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Synthesis of Nitroxy-Functionalized Polybutadiene by Anionic Polymerization Using a Nitroxy-Functionalized Terminator

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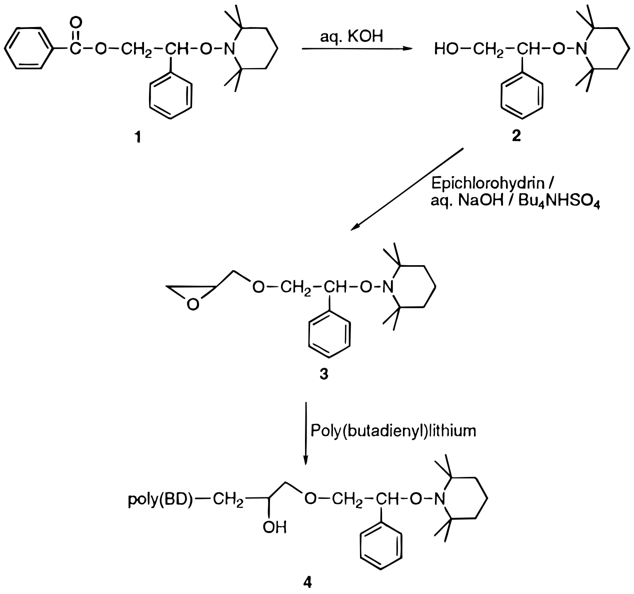
Introduction. Polymerizations initiated by alkoxyamines at elevated temperatures involve propagating free radicals but exhibit characteristics of “living” polymerizations. Thus, molecular weights of the polymers produced increase with conversion and the molecular weight distributions are narrower than those of conventional radical polymerizations ($M_w/M_n < 1.3$). This behavior is attributed to the ability of nitroxyl free radicals derived from the initiators to combine reversibly with propagating polymer radicals and thereby moderate their growth.[1−11]

The use of nitroxyl free radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and di-*tert*-butyl nitroxide (DBN) to moderate free radical polymerizations was first reported by Rizzardo *et al.*[1] Georges *et al.*[2] have done much to develop this approach, including its application to random and block copolymer syntheses. The alkoxyamines required for such polymerizations were initially prepared *in situ* by decomposing conventional free radical initiators such as 2,2′-azobis(isobutyronitrile) or benzoyl peroxide (BPO) in the presence of monomer and nitroxyl radicals (typically, TEMPO and DBN).[2,3] This led to unimer or low molecular weight polymers with alkoxyamine ends that then initiated styrene (ST) polymerization at temperatures of 120 °C and above.

The unimer alkoxyamine initiator, **1**, that corresponds to the adduct produced by addition of TEMPO with the primary propagating radical initiated with BPO was first found by Moad *et al.*[4] in spin-trapping experiments, but methods for forming this and similar materials in high purity and high yield have only recently been developed.[5−8] Since the alkoxyamine moiety has rather good chemical stability, derivatives of **1** have been prepared and used as initiators for synthesis of polymers and copolymers with useful end functionality, multiarm star polymers, hyperbranched polymers, and dendritic linear block copolymers.[6,9]

Free radical reactions have been used to prepare polymers and polymer segments for block copolymers in all of these processes. It would seem desirable to develop ways to prepare polymeric alkoxyamines by functionalizing living polymers prepared via ionic or coordination polymerization reactions and thereby extend the synthetic scope of alkoxyamine-initiated, nitroxide-mediated polymerizations. Yoshida *et al.*[12] seem to be the first to have attempted this by functionalizing poly(styryl)lithium with an oxoaminium salt. Although the nitroxyl groups were not introduced quantitatively using the oxoaminium salt alone, quantitative functionalization was achieved by carrying out the reaction in the presence of nitroxyl radicals.

Scheme 1



In this communication, we describe the synthesis of an epoxy-functional alkoxyamine, **3**, and its use as a terminator for the living anionic polymerization of butadiene (BD). The general approach is indicated by Scheme 1.

The use of poly(BD) terminated with **3** as a macroinitiator for preparing block copolymers containing a poly(BD) segment will be discussed in a subsequent publication.

Results and Discussion. In initial studies on the formation of **1** from the reaction of BPO, ST, and TEMPO, Moad *et al.*[4] found that three unimers are formed, these being the results of initial attack of benzoyloxy radicals at the unsubstituted olefin (**1**, ca. 80%), substituted olefin (ca. 15%), and aromatic carbons of ST (ca. 5%) along with trace amounts of dimers and trimers, etc. Apparently, the presence of minor products of this reaction prevented **1** from crystallizing when it was prepared in large scale (19% yield based on TEMPO) by Hawker *et al.*[6] By heating a solution of BPO (4.7 g) and TEMPO (3.0 g) in ST (300 mL) at 90−95 °C under nitrogen for 30 min and then removing excess ST and BPO, we obtained **1** as a solid that was purified by recrystallization from ethanol. The yield was 3.6 g (50% based on TEMPO), mp = 72.2−72.6 °C. The ^{1}H-NMR spectrum of the product was similar to that reported by Hawker *et al.*[6] Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.64; H, 8.49; N, 3.64.

1 was hydrolyzed by heating a solution of it (2.4 g) under reflux in a mixture of ethanol (35 mL) and 2 N KOH (8.5 mL) under nitrogen at 80 °C for 5 h, as described by Hawker *et al.*[6] The reaction mixture was concentrated to remove ethanol, diluted with water, and extracted with methylene chloride. The extract was dried over $MgSO_4$, and methylene chloride was removed by distillation to obtain **2** as a slightly yellow liquid (1.7 g) in quantitative yield.

The preparation of **3** followed a procedure reported for the preparation of phenethyl glycidyl ether from phenethyl alcohol.[13] Epichlorohydrin (2.8 g) was added dropwise to a mixture of 50% aqueous NaOH (4.3 mL) and Bu_4NHSO_4 (0.085 g). The solution was stirred vigorously at room temperature for 2 h, and then **2** (1.7 g) was added in portions over 1 h at room temperature.

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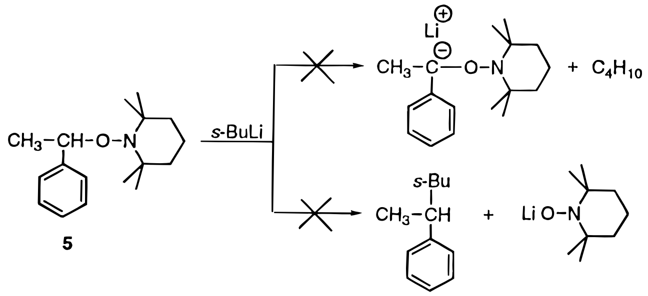
Scheme 2



The mixture was stirred overnight. The reaction mixture was diluted with water and extracted with methylene chloride, and the extract was dried over $MgSO_4$. After removal of methylene chloride by distillation, **3** was purified by recrystallization from methanol. The yield was 1.5 g (70%), mp = 35−36 °C. ^{1}H-NMR ($CDCl_3$):[14] $\delta = 0.5{-}2.0$ (complex, 18H, CH_2 and CH_3 of TEMPO group), 2.48 (dd, $J = 2.9$ and 5.2 Hz, 1H, methylene CH of oxirane ring), 2.69 (dd, $J = 4.3$ and 5.2 Hz, 1H, methylene CH of oxirane ring), 3.01 (m, $J = 2.9$, 3.1, 4.3, and 5.0 Hz, 1H, CH of oxirane ring), 3.31 and 3.37 (dd, $J = 5.0$ and 11.6 Hz, 1H, methylene CH of glycidyl group), 3.58 and 3.64 (dd, $J = 3.1$ and 11.6 Hz, 1H, methylene CH of glycidyl group), 3.68 and 3.75 (dd, $J = 6.6$ and 10.0 Hz, 1H, $C\mathit{H}_2CHPh$), 4.00 and 4.06 (dd, $J = 5.2$ and 10.0 Hz, 1H, $C\mathit{H}_2CHPh$), 4.80 (dd, $J = 5.2$ and 6.6 Hz, 1H, $C\mathit{H}Ph$), 7.0−7.5 (complex, 5H, phenyl). Anal. Calcd for $C_{20}H_{31}NO_3$: C, 72.04; H, 9.37; N, 4.20. Found: C, 72.14; H, 9.59; N, 4.32.

A requisite for the use of **3** as a terminator for anionic polymerizations is that its alkoxyamine group be stable to alkyllithiums and other strong bases. This was investigated by allowing 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine, **5**, to react with *sec*-butyllithium in cyclohexane solution for 24 h at room temperature. The solution was colorless throughout the reaction. Upon workup of the reaction mixture by methanolysis, water washing, extraction with methylene chloride, and evaporation, **5** was recovered unchanged in quantitative yield. This demonstrates that the alkoxyamine group is stable to alkyllithiums and that compounds containing such groups may be employed in anionic polymerizations.

A 1.2-fold excess of **3** in cyclohexane was then added to a poly(butadienyl)lithium solution in cyclohexane that been prepared using *sec*-butyllithium as initiator ([BD]/[*s*-BuLi] = 60). The reaction mixture was allowed to stand for 24 h and was then worked up by precipitation into methanol containing *p*-*tert*-butylcatechol. The polymer was reprecipitated several times to ensure the removal of any unreacted **3**. The resulting polymer was shown by size-exclusion chromatography to have M_n and M_w values of 3840 and 3930, respectively.[15]

Figure 1 shows the ^{1}H-NMR spectrum of the polymer.[14] It is typically that of an alkyllithium-initiated poly(BD) that is prepared in hydrocarbon solvents (i.e., 90% of 1,4-structure) except for the presence of resonances that are attributable to end groups derived from **3**. The resonances in the $\delta = 7.3{-}7.5$ ppm and $\delta = 3.0{-}4.0$ ppm region are easily measured. Their relative areas, when compared to the areas of the other resonances in the spectrum, indicate a ratio of BD units to ends derived from **3** of 62. This compares favorably with the degree of polymerization of the polymer (64) that is based on its M_n value, indicating a high degree of end-functionalization.

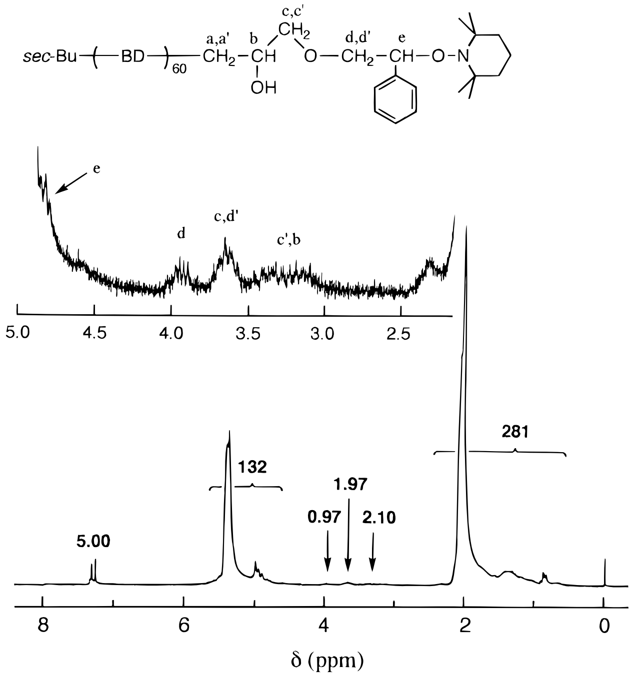


Figure 1. ^{1}H-NMR spectrum of poly(BD) terminated with **3**. The numbers in the spectrum indicate intensities of respective resonances.

The polymer was analyzed by thin layer chromatography using SiO_2-coated plates and toluene as the eluent. Although unfunctionalized poly(BD) would be observed as a spot having an $R_f > 0.9$, no such spot was detected from the resulting polymer. Instead, the polymer migrated as a spot having an R_f of 0.15. The hydroxy groups present on the functionalized polymer are responsible for its enhanced retention by the plate. These results also indicate that the functionalization reaction occurs nearly completely.

In conclusion, compound **3**, which contains oxirane and alkoxyamine functionalities, has been prepared and used to functionalize the living end of poly(butadienyl)-lithium efficiently. We are presently investigating polymers functionalized with **3** as macroinitiators for the preparation of block copolymers with controlled molecular weights and molecular weight distributions.

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(14) ^{1}H-NMR spectra were recorded on a Varian Gemini-200 spectrometer and deuteriochloroform was used as the solvent.

(15) The M_n and M_w of the polymers were determined by size-exclusion chromatography (Waters system) calibrated with poly(BD) standard samples (American Polymers Standards Corp.) in tetrahydrofuran.

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