5H, phenyl group). ^{13}C NMR ($CDCl_3$): δ = 17.3, 20.5, 32.4, 40.7, 60.2 (C, CH_2, and CH_3 of TEMPO group), 36.8 ($BrCH_2$), 85.6 (CH−ON), 128.0, 128.3, 140.8 (phenyl group).

2,2,6,6-Tetramethyl-1-(2-cumyloxy-1-(chloromethylphenyl)ethoxy)piperidine (2). Synthesis of **2** was achieved by allowing CMST to react with dicumyl peroxide (DCP) in the presence of TEMPO as follows. TEMPO (3.0 g, 19 mmol) dissolved in benzene was added dropwise to the reaction mixture including DCP (20 g, 74 mmol) and CMST (43 g, 28 mmol) under nitrogen at 100 °C. After reaction for 8 h, the excess CMST and benzene were removed by evaporation. Hexane was added to the residual oil, and then a hexane-insoluble part was separated by filtration. The hexane extract was dried over $MgSO_4$, and hexane was then removed by evaporation to obtain the crude product. The product was purified by silica gel column chromatography using methylene chloride as the eluent followed by recrystallization from methanol. The yield of **2** was 1.0 g (12% based on TEMPO): mp = ca. 52 and ca. 75 °C (meta and para mixtures). ^{1}H NMR ($CDCl_3$): δ = 0.5−2.0 (complex, 18H, CH_2 and CH_3 of TEMPO group), 1.38 (s, 3H, CH_3 of cumyl group), 1.42 (s, 3H, CH_3 of cumyl group), 3.28 (*p*) and 3.29 (*m*) (q, 1H, methylene CH), 3.68 (*p*) and 3.69 (*m*) (q, 1H, methylene CH), 4.60 (*m*) and 4.62 (*p*) (s, 2H, CH_2Cl), 4.77 (t, 1H, CH), 6.8−7.4 (complex, 9H, phenyl). ^{13}C NMR ($CDCl_3$): δ = 17.3, 20.5, 32.2, 40.7, and 60.1 (C, CH_2, and CH_3 of TEMPO group), 28.2 and 28.3 (CH_3 of cumyl group), 46.6 (*p*) and 46.7 (*m*) (CH_2Cl), 65.6 (*m*) and 65.8 (*p*) (OCH_2), 76.7 (C−O), 85.8 (*p*) and 85.9 (*m*) (CH−ON), 126.0, 126.8, 127.5, 120.2, 128.5, 136.4, 137.0, 143.0, 143.3, and 146.6 (phenyl group).

Anionic Polymerization of BD. Anionic polymerizations of BD in heptane were carried out for 24 h at room temperature in all-glass, sealed reactors using break-seals and standard high-vacuum techniques.[11] A portion of each polymerization mixture was collected and quenched with methanol to obtain material for molecular weight measurements. Termination reactions of the PBD-Li were carried out during 24 h using a 1.2-fold molar excess of the terminator in a heptane/THF mixture at ambient temperature or at −78 °C. The polymerization mixtures were poured into methanol to precipitate the polymers. The polymers were purified by reprecipitation from hexane solution into methanol and dried under vacuum. The molecular weights of the polymers were determined using gel permeation chromatographic (GPC) analysis, and the results are shown in Table 1.

Table 1. Anionic Polymerization of BD[a]

terminator	temp (°C)	M_n (calcd)	M_n (GPC)	M_w (GPC)	M_w/M_n (GPC)
methanol	rt	902	990	1030	1.04
1	−78	1160[b]	1170	1200	1.03
1	rt	1160[b]	1600	1760	1.10
2	−78	1382[b]	1480	1530	1.03

[a] [BD]/[*sec*-BuLi] = 15.6. [b] The value expected for benzyloxyamine-functionalized PBD.

NMR Measurement. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 NMR spectrometer using deuteriochloroform and tetramethylsilane as solvent and internal standard, respectively.

Gel Permeation Chromatography (GPC). Number- and weight-average molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polymers were measured by GPC analysis at 35 °C using THF as the eluent. GPC was performed using a Waters system equipped with a Waters 510 HPLC pump, Waters Styragel columns (HR-5E, HR-4E, and HR-1 connected in this order), a Waters 410 differential refractometer, and a Viscotek differential viscometer model 100. The universal calibration curve was used to calculate M_n and M_w.

Results and Discussion

In our previous paper, it was reported that PBD-Li reacts with a glycidyl functional benzyloxyamine in hydrocarbon solvent at room temperature to form a benzyloxyamine-functionalized PBD.[9] The nitroxy-functionalized PBD was used as a macroinitiator for NMRP of styrene.[10b] Another possibility to make a nitroxy-functionalized PBD is to use a halogen-containing benzyloxyamine as a terminator for PBD-Li. Therefore, we synthesized two different types of halogen functional benzyloxyamines and investigated their use as terminators.

Termination of PBD-Li with 1. Previously, we reported the synthesis of **1**[12] by allowing styrene to react with 1-oxo-2,2,6,6-tetramethylpiperidinium bromide, which is prepared from TEMPO and bromine.[12] 2,2,6,6-Tetramethyl-(2-chloro-1-phenylethoxy)piperidine can be synthesized by the same method using chlorine instead of bromine.[12] However, the chloro derivative was obtained as a liquid, whereas the bromine derivative is a solid. Therefore, the chloro derivative is difficult to obtain in high purity, making it unsuitable as a terminator for anionic polymerization.

Anionic polymerization of BD was carried out using *sec*-butyllithium as the initiator in heptane at room temperature ([BD]/[*sec*-BuLi] = 15.6). A portion of the polymerization mixture was quenched with methanol to obtain information about the molecular weight, molecular weight distribution, and microstructure of the polymer. The resulting unfunctionalized PBD had a M_n of 990 and a M_w/M_n of 1.04 as shown in Table 1. Its M_n value was in agreement with the value expected (902) based on the 15.6:1 molar ratio of BD to *sec*-butyllithium employed. The ^{1}H NMR spectrum of the unfunctionalized PBD is shown in Figure 1. It is known that the microstructure of BD (1,2- and 1,4-microstructures) can be estimated by comparing the relative intensities of the resonances at δ = 4.5−5.1 ppm and δ = 5.1−6.0 ppm in the ^{1}H NMR spectrum.[13] The former resonances correspond to two olefinic protons of 1,2-units, and the latter resonances correspond to one olefinic proton of 1,2-units and two olefinic protons of 1,4-units. The 1,4-content of the polymer was estimated to be 74% from the ^{1}H NMR spectrum in Figure 1. In general, a high molecular weight PBD prepared using hydrocarbon

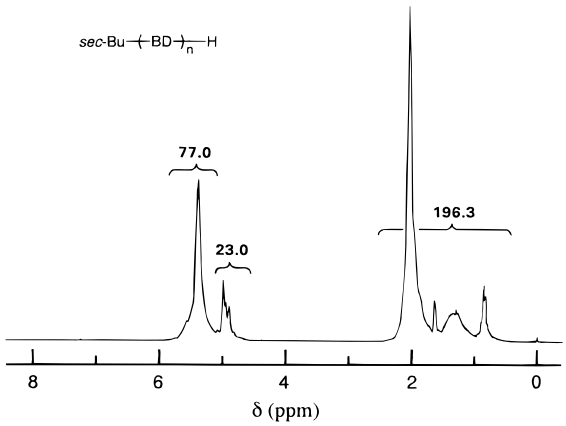

Figure 1. ^{1}H NMR spectrum of the unfunctionalized PBD. The numbers in the spectrum indicate intensities of respective resonances.

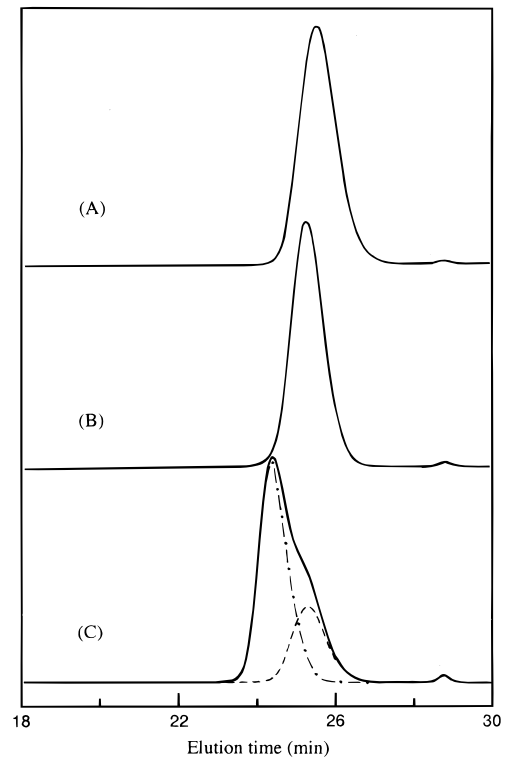

Figure 2. GPC elution curves of the unfunctionalized PBD (A) and benzyloxyamine-functionalized PBDs terminated with **1** at −78 °C (B) and room temperature (C). (C) includes 27 wt % of the benzyloxyamine-functionalized PBD (- - -) and 73 wt % of a dimeric PBD (− • −).

solvent has ca. 90% 1,4-units.[13] The PBD in this study seems to have a lower content of 1,4-units because of the high concentration of initiator employed.

The PBD produced by termination at −78 °C using **1** had a narrow molecular weight distribution (M_w/M_n = 1.03) (Figure 2) and a M_n of 1170, which agreed well with that expected for the functionalized polymer (1160). Figure 3 shows a ^{1}H NMR spectrum of the resulting PBD. It contains resonances in the δ = 0.2−1.5, 4.6, and 7.0−7.4 ppm range that are assignable to the protons of the nitroxy group, the methine proton next to the nitroxy group, and the phenyl protons of the terminating group, respectively. 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 14.1 BD units per nitroxy

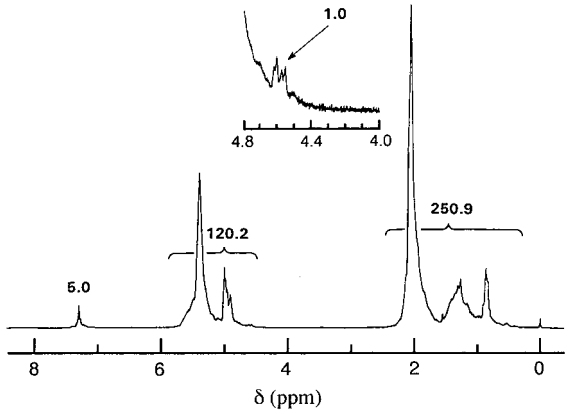

Figure 3. ^{1}H NMR spectrum of the benzyloxyamine-functionalized PBD teminated with **1** at −78 °C. The numbers in the spectrum indicate intensities of respective resonances.

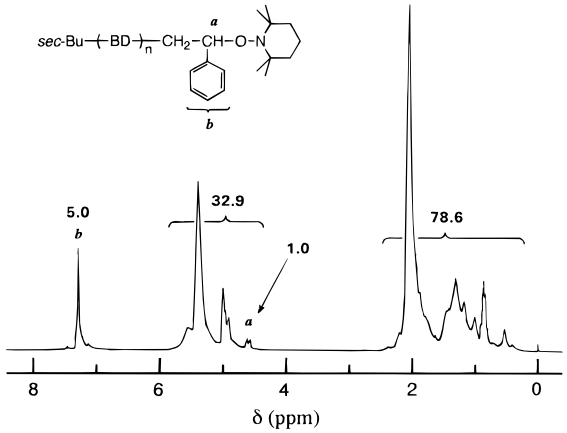

Figure 4. ^{1}H NMR spectrum of PBD-Li terminated with **1** at room temperature. The numbers in the spectrum indicate intensities of respective resonances.

end group in the polymer. Since the degrees of polymerization of the unfunctionalized and functionalized PBDs, determined by GPC measurements, were 17.2 and 15.8, respectively, it may be concluded that a high proportion (>90%) of the PBD-Li chains was functionalized by reaction with **1**.

When the termination reaction using **1** was carried out at room temperature, the color of the polymerization mixture changed to a pale yellowish solution and then gradually disappeared. After 5 min, the color completely disappeared. After quenching with methanol, the material had a slightly broad molecular weight distribution (M_w/M_n = 1.10) (Figure 2) and a M_n of 1600. It is known that lithium−halogen exchange occurs when poly(alkyl)-lithiums react with halogen-containing compounds at room temperature.[13] As a result, a PBD having a halogen atom on the chain end reacted with PBD-Li to form a dimeric PBD. Figure 4 shows the ^{1}H NMR spectrum of the resulting material. It contains the same resonances in the δ = 0.2−1.5, 4.6, and 7.0−7.4 ppm range as present in the spectrum of the derivative prepared at −78 °C, but their intensities are much lower. By comparing the relative intensities of these resonances to those at δ = 4.3−6.0 ppm, it was estimated that 27 wt % of the polymer was functionalized with benzyloxyamine groups. The GPC elution curves of the benzyloxyamine-functionalized PBD (27 wt %) and the dimeric PBD (73 wt %) are illustrated in Figure 2C.

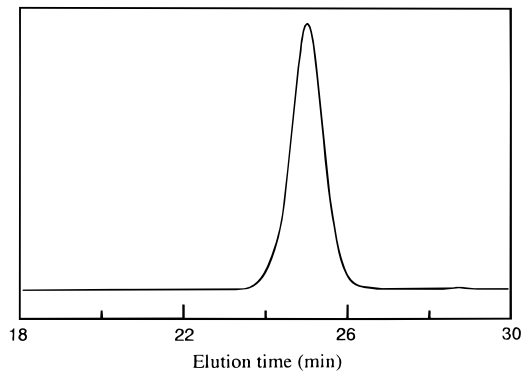

Figure 5. GPC elution curve of the benzyloxyamine-functionalized PBD terminated with **2** at −78 °C.

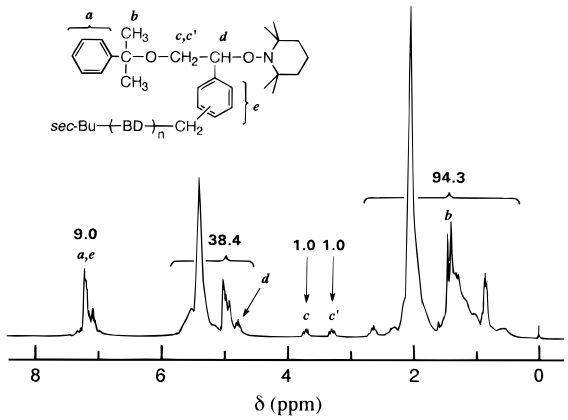

Figure 6. ^{1}H NMR spectrum of the benzyloxyamine-functionalized PBD terminated with **2** at −78 °C. The numbers in the spectrum indicate intensities of respective resonances.

Termination of PBD-Li with 2. Previously, we reported that the yield of 2,2,6,6-tetramethyl-(2-benzoyloxy-1-phenylethoxy)piperidine obtained by reaction of benzoyl peroxide with styrene in the presence of TEMPO could be improved by dilution of the reaction mixture.[9] Dilution reduces the rate at which TEMPO undergoes a redox reaction with benzoyl peroxide.[14] In our best conditions, 2,2,6,6-tetramethyl-(2-benzoyloxy-1-phenylethoxy)piperidine was obtained in 50% yield based on TEMPO.[9]

During the preparation of **2**, we wanted to keep the temperature <110 °C to minimize the decomposition of **2** as it formed. It is well-known that α-phenethyloxyamines such as **2** are thermally unstable at elevated temperatures.[15] Since the 1 h half-life decomposition temperature for DCP is ∼135 °C, a large excess of DCP vs TEMPO was used because the reaction of DCP with CMST was carried out for only 8 h at 100 °C. Thus, only a fraction of the DCP present would decompose under these conditions. The reason for the low (12%) yield of **2** based on TEMPO is likely due to lack of formation of enough CMS radicals to consume all of the TEMPO. A higher yield may have been obtained by carrying out the reaction at higher temperature or for an extended time.

Termination of PBD-Li at −78 °C using **2** resulted in the formation of a material having a narrow molecular weight distribution ($M_w/M_n = 1.03$) (Figure 5) and a M_n of 1480, which agreed well with that expected for the functionalized polymer (1382). Figure 6 shows the ^{1}H NMR spectrum of the resulting PBD. It contains resonances in the $\delta = 0.2-1.5$, 2.6, 3.3, 3.7, 4.7, and 6.8−7.4 ppm range that are assignable to the protons of the terminating group. By comparing the relative intensities of these resonances to those at $\delta = 4.3-6.0$ ppm, which are due to the olefinic protons of BD units, it was estimated that there were 16.5 BD units per benzyloxyamine end group in the polymer. Since the degrees of polymerization of the unfunctionalized and functionalized PBDs, determined by GPC measurements, were 17.2 and 17.0, respectively, it may be concluded that a high proportion (>90%) of the PBD-Li chains was functionalized by reaction with **2**.

Conclusion

Two different types of halogen-containing benzyloxyamines have been synthesized and investigated as terminators for PBD-Li to prepare benzyloxyamine-functionalized PBD. Both benzyloxyamines worked as terminators in high yield by reaction with PBD-Li at −78 °C, but poor yield was obtained when the termination reaction was carried out at ambient temperature.

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