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End-Quenching of Quasi-Living Isobutylene Polymerizations with Alkoxybenzene Compounds

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Introduction. Since the development of living carbocationic polymerization of isobutylene, in situ quenching of the living chain ends to produce end-functional polymers has been a topic of great interest. However, relatively few classes of compounds have been discovered that yield quantitative end-functionalization. Hard, σ-nucleophiles such as nonhindered alcohols or amines react with the more abundant Lewis acid catalyst and return only *tert*-chloride polyisobutylene (PIB) chain ends.[1,2] Soft π-nucleophiles, on the other hand, can be induced under the proper conditions to react with the carbocations, yielding functional groups other than *tert*-chloride. Among π-nucleophiles, two particularly useful classes have emerged: non-homopolymerizable olefins[2−8] and highly reactive aromatic substrates.[9−12] The former class may be divided among those olefins yielding quantitatively ionized chain ends, e.g., 1,1-diphenylethylene,[3] and those that add once and then terminate the chain, through either collapse,[4,5] e.g., butadiene, or fragmentation,[2,6−8] e.g., allyltrimethylsilane. The latter class consists of heterocyclic aromatic compounds, including 2-alkylfurans,[9] thiophene,[10] and N-substituted pyrroles,[11,12] that undergo quantitative Friedel−Crafts alkylation by quasi-living PIB.

A promising new development in this field is the use of a single type of end-quenching reaction, for example, alkylation of an N-substituted pyrrole, to fit various end-functionalities onto the chain ends. Thus, Storey et al.[12] tethered either primary alkyl chloride or bromide to the nitrogen atom of pyrrole and obtained quantitative alkylation of both of the resulting N-substituted pyrroles by reaction with quasi-living PIB. Obviously, groups other than halogen may be contemplated for attachment in this fashion. Binder et al.[13] demonstrated a similar approach using a non-homopolymerizable olefin; these authors attached a primary bromide to 1,1-diphenylethylene via a three-carbon tether and used the resulting monomer to quench quasi-living PIB and thereby create primary bromide-terminated PIB.

Although highly reactive heterocyclic aromatics such as furan, thiophene, and pyrrole have proven to be excellent quenching agents for quasi-living PIB, there have been few reports of end-capping by less reactive arenes. Over the years, reports have appeared describing postpolymerization Friedel−Crafts alkylation reactions of *tert*-chloride- and/or olefin-terminated PIB with benzene-based aromatic compounds. Kennedy et al. reported successful alkylation of both phenol[14] and anisole[15] in the presence of BF_3-OEt_2, using either *tert*-chloride or *exo*-olefin-terminated PIB. The reactions were carried out in refluxing hexane and required ~2 days for quantitative conversion. Later, Bergbreiter et al.[16] reported the alkylation of highly activated benzene derivatives, such as phenol, with *exo*-olefin-terminated PIB in the presence of concentrated sulfuric acid. Reactions on less activated alkylbenzenes were unsuccessful. Recently, Zhang et al.[17] reported Friedel−Crafts alkylation of triphenylamine at 50 °C by a mixture of *tert*-chloride- and *exo*-olefin-terminated PIB that had been synthesized from an $H_2O/TiCl_4$ initiating system at −40 °C. The alkylations were performed both in situ and postpolymerization on a purified polymer. In either case, the maximum capping efficiency was 70−80%, and the process was plagued by competitive *exo*-olefin formation. The latter problem was a predictable outcome for the use of an aromatic amine, since Storey et al.[18] have shown that quenching with hindered amines can lead to quantitative *exo*-olefin-terminated PIB.

Herein, we report our discovery that alkoxybenzenes represent a versatile new class of capping agents for quasiliving PIB. The alkoxy group is one of the more strongly activating groups toward electrophilic aromatic substitution (EAS); however, as opposed to amino and substituted amino, alkoxy does not react or strongly complex with Lewis acid, nor does it tend to induce elimination at the chain end. Since primary bromide-terminated PIB is currently of great interest[12,13,19−22] due to its ease of transformation into other useful functionality,[22−24] we have chosen to demonstrate the utility of alkoxybenzene quenching with 3-bromopropoxybenzene as a representative member of this class of compounds. However, alkoxybenzene quenching has been found to be tolerant to a surprisingly broad range of tethered functional groups, and a more detailed report on the scope of this useful new method will appear in a forthcoming publication.

Results and Discussion. Figure 1 shows the scheme for end-quenching quasi-living PIB with an ω-haloalkoxybenzene. In general, we have observed that alkylation reactions on alkoxybenzenes are slower than with heterocyclic aromatics, which are so reactive that chain end ionization is typically rate limiting.[12] Nonetheless, reactivity of the alkoxybenzenes is sufficiently high to obtain quantitative capping before any loss of functionality through spontaneous termination processes such as chain end rearrangement.[25] To ensure solubility of the more polar alkoxybenzenes, and also to increase the rate of quenching, we have used a more polar solvent mixture (40/60, v/v, hexane/methyl chloride) compared to the 60/40 hexane/methyl chloride mixture typically used for $TiCl_4$-catalyzed isobutylene polymerizations. The proportion of polar solvent can in fact be further increased, but at the expense of broader molecular weight distributions, particularly for low target molecular weights.

Quantitative end-capping was attained by directly charging an excess (2.5 equiv per chain end) of 3-bromopropoxybenzene to $TiCl_4$-catalyzed quasi-living polyisobutylene in 40/60 (v/v) hexane/methyl chloride at −70 °C. A greater (or lesser) excess of quencher can be used, resulting in shorter (or longer) quenching times. We found that 2.5:1 is a good compromise between rate of quenching and quencher consumption for laboratory preparations. Figure 2 (spectrum A) shows a ^1H NMR spectrum of the resulting difunctional polyisobutylene bearing primary bromide end groups. Alkylation of 3-bromopropoxybenzene by PIB is evident from the disappearance of the resonances at 1.68 and 1.96 ppm due to

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the *gem*-dimethyl and methylene protons of the ultimate repeat unit in *tert*-chloride PIB. Monoalkylation occurs exclusively *para* to the alkoxy moiety, and a new resonance for the ultimate PIB methylene unit appears at 1.79 ppm as well as resonances at 3.60 (triplet), 2.3 (quintet), 4.07 (triplet), 6.83 (doublet), and 7.27 ppm (doublet) due to the 4-alkylated 3-bromopropoxyphenyl moieties. Integration of these resonances (see integration data, Figure 2, spectrum A) in comparison with the aromatic initiator resonance at 7.17 ppm indicates quantitative capping and production of difunctional, telechelic primary bromide PIB.

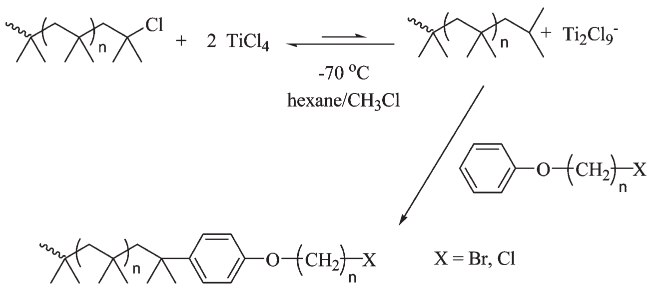

Figure 1. End-quenching of quasi-living polyisobutylene with an ω-haloalkoxybenzene.

Figure 3 shows gel permeation chromatography (GPC) traces for the difunctional PIB immediately before quenching with 3-bromopropoxybenzene and after complete capping of the chain ends. Number-average molecular weights (and polydispersities) calculated from the chromatograms were 3.1×10^3 g/mol (1.13) immediately before and 3.5×10^3 g/mol (1.11) after quenching. The chromatograms do not show any evidence of chain coupling due to double alkylation of a single ring. The absence of any apparent

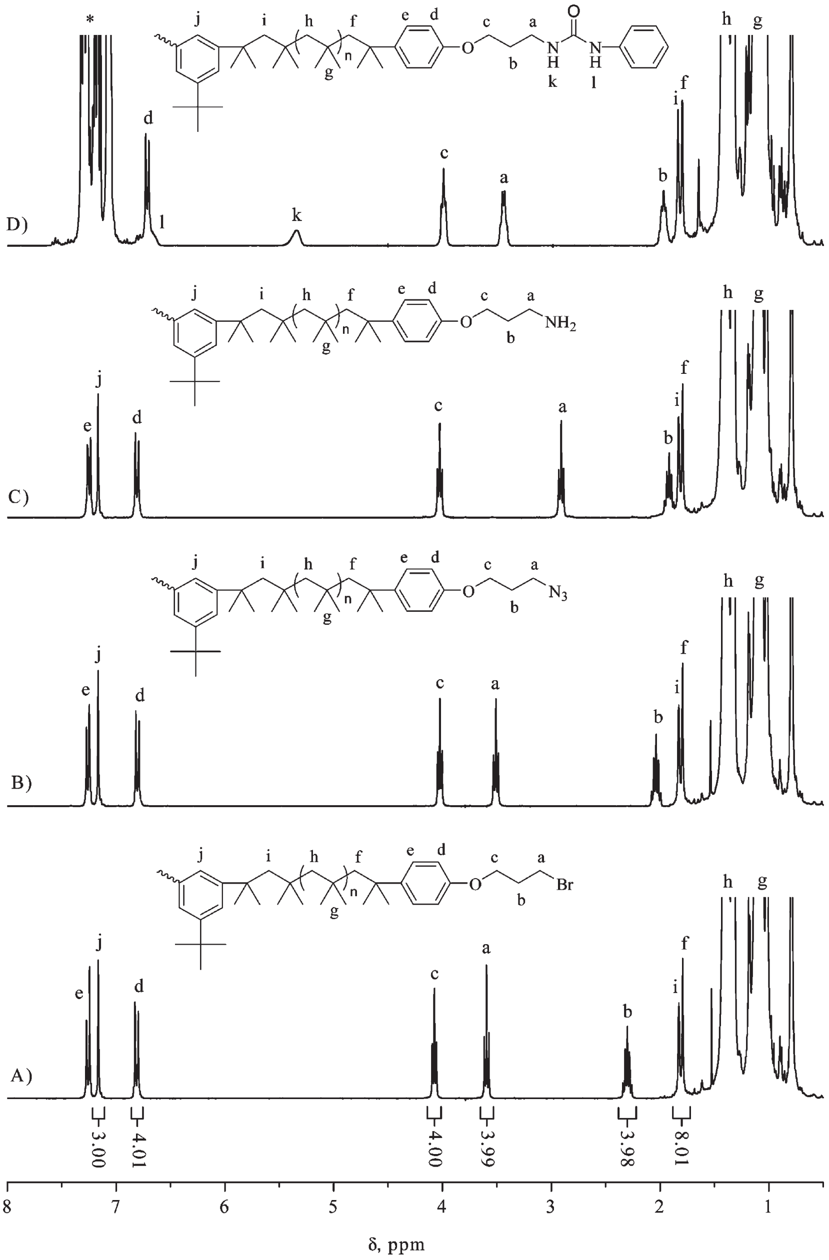

Figure 2. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) spectra of (A) α,ω-bis[4-(3-bromopropoxy)phenyl]polyisobutylene with peak integrations, (B) α,ω-bis[4-(3-azidopropoxy)phenyl]polyisobutylene, (C) α,ω-bis[4-(3-aminopropoxy)phenyl]polyisobutylene, and (D) the reaction product of α,ω-bis[4-(3-aminopropoxy)phenyl]polyisobutylene and excess phenyl isocyanate (*).

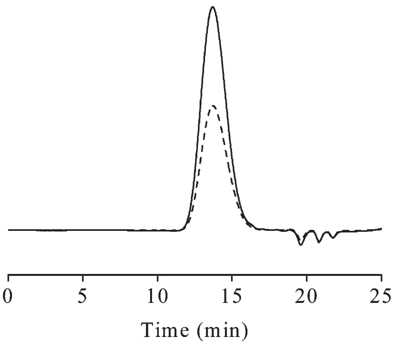

Figure 3. GPC differential refractive index traces of PIB before (dotted line) and after (solid line) quenching with 3-bromopropoxybenzene.

tendency toward coupling, even for a difunctional PIB, suggests that the overall concentration of the system can be increased for process optimization without ill effect.

To further illustrate the utility of end-capping polyisobutylene with 3-bromopropoxybenzene, we have demonstrated the facile conversion of the primary bromide terminus to azide and, subsequently, primary amine. Sodium azide was found to rapidly displace the terminal bromide when reacted with the polymer in 50/50 (v/v) heptane/DMF under reflux. Figure 2 (spectrum B) shows a ^{1}H NMR spectrum of the resulting polymer, where evidence of quantitative conversion to azide is represented in an upfield shift in the resonances due to the tether methylene units, notably 3.6−3.51 ppm (labeled a) and 2.3−2.04 ppm (labeled b). The terminal primary azide was readily converted to primary amine via hydrogenation in the presence of Pd on activated carbon. Figure 2 (spectrum C) shows a ^{1}H NMR spectrum of the resulting telechelic primary amine PIB; quantitative reduction of the azide is evidenced by an upfield shift in the resonances due to the tether methylene units, 3.51−2.91 ppm (a) and 2.04−1.92 ppm (b). Saturation of the aromatic initiator and quencher residues in the polymer did not occur under the conditions for reduction of the azide. Presence of primary amine at the chain end was further confirmed by addition of excess phenyl isocyanate to the amine telechelic PIB in chloroform-*d* at room temperature. The amine rapidly and quantitatively reacted to form a urea, and as shown in Figure 2 (spectrum D), the terminal methylene resonance shifted from 2.91 to 3.44 ppm (a), and the signal was split into a quartet due to coupling with the adjacent urea proton.

Experimental Section. 3-Bromopropoxybenzene (96%), palladium (Pd) on activated carbon (10% Pd by weight dry loading), sodium azide (99.5%), and phenyl isocyanate (98%) were purchased from Sigma-Aldrich and used as received. Other materials and polymer characterization have been previously described.[12,26,27]

Preparation of α,ω-*Bis*[*4-*(*3-Bromopropoxy*)*phenyl*]*polyisobutylene*. Under a N_2 atmosphere, 60 mL of hexane and 90 mL of methyl chloride were chilled to −70 °C and placed in a four-neck 250 mL round-bottom flask equipped with an overhead stirrer, thermocouple, and infrared probe. To the 40/60 (v/v) hexane/methyl chloride solvent mixture were added 2.74 g (9.6 mmol) of 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene initiator (bDCC), providing a chain end concentration of 0.1 M, and 0.11 mL (1 mmol) of 2,6-lutidine. A final molecular weight near 3000 g/mol was targeted by charging the reactor with 32.7 mL (401 mmol) of isobutylene. After thermal equilibration, the polymerization was initiated with 0.125 mL (1.14 mmol) of $TiCl_4$. After the initial reaction exotherm had passed, a second 0.125 mL charge of $TiCl_4$ was added at 35 min to lessen the total polymerization time. Complete monomer conversion was attained after ~90 min, at which point 7.52 mL (47.8 mmol, 2.5 equiv per chain end) of 3-bromopropoxybenzene was charged to the reactor along with an additional 2.1 mL (19.1 mmol) of $TiCl_4$ to increase the rate of 3-bromopropoxybenzene alkylation. After 3.5 h, the catalyst was destroyed by addition of excess methanol, and the PIB was isolated by precipitation from hexane into methanol/acetone.

Preparation of α,ω-*Bis*[*4-*(*3-Azidopropoxy*)*phenyl*]*polyisobutylene*. Difunctional primary bromide-terminated PIB (10 g) was dissolved in 100 mL of a 50/50 (v/v) mixture of heptane and DMF. To this biphasic mixture was added 4.33 g (66.6 mmol) of sodium azide. The mixture was heated to 90 °C, upon which it became monophasic, and allowed to react for 2.5 h. After cooling and phase separation, the heptane layer was washed with deionized water; the polymer was precipitated into methanol, and the residual solvent was removed under vacuum.

Preparation of α,ω-*Bis*[*4-*(*3-Aminopropoxy*)*phenyl*]*polyisobutylene*. Difunctional primary azide-terminated PIB (1.5 g) was dissolved in 15 mL of hexane. To this solution was added 0.04 g of Pd on activated carbon. The solution was pressurized with 50 psig of H_2 for 6 h on a Parr shaker-type hydrogenation apparatus. After settling of the catalyst, the supernatant was passed through a 0.2 μm pore diameter PTFE filter, and the solvent was removed under vacuum.

Preparation of α,ω-*Bis*{*4-*[*3-*(*phenyliminocarbonylimino*)*propoxy*]*phenyl*}*polyisobutylene*. One drop of neat phenyl isocyanate was added to a solution (0.02 mol/L) of difunctional primary amine-terminated PIB in chloroform-*d* within a 5 mm NMR tube at room temperature.

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