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End-Quenching of $TiCl_4$-Catalyzed Quasiliving Polyisobutylene with Alkoxybenzenes for Direct Chain End Functionalization

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ABSTRACT: Alkoxybenzenes were used to end-quench $TiCl_4$-catalyzed quasiliving isobutylene polymerizations initiated from 2-chloro-2,2,4-trimethylpentane or 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene at −70 °C in 40/60 (v/v) hexane/methyl chloride. The alkoxybenzene/chain end molar ratios were in the range 2.5−4. Effective alkoxybenzene quenchers included those with simple alkyl groups, such as anisole and isopropoxybenzene, haloalkyl tethers, such as (3-bromopropoxy)benzene and (2-chloroethoxy)benzene, and even those with hydroxyl and amine functionality, such as 4-phenoxy-1-butanol and 6-phenoxyhexylamine. Alkylation was generally quantitative and occurred exclusively in the *para* position; multiple alkylations on the same alkoxybenzene were not observed. The alkylation reactions were tolerant of temperatures ranging from −70 to −30 °C and were unimpeded by the presence of *endo*- or *exo*-olefin termini. *In situ* cleavage of the ether linkage of anisole and isopropoxybenzene termini allowed single pot syntheses of phenol-terminated polyisobutylenes.

Introduction

Polyisobutylene (PIB) is a versatile material with properties desirable for applications ranging from lubricant additives[1] to biomaterials.[2] However, the use of PIB in preparation of more complex materials may require introduction of a reactive and/or polar functionality at the chain end. For most commercially produced PIBs the available starting functionality is olefin, which arises naturally from β-proton expulsion in chain transfer dominated polymerization processes. In BF_3-catalyzed polymerizations the content of highly reactive methylvinylidene or *exo*-olefin chain ends can be as high as 70−90%; however, protic initiation causes these PIBs to contain only a single reactive terminus.[3,4] With the development of methods enabling controlled polymerization of isobutylene from multifunctional initiators,[5] synthesis of telechelic PIBs became possible. These processes, mainly involving BCl_3 or $TiCl_4$ co-initiators, are generally conducted under conditions whereby the growing chain ends are in equilibrium between dormant and active states.[6] Such conditions naturally lead to *tert*-chloride functionality at the chain end,[7] and post-polymerization dehydrochlorination would still be required to synthesize *exo*-olefin telechelic PIB.[8−10]

Olefin-terminated PIB has been subjected to numerous post-polymerization transformations, including hydroboration−oxidation,[11] hydroformylation,[12] epoxidation,[13] ozonolysis,[14,15] lithiation,[16] sulfonation,[17] hydrosilylation,[18] and hydrobromination.[19] The terminal unsaturation has also been used as a Friedel−Crafts alkylating agent[20] and a substrate for the free radical addition of thiols.[21] These and subsequent postpolymerization transformations provide useful chain end functionality, but often with difficultly and/or significant expense. That has provided impetus for the development of technology aimed at obtaining functionalities other than *tert*-chloride and/or *exo*-olefin directly from isobutylene polymerizations. Two approaches to *in situ* functionalization have been taken; one is to begin the polymerization with a functional initiator, and the other is addition of suitable nucleophiles to the polymerization at full monomer conversion (end-quenching).

Functional initiators reported for isobutylene polymerization have included structures with nonpolymerizable olefins,[22−24] acetates,[25] protected[26] and unprotected[27] phenols, and silyl chlorides.[28−31] Other reported initiators have involved cyclic moieties such an epoxide[32] or lactone[33] that ring open in the presence of $TiCl_4$ to provide hydroxyl and ester functionality, respectively. Unfortunately, functional initiators only provide the desired functionality at the initiation site, and the PIB chain terminus remains *tert*-chloride unless subsequently modified or a coupling strategy is employed.

The approach of quenching an isobutylene polymerization with a nucleophile that either adds to or modifies the chain end has been somewhat more successful due to avoidance of complications that could arise during initiation and propagation from a functional initiator. However, a judicious choice of nucleophile is required because of rapid and often overwhelming interaction with the Lewis acid catalyst, rendering one or both unreactive. Soft π-nucleophiles, such as nonpolymerizable monomers[34−38] and heterocyclic aromatic substrates,[39−41] have been used to successfully cap $TiCl_4$-catalyzed quasiliving PIB. In addition, certain hindered organic nitrogen bases,[42,43] ethers/alkoxysilanes,[44] and (di)sulfides[45] have proven useful for *in situ* transformation of the PIB chain end to olefin. Despite many advances in quenching technology, large scale practicability may be limited due to reagent expense as well as requirements for low temperatures and/or dilute reaction systems.

In cationic polymerization systems, alkylation of arenes was recognized early but was generally regarded as a chain transfer/termination reaction only useful for controlling molecular weight. For example, Plesch et al. reported that polystyrene polymerizations catalyzed by $TiCl_4$ in toluene resulted in polymers with tolyl end groups[46] and that anisole may act as chain terminating agent for $TiCl_4$-catalyzed isobutylene polymerization, as evidenced by *p*-methoxyphenyl end groups.[47] Similarly, Overberger et al.[48−50] found that a wide variety of mono- and

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dialkyl-substituted aromatics function as chain-terminating agents in $SnCl_4$-catalyzed polymerization of styrene at 0 °C. When Russell et al.[51−56] conducted $SnCl_4$-catalyzed isobutylene polymerizations in ethyl chloride at −78.5 °C with phenol and substituted phenols as cocatalysts (initiators), they found evidence of phenolic end groups; however, proton expulsion was also a significant chain breaking event, leading to terminal unsaturation.[57]

The first attempts at controlled termination of carbocationic polymerizations with an arene were reported by Kennedy et al.[58−61] when they used a triphenylaluminum/*tert*-alkyl chloride initiating system. The arylaluminum acted as both a catalyst and chain terminating agent, yielding α,ω-diphenyl PIBs with 0.7−1.7 phenyl groups per chain. For polystyrene, Hunter et al.[62] demonstrated that 40−70% of the chain ends may be capped by alkylphenols under $AlCl_3$ catalysis. Zhang et al.[63] reported direct addition of triphenylamine to PIB synthesized from a H_2O/$TiCl_4$ initiating system. The maximum capping efficiency was in the 70−80% range, and the process was plagued by competitive *exo*-olefin formation due to the presence of the basic amine.[42] Fujisawa et al.[64] disclosed quenching of $SnCl_4$-catalyzed isobutylene polymerizations with vinylalkoxybenzenes. The alkylation reactions were performed in methylene chloride from −30 °C to room temperature, and vinyl end group functionalities from 76 to 90% were obtained.

Because of limited success at *in situ* alkylation/incorporation of arenes, namely phenol, at the PIB chain end, much attention has been given to postpolymerization Friedel−Crafts alkylations. Conventional PIBs made from $AlCl_3$ catalysis have relatively high amounts of tri- and tetra-substituted olefin end groups, and the harsh acid catalysis required to induce alkylation via the olefin end group may also induce fragmentation of the polymer chain. Selection of appropriate alkylation catalysts[65,66] and conditions or modification of the polymer chain end[67] can minimize these problems. However, arene alkylation with the olefin terminus became more practical with the commercial availability of high methyl vinylidene (>70%) PIB. With the highly reactive isomer, alkylation can be carried out in the absence of molecular weight degradation.[68] Typical alkylation catalysts include Lewis acids (e.g., $AlCl_3$, BF_3, and BF_3 complexes), trifluoromethanesulfonic acid, and acidic molecular sieves (e.g., Amberlyst 36).

The discovery of conditions that allowed for controlled quasiliving polymerization of isobutylene also led to polymers with quantitative chain end functionality. Kennedy et al. made use of these telechelic polyisobutylenes and reported postpolymerization alkylation of phenol,[69,70] anisole,[71] benzene, toluene, and xylene[72] with both *tert*-chloride- and *exo*-olefin-terminated PIB. The Friedel−Crafts alkylations were most often catalyzed by BF_3−etherate in hexanes or aromatic/dichloromethane solvent mixtures at temperatures from 20 to 55 °C; unfortunately, warmer temperatures, especially above 60 °C, apparently favored cracking and depolymerization. Even with the more reactive arenes, phenol and anisole, reaction times of 2 days were required for complete conversion of the chain ends. Bergbreiter et al.[73] also reported the alkylation of highly activated benzene derivatives with *exo*-olefin-terminated PIB in the presence of concentrated sulfuric acid, but the reactions required 60 h for complete conversion. Marechel et al.[27,74] reported $SnCl_4$-catalyzed alkylation of phenol with *exo*-olefin-terminated PIB at temperatures from −50 to 0 °C in dichloromethane within 1−3 h; however, polymer degradation was observed, becoming more severe at higher temperatures. Kennedy et al.[72,75] have reported alkylation of less reactive arenes such as benzene, toluene, and 2-bromoethylbenzene by *tert*-chloride-terminated PIB in fewer than 5 h using aluminum trichloride catalysis at temperatures between −50 and −80 °C. In these and all other alkylation reactions involving arenes and PIB, selection of catalyst, solvent, and reaction temperature is critical to prevent unwanted degradation and/or cracking of PIB. Unfortunately, the conditions necessary for the Friedel−Crafts alkylation reactions are usually not the same as those required for quasiliving carbocationic polymerization of isobutylene, and therefore, arene-functionalized PIBs have predominately been prepared in multistep processes.

Here, we report the successful alkylation of a range of alkoxybenzene compounds with $TiCl_4$-catalyzed quasiliving PIB, leading to quantitative capping of the chain ends. Alkylation and subsequent *in situ* deprotection of simple alkyl phenols allowed for direct synthesis of phenolic PIBs. In addition, important functionalities such as primary halide, hydroxyl, and amine were obtained at the PIB chain end in a single step via end-quenching of the polymerization. The alkylations were remarkably tolerant of changes in temperature, e.g., up to −30 °C, as well as the presence both *endo*- and *exo*-olefin-terminated PIB.

Experimental Section

Materials. Hexane (anhydrous, 95%), titanium tetrachloride ($TiCl_4$) (99.9%), boron tribromide (BBr_3) (99.9%), 2,6-lutidine (redistilled, 99.5%), phenol (99%), anisole (anhydrous, 99.7%), (2-chloroethoxy)benzene (98%), (2-bromoethoxy)benzene (98%), (3-bromopropoxy)benzene (96%), allyl phenyl ether (99%), 2,6-di-*tert*-butylphenol (99%), 2-bromopropane (99%), phenyl propargyl ether (90%), chlorotrimethylsilane (97%), tetrahydrofuran (THF) (anhydrous, 99.9%), methyllithium (1.6 M in diethyl ether), calcium hydride (CaH_2) (95%), 4-phenoxybutyric acid (98%), lithium aluminum hydride ($LiAlH_4$) (powder, 95%), 1,6-dibromohexane (96%), zinc (dust, 98%), butyl phenyl ether (99%), potassium benzoate (99%), potassium *tert*-butoxide (95%), tetrabutylammonium fluoride (1 M in THF) (TBAF), and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. 3-Phenoxypropyldimethylchlorosilane was purchased from Gelest and used as received. Dimethylformamide (DMF) (99.8%), heptane, diethyl ether, ethyl acetate, ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), concentrated sulfuric acid (H_2SO_4), anhydrous magnesium sulfate ($MgSO_4$), anhydrous sodium sulfate (Na_2SO_4), sodium bicarbonate ($NaHCO_3$), and ammonium chloride (NH_4Cl) were purchased and used as received from Fisher Scientific. Isobutylene (BOC Gases) and methyl chloride (Alexander Chemical Corp.) were dried by passing the gases through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glovebox immediately prior to use. Boron trichloride (BCl_3) purchased from Matheson was also condensed immediately prior to use. The monofunctional initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), was prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich) at 0 °C. The HCl-saturated TMPCl was stored at 0 °C, and immediately prior to use it was neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The difunctional initiator, 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-DCC), was synthesized as previously reported[76] and stored at 0 °C.

Isopropoxybenzene. Isopropoxybenzene was synthesized by reaction of phenolate with 2-bromopropane. Typically, 30 g (319 mmol) of phenol, 36 mL (383 mmol) of 2-bromopropane, and 15.3 g (383 mmol) of NaOH were combined in 100 mL of DMF and heated to reflux in a 70 °C oil bath. After 16 h, the reaction was cooled, and the product was extracted into diethyl ether, washed with deionized water, and dried over $MgSO_4$. Removal of solvent under reduced pressure and vacuum distillation from CaH_2 provided 44 g (86%) of a colorless liquid. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.36 (d, methyl, J = 6.06 Hz, 6H), 4.57 (m, methine, J = 6.06 Hz, 1H), 6.92 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.29 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 22.1 (methyl), 69.7 (methine), 115.9, 120.5, 129.5, 157.9 (aromatic).

Trimethyl(3-phenoxy-1-propynyl)silane. The alkyne moiety of phenyl propargyl ether was protected with trimethylsilane.

Typically, 12.3 mL (95.5 mmol) of phenyl propargyl ether was dissolved in 50 mL of THF and chilled to −30 °C. To this solution was added dropwise 66 mL (106 mmol) of methyllithium as a 1.6 M solution in diethyl ether. After 15 min, 24 mL (189 mmol) of chlorotrimethylsilane was slowly charged to the reactor. After the initial exotherm, the reaction was allowed to warm and sit overnight at room temperature. The reaction mixture was filtered and concentrated on a rotary evaporator. Vacuum distillation from CaH_2 afforded 15.6 g (80%) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.20 (s, methyl, 9H), 4.69 (s, methylene, 2H), 6.99 (d, aromatic, 2H), 7.02 (d, aromatic, 1H), 7.31 (t, aromatic, 2H). ^{13}C NMR δ (ppm): −0.3 (methyl), 56.7 (methylene), 92.6 (*C*-Si), 100.1 (CH_2C), 114.9, 121.4, 129.4, 158.7 (aromatic).

4-Phenoxy-1-butanol. 4-Phenoxy-1-butanol was synthesized by $LiAlH_4$ reduction of 4-phenoxybutyric acid. Typically, 50 g (277 mmol) of 4-phenoxybutyric acid in 100 mL of THF was added dropwise to 10.5 g (277 mmol) of $LiAlH_4$ in 150 mL of THF at room temperature under N_2. After the initial exotherm, controlled by refluxing THF, the reaction sat overnight at room temperature. An aqueous solution of hydrochloric acid (0.1 M) was added to release the product, which was then extracted into diethyl ether and washed with deionized water until neutral. The organic layer was dried with Na_2SO_4, and the solvent was removed under vacuum. Vacuum distillation from calcium hydride afforded 33 g (72%) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.73 (m, $-CH_2CH_2OH$, 2H), 1.86 (m, $C_6H_5O-CH_2CH_2-$, 2H), 3.68 (t, $-CH_2OH$, J = 6.17 Hz, 2H), 3.98 (t, $C_6H_5O-CH_2-$, J = 6.17 Hz, 2H), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 25.8 ($C_6H_5O-CH_2CH_2-$), 29.5 ($-CH_2CH_2OH$), 62.4 ($-CH_2OH$), 67.7 ($C_6H_5O-CH_2-$), 114.5, 120.5, 129.4, 159.0 (aromatic).

6-Phenoxyhexylamine. 6-Phenoxyhexylamine was synthesized by reaction of phenolate with excess 1,6-dibromohexane, followed by displacement of bromide with azide and reduction of azide. Typically, 19.3 g (205 mmol) of phenol and 8.6 g (215 mmol) of NaOH were combined in 200 mL of DMF, and the reaction flask was heated to 80 °C. After 10 min, 100 g (410 mmol) of 1,6-dibromohexane was charged to the reaction. After 1 h, the reaction mixture was cooled, and the product was extracted into diethyl ether and washed with deionized water. Fractional vacuum distillation from CaH_2 provided 25.1 g (48%) of (6-bromohexoxy)benzene as a colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.5 (m, methylene, 4H), 1.8 (m, methylene, 2H), 1.9 (m, methylene, 2H), 3.41 (t, $-CH_2Br$, 2H), 3.95 (t, $C_6H_5O-CH_2-$, 2H), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 25.3, 28.0, 29.1, 32.7 (methylene), 33.9 ($-CH_2Br$), 67.6 ($C_6H_5O-CH_2-$), 114.5, 120.5, 129.4, 159.0 (aromatic).

In conversion of bromide to azide, 25.1 g (97.6 mmol) of (6-bromohexoxy)benzene and 19 g (293 mmol) of sodium azide were placed in 100 mL of DMF, and the mixture was heated at 90 °C for 3 h. The product was extracted into diethyl ether, washed with H_2O, and dried over Na_2SO_4, and the residual solvents were removed under vacuum to yield 17.7 g (83%) of (6-azidohexoxy)benzene. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.5 (m, methylene, 4H), 1.64 (m, methylene, 2H), 1.8 (m, methylene, 2H), 3.28 (t, $-CH_2N_3$, 2H), 3.96 (t, $C_6H_5O-CH_2-$, 2H), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 25.7, 26.5, 28.8, 29.2 (methylene), 51.4 ($-CH_2N_3$), 67.6 ($C_6H_5O-CH_2-$), 114.5, 120.5, 129.4, 159.0 (aromatic).

In reduction of the azide,[77] 17.7 g (80.7 mmol) of (6-azidohexoxy)benzene and 8.6 g (161 mmol) of ammonium chloride were placed into 100 mL of ethyl acetate at room temperature. While vigorously stirring, 7.9 g (121 mmol) of zinc dust was slowly added, and the exotherm was controlled by refluxing ethyl acetate. After 15 min, the reaction mixture was washed with NH_4OH and then deionized water. Removal of the solvent under vacuum, followed by vacuum distillation from calcium hydride provided 14.3 g (92%) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.45 (m, methylene, 6H), 1.77 (m, $C_6H_5O-CH_2CH_2-$, 2H), 2.67 (t, $-CH_2NH_2$, J = 6.84 Hz, 2H), 3.93 (t, $C_6H_5O-CH_2-$, J = 6.49 Hz, 2H), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 26.0 ($C_6H_5O-CH_2CH_2CH_2-$), 26.7 ($-CH_2CH_2CH_2NH_2$), 29.3 ($C_6H_5O-CH_2CH_2-$), 33.7 ($-CH_2CH_2NH_2$), 42.1 ($-CH_2NH_2$), 67.7 ($C_6H_5O-CH_2-$), 114.5, 120.5, 129.4, 159.0 (aromatic).

6-Phenoxy-1-hexanol and 8-Phenoxy-1-octanol. The longer chain phenoxyalkanols were synthesized by reaction of phenolate with haloalkanols. For synthesis of 6-phenoxy-1-hexanol, 18.9 g (0.201 mol) of phenol and 18.3 g (0.457 mol) of NaOH were combined in 100 mL of DMF and heated to 80 °C. To the heated solution was charged 25 g (0.183 mol) of 6-chloro-1-hexanol. After 3 h, the reaction mixture was neutralized with HCl, and the product was extracted into diethyl ether and washed with deionized water. Vacuum distillation provided 34.8 g (78%) of a crystalline solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.47 (m, methylene, 4H), 1.61 (m, $-CH_2CH_2OH$, 2H), 1.80 (m, $C_6H_5O-CH_2CH_2-$, 2H), 3.65 (m, $-CH_2OH$, 2H), 3.96 (t, $-CH_2-OC_6H_5$, J = 6.48 Hz, 2H), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H). ^{13}C NMR δ (ppm): 25.6 ($-CH_2CH_2CH_2-OH$), 25.9 ($C_6H_5O-CH_2CH_2CH_2-$), 29.3 ($-CH_2CH_2-OH$), 32.7 ($C_6H_5O-CH_2CH_2-$), 62.9 ($-CH_2OH$), 67.7 ($C_6H_5O-CH_2-$), 114.5, 120.5, 129.4, 159.0 (aromatic). A similar reaction with 8-chloro-1-octanol yielded 8-phenoxy-1-octanol.

Instrumentation. Nuclear magnetic resonance (NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Standard ^{1}H and ^{13}C pulse sequences were used. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^{1}H chemical shifts were referenced to TMS (0 ppm), and all ^{13}C shifts were referenced to the $CDCl_3$ solvent resonance (77.0 ppm). Samples were prepared by dissolution in $CDCl_3$ (20−50 mg/mL) and charging this solution to a 5 mm NMR tube.

Number-average molecular weights ($\overline{M}_n$) and polydispersities (PDI = $\overline{M}_w/\overline{M}_n$) were determined with a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an online multiangle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (Optilab rEX, Wyatt Technology Inc.) operating at 35 °C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed E columns (pore size range 50−10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were ca. 15−20 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a dn/dc calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Real-time ATR-FTIR monitoring of isobutylene polymerizations was performed using a ReactIR 4000 (Mettler-Toledo) integrated with a N_2-atmosphere glovebox (MBraun Labmaster 130).[78] Isobutylene conversion during polymerization was determined by monitoring the area, above a two-point baseline, of the absorbance centered at 887 cm^{-1}, associated with the $=CH_2$ wag of isobutylene.

Polymerization, Quenching, and Postpolymerization Reactions. Table 1 lists conditions for polymerization and quenching reactions used to produce the various PIBs reported herein and molecular weight data for the resulting prequench *tert*-chloride PIBs, quenched PIBs, and further derivatives. Polymerization and quenching reactions were performed within a N_2-atmosphere glovebox equipped with cryostated heptane bath. Total reaction volumes of 100−200 mL, typically comprising a 40/60 (v/v) hexane/methyl chloride mixture, were contained in 250 mL round-bottom flasks equipped with an overhead stirrer, thermocouple, and ReactIR probe. $TiCl_4$-catalyzed polymerizations

Table 1. Conditions for Quasiliving Isobutylene Polymerizations and Alkylation (Quenching) Reactions

		component concentration (mol/L)[a]					reaction time (h)		
entry	quencher	initiator	IB	$TiCl_4$ pzn	quencher	$TiCl_4$ quench	pzn	quench	$\overline{M}_n \times 10^{-3}$ (PDI)[f]
1	anisole	0.025[b]	1.14	0.016	0.125	0.066	0.36	3.63	2.9 (1.14), 3.1 (1.10), 3.2 (1.08)[g]
2	isopropoxybenzene	0.025[b]	1.12	0.015	0.125	0.115	0.36	2.05	3.4 (1.05), 3.4 (1.04), 3.5 (1.03)[g]
3	2,6-di-*tert*-butylphenol	0.025[c]	0.75	0.017	0.100	0.167	0.71	1.06	2.0 (1.14), 2.2 (1.09)
4	allyl phenyl ether	0.050[c]	1.75	0.015	0.150	0.100	0.56	2.16	2.7 (1.34), 2.9 (1.31)
5	(2-chloroethoxy)benzene	0.040[c]	1.59	0.012	0.100	0.092	1.42	3.42	3.0 (1.21), 2.9 (1.23), 3.0 (1.22)[h]
6	(3-bromopropoxy)benzene	0.050[b]	2.08	0.012[e]	0.250	0.112	1.58	3.42	3.1 (1.13), 3.5 (1.04), 3.5 (1.12)[i]
7	3-phenoxypropyldimethylchlorosilane[d]	0.010[b]	0.76	0.100	0.060	0.100	0.33	1.50	4.9 (1.01), 5.6 (1.05)
8	trimethyl(3-phenoxy-1-propynyl)silane	0.025[c]	0.75	0.017	0.100	0.167	0.68	5.35	2.2 (1.19), 2.5 (1.18), 2.5 (1.16)[j]
9	4-phenoxy-1-butanol	0.024[b]	1.05	0.014	0.144	0.494	0.40	7.70	2.9 (1.07), 3.2 (1.05)
10	6-phenoxyhexylamine	0.025[b]	1.09	0.015	0.125	0.190	0.48	9.00	3.1 (1.07)

[a] Polymerization and alkylation reactions at −70 °C in 40/60 (v/v) hexane/methyl chloride in the presence of 0.005 M 2,6-lutidine. [b] Initiated from bDCC. [c] TMPCl. [d] 60/40 (v/v) hexane/methyl chloride. [e] Added in two equal portions to control exotherm. [f] Molecular weight prior to alkylation, after alkylation, and after further modification (see Experimental Section) to phenolic (g), vinyl ether (h), hydroxyl (i), and alkynyl functional PIB (j).

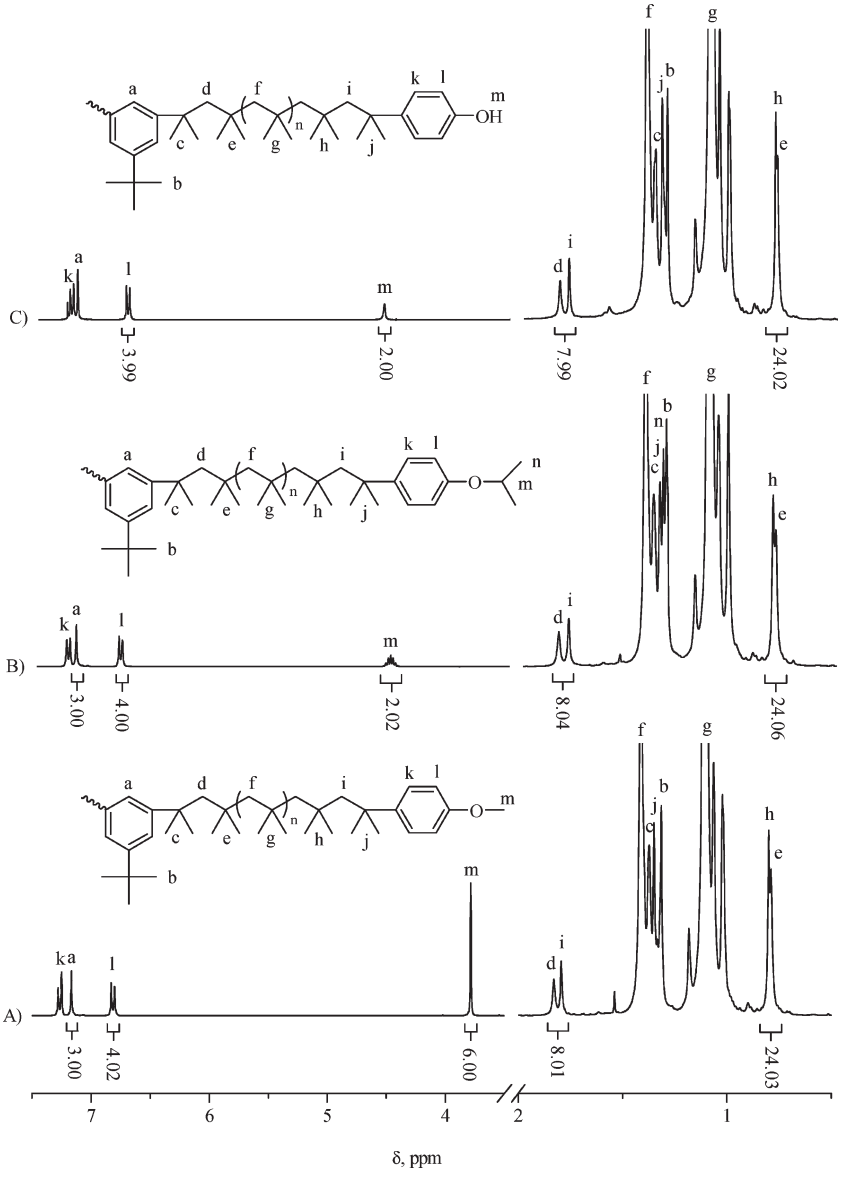

Figure 1. ^1H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis(4-methoxyphenyl)polyisobutylene and (B) α,ω-bis(4-isopropoxyphenyl)polyisobutylene obtained by direct addition of anisole and isopropoxybenzene, respectively, to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations and (C) α,ω-bis(4-hydroxyphenyl)polyisobutylene obtained by *in situ* demethylation or deisopropylation (Table 1, entries 1 and 2).

of isobutylene at −70 °C in the presence of 2,6-lutidine (0.005 M) were initiated from either TMPCl or *t*-Bu-*m*-DCC at concentrations of 0.01−0.05 M. Isobutylene charges were chosen to target molecular weights of 2000−5000 g/mol. The $TiCl_4$ polymerization catalyst, typically around 0.015 M, resulted in polymerization times from 20 to 90 min, depending on the initiator and its

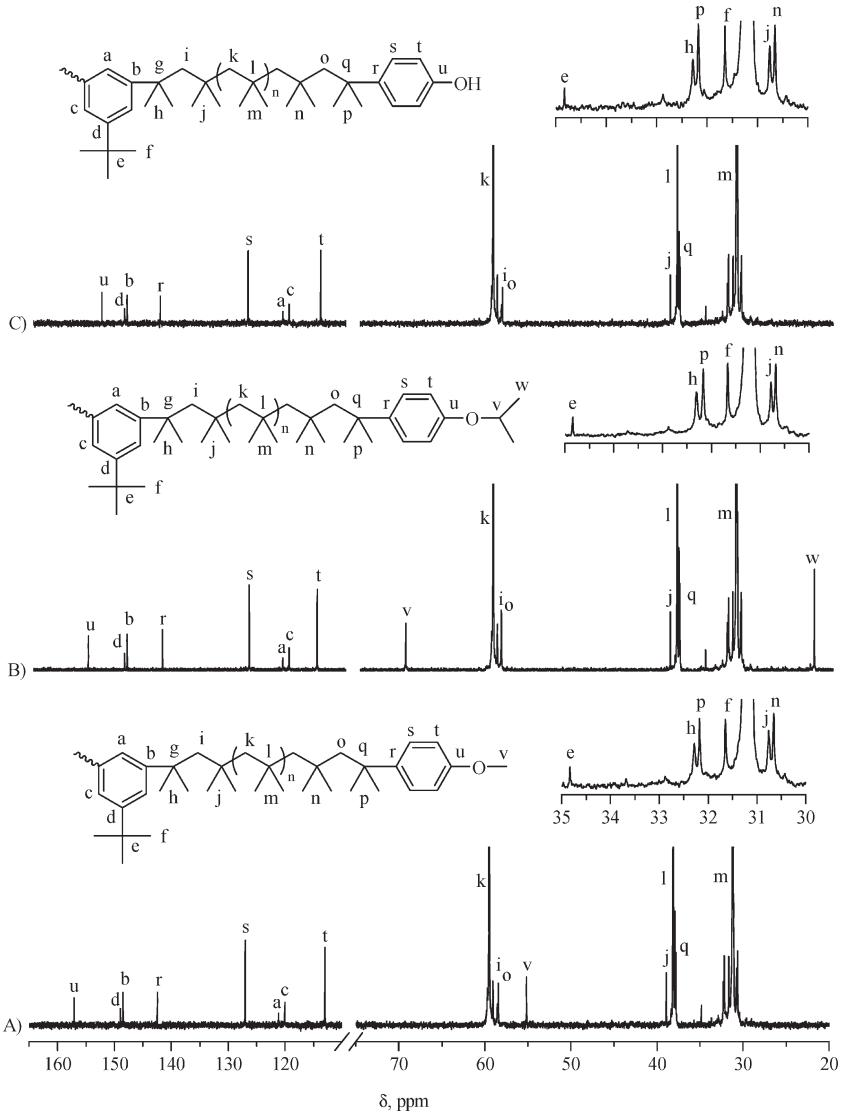

Figure 2. ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis(4-methoxyphenyl)polyisobutylene and (B) α,ω-bis(4-isopropoxyphenyl)polyisobutylene obtained by direct addition of anisole and isopropoxybenzene, respectively, to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations and (C) α,ω-bis(4-hydroxyphenyl)polyisobutylene obtained by *in situ* demethylation or deisopropylation (Table 1, entries 1 and 2).

concentration. At full monomer conversion, the alkoxybenzene quenchers were charged to the reaction, typically at 2.5−4 equiv per chain end. Additional $TiCl_4$ (1−6 equiv per chain end) was added to catalyze the alkylations reactions, resulting in overall $TiCl_4$ concentrations near 0.1 M. For alkoxybenzenes such as 4-phenoxy-1-butanol and 6-phenoxyhexylamine the $TiCl_4$ concentrations were augmented to account for complexation of the hydroxyl and amine moieties, respectively. Alkylations were allowed to proceed from 1 to 4 h in most cases; however, the highly complexing alkoxybenzenes required 7−9 h for complete capping of the chain ends. Finally, the catalysts were destroyed by addition of excess methanol, and the PIBs were isolated by precipitation from hexane into methanol.

With anisole and isopropoxybenzene an additional deblocking step was required before destruction of the catalyst to obtain phenolic PIB. For anisole, cleavage of the terminal methyl ether involved charging the reactor with an excess (6 equiv per chain end) of BBr_3 and allowing the reaction to warm at room temperature for 22 h. For isopropoxybenzene, additional $TiCl_4$ (2 eq per chain end) and H_2SO_4 (0.3 mL) were charged to the reactor, and it was allowed to warm at room temperature for 5.5 h.

The primary chloride functional PIB obtained via quenching with (2-chloroethoxy)benzene was converted to a vinyl ether by dehydrochlorination with potassium *tert*-butoxide. Typically, 15 mL of heptane was used to dissolve 1.6 g of monofunctional primary chloride PIB (2.9×10^3 g/mol), and to this mixture was added an equal volume of DMF and 0.62 g (10 equiv per chain end) of potassium *tert*-butoxide. The two-phase reaction mixture was heated, upon which it became monophasic, and the reaction was conducted at reflux for 1 h. The reaction mixture was cooled, whereupon a biphasic mixture re-formed, and the heptane and DMF layers were separated. The heptane layer was washed with deionized water, dried over $MgSO_4$, and filtered, and finally the solvent was removed under vacuum.

The primary bromide functional PIB obtained via quenching with (3-bromopropoxy)benzene was converted to primary hydroxyl by displacement with benzoate, followed by hydrolysis. Typically, 2.5 g of difunctional primary bromide PIB (3.5×10^3 g/mol) was dissolved in 25 mL of heptane. This solution was added to 1.83 g (8 equiv per chain end) of potassium benzoate in 25 mL of DMF. The two-phase system was heated, upon which it became monophasic, and the reaction was conducted at reflux for 4 h. After cooling, the heptane layer was separated from the DMF layer and subsequently contacted with 2.2 g of NaOH in 25 mL of DMF. The reaction was again heated to reflux for 12 h. After cooling and phase separation, the heptane layer was washed with deionized water and dried over Na_2SO_4, and the solvent was removed under vacuum.

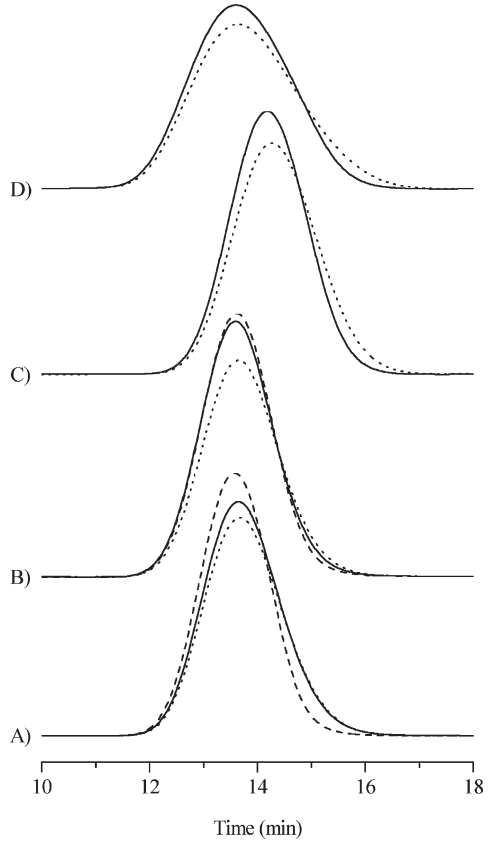

Figure 3. GPC differential refractive index traces of PIB obtained from $TiCl_4$-catalyzed quasiliving isobutylene polymerizations quenched with (A) anisole, (B) isopropoxybenzene, (C) 2,6-di-*tert*-butylphenol, and (D) allyl phenyl ether: prequench (dotted); postquench (solid); and after deblocking (dashed) to provide phenolic PIB (A and B only) (Table 1, entries 1−4).

The trimethylsilyl protecting group on PIB capped with trimethyl(3-phenoxy-1-propynyl)silane was removed with TBAF. Typically, 0.4 g of trimethyl(3-phenoxy-1-propynyl)silane-capped PIB (2.5×10^3 g/mol) was contacted with 10 mL of 1 M TBAF solution for 3 h at room temperature. The polymer solution was washed with deionized water, dried with $MgSO_4$, and filtered, and the solvent was removed under vacuum.

Results and Discussion

Anisole. Direct addition of anisole to a $TiCl_4$-catalyzed isobutylene polymerization at −70 °C in a 40/60 (v/v) hexane/methyl chloride solvent system resulted in alkylation of anisole and quantitative end-capping of the polyisobutylene chains. Exclusively monoalkylation, *para* to the alkoxy moiety, was observed. This is consistent with previous reports of $TiCl_4$-catalyzed Friedel−Crafts alkylation of arenes with *tert*-butyl and *tert*-amyl chlorides, which suggested that *para* substitution products dominate.[79] As shown by the ^{1}H NMR spectrum in Figure 1A, resonances that would otherwise appear at 1.69 and 1.96 ppm due to the ultimate *gem*-dimethyl and methylene unit of *tert*-chloride PIB were absent, and a new resonance appeared at 1.79 ppm due to the ultimate PIB methylene unit adjacent to anisole, as well as resonances at 6.82, 7.27, and 3.79 ppm, due to the alkylated anisole. Integration of the anisole moiety resonances in comparison with the aromatic initiator resonance at 7.17 ppm indicated quantitative capping of the chain ends. Further evidence of anisole alkylation is shown by the ^{13}C NMR spectrum in Figure 2A. Resonances at 71.9 and 35.2 ppm,

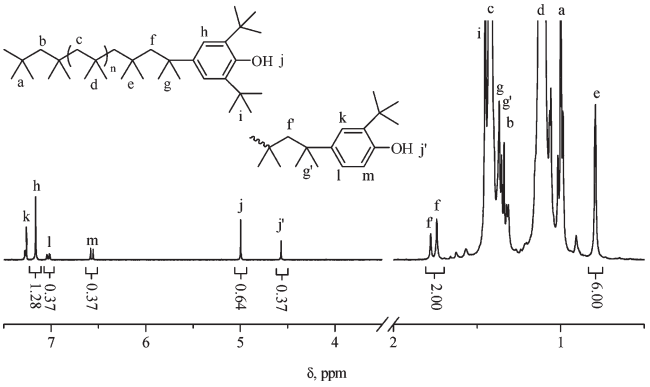

Figure 4. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectrum of 2,6-di-*tert*-butyl-4-polyisobutylphenol and 2-*tert*-butyl-4-polyisobutylphenol obtained by direct addition of 2,6-di-*tert*-butylphenol to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization (Table 1, entry 3).

representing the ultimate quaternary and *gem*-dimethyl carbons of *tert*-chloride PIB, respectively, were not present after the alkylation reaction and were replaced by a new set of resonances in the aromatic region and a resonance at 55.15 ppm due to the anisole methyl carbon.

The anisole end group by itself is not particularly useful, but demethylation via cleavage of the terminal ether would provide phenolic PIB, a product of significant importance. Ether cleavage is often performed under strongly acidic conditions; however, methyl ethers are relatively difficult to cleave.[80] Under the conditions used for quasiliving isobutylene polymerization and quenching, i.e., with $TiCl_4$ present at −70 °C, no cleavage of the terminal ether was observed. To achieve quantitative ether cleavage to phenolic end groups required addition of excess BBr_3 and 22 h at room temperature. Figure 1C shows the ^{1}H NMR spectrum of phenolic PIB obtained from the BBr_3-assisted demethylation of anisole-capped PIB. The resonance at 3.79 ppm due to the terminal methyl group was replaced by a new resonance at 4.57 ppm with 1/3 the intensity due to the phenolic proton. Demethylation was also evidenced in the ^{13}C NMR spectrum of Figure 2C by a disappearance of the methyl resonance at 55.15 ppm and an upfield shift of the resonance due to the aromatic carbon adjacent to oxygen from 157.1 to 152.9 ppm. The GPC traces of Figure 3A indicated no coupling during the alkylation/quenching reaction and no significant polymer degradation or depolymerization during BBr_3-assisted deblocking.

Isopropoxybenzene. The *in situ* demethylation of anisole-capped PIB to provide phenolic end groups required harsh conditions, i.e., addition of BBr_3, due to the strength of the methyl ether bond. More facile ether cleavage would be possible with bulkier alkyl groups; therefore, isopropoxybenzene was alkylated by quasiliving PIB under conditions similar to those used with anisole. Other alkyl groups could be used to protect phenol, but they must be stable under the alkylation reaction conditions.

A ^{1}H NMR spectrum of the isopropoxybenzene-capped PIB is shown in Figure 1B. Resonances due to the alkylated isopropoxybenzene ring appear at 6.79 and 7.23 ppm, and a resonance for the methine proton of the isopropyl moiety appears at 4.51 ppm. Evidence of isopropoxybenzene alkylation is also given by the ^{13}C NMR spectrum of Figure 2B by resonances in both the aromatic region and at 22.2 and 69.7 ppm due to the terminal isopropyl moiety.

Attempted cleavage of the terminal isopropyl ether with excess $TiCl_4$ (5 equiv per chain end) at room temperature for 30−48 h resulted in near quantitative (91%) phenol functionality.

However, subsequent experiments with the addition of excess BBr_3 (5 equiv) or BCl_3 (15 equiv) quantitatively cleaved the ether in less than 3 h while warming from −70 °C. The simplest approach found for rapid cleavage of the isopropyl ether was the addition of protic acid, namely H_2SO_4. With $TiCl_4$ and H_2SO_4 present in the reactor, less than 5 h was required to obtain quantitative phenol functional PIB. NMR spectra of the polymer obtained by H_2SO_4-assisted deblocking of isopropoxybenzene-capped PIB were identical to those in Figures 1C and 2C. Again, GPC traces of Figure 3B indicated no chain coupling and no polymer degradation during quenching and deblocking.

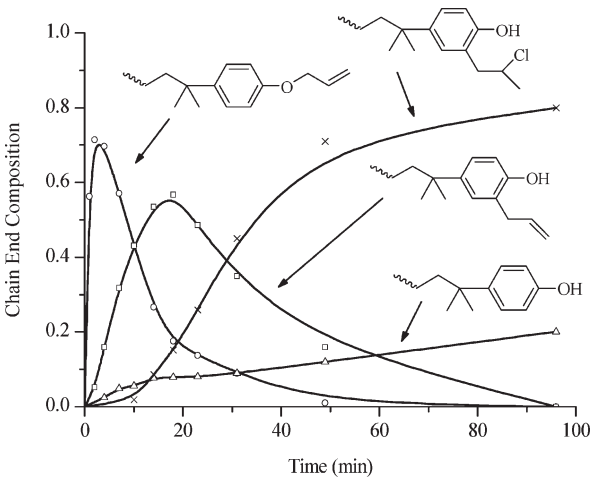

Figure 5. PIB chain-end composition after direct addition of allyl phenyl ether to a $TiCl_4$-catalyzed isobutylene polymerization. Alkylation of allyl phenyl ether (○) is accompanied by Claisen rearrangement to form 2-allylphenol end groups (□) and ether cleavage to form phenol end groups (Δ). The allyl functionality is also hydrochlorinated to provide 2-(2-chloropropyl)phenol end groups (×) (Table 1, entry 4).

2,6-Di-*tert*-butylphenol. Addition of phenol and various ring-alkylated phenols, such as 2-*tert*-butyl phenol, to $TiCl_4$-catalyzed isobutylene polymerizations did not yield alkylated chain ends. Failure of alkylation was probably due to insolubility of the phenolic−$TiCl_4$ complexes in the polymerization cosolvents in combination with deactivation of the Lewis acid catalyst, as evidenced by the near quantitative return of *tert*-chloride PIB. Only with the highly hindered phenol, 2,6-di-*tert*-butylphenol, did alkylation proceed at −70 °C in the 60/40 (v/v) methyl chloride/hexane solvent system. Monoalkylation occurred in the *para*-position; however, de-*tert*-butylation from the *ortho* position was also observed. De-*tert*-butylation on arenes is known to occur in the presence of Lewis acids,[81] and under appropriate conditions, selective *ortho*-de-*tert*-butylation of substituted phenols has been demonstrated.[82] As shown by the ^{1}H NMR spectrum in Figure 4, 37% of the chain ends were de-*tert*-butylated in about 1 h, and this amount increased over time: 44% at 5 h and 57% at 7 h. GPC traces shown in Figure 3C indicate the absence of chain coupling.

Allyl Phenyl Ether. Quenching with an alkoxybenzene whose alkoxy group contains a terminal olefin would represent a potential means of obtaining PIBs with an α-olefin terminus. Unfortunately, alkylation of the simplest alkoxybenzene with α-olefin functionality, allyl phenyl ether, was accompanied by simultaneous Claisen rearrangement and ether cleavage. Narasaka et al.[83] reported on the usefulness of $TiCl_4$ in catalyzing the [3,3]-sigmatropic concerted pericylic rearrangement of allyl aryl ethers and found that hydrochloric acid generated during the reaction often resulted in

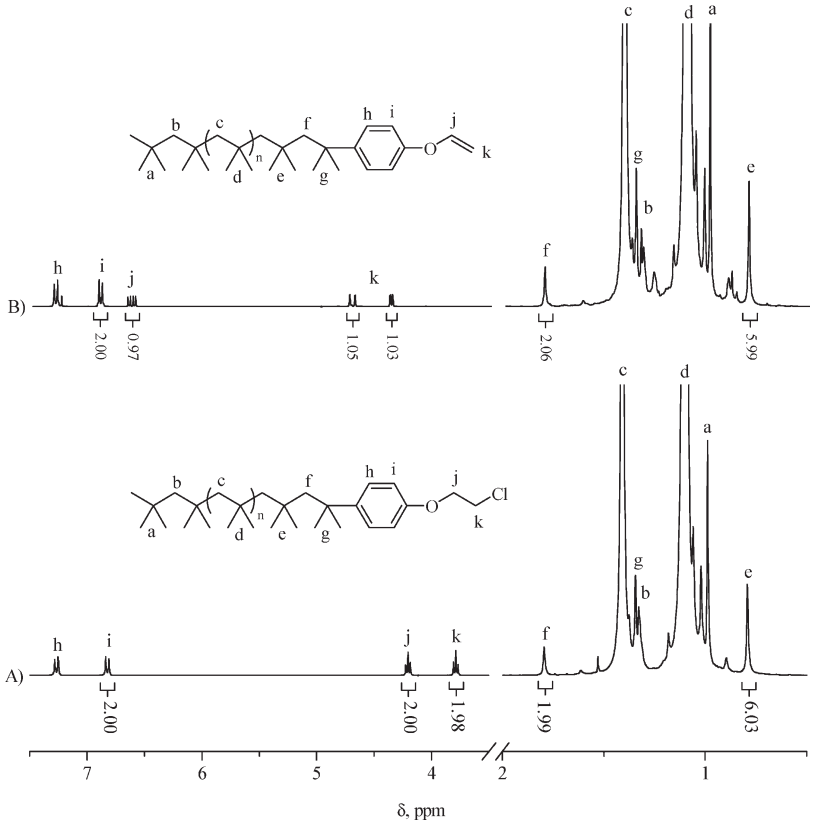

Figure 6. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of (A) 1-(2-chloroethoxy)-4-polyisobutylbenzene and (B) 1-vinyloxy-4-polyisobutylbenzene obtained by direct addition of (2-chloroethoxy)benzene to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent postpolymerization dehydrochlorination of the primary halide terminus (Table 1, entry 5).

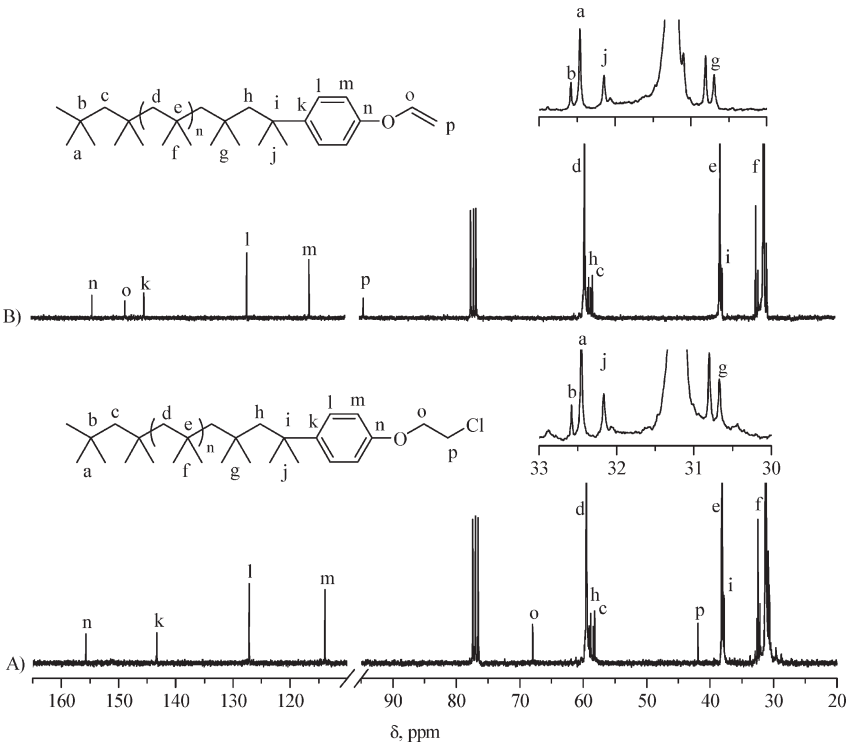

Figure 7. ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) spectra of (A) 1-(2-chloroethoxy)-4-polyisobutylbenzene and (B) 1-vinyloxy-4-polyisobutylbenzene obtained by direct addition of (2-chloroethoxy)benzene to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent postpolymerization dehydrochlorination of the primary halide terminus (Table 1, entry 5).

concomitant hydrochlorination of the newly formed *o*-allylphenol. As shown in Figure 5, simultaneous Claisen rearrangement and hydrochlorination were observed in addition to ether cleavage to provide chain ends capped with 2-(2-chloropropyl)phenol and phenol functionality. The GPC traces shown in Figure 3D indicate that the α-olefin was unreactive toward polymerization and chain coupling. Higher α-olefin homologues were not investigated because olefin functionality can more easily be obtained via dehydrohalogenation of a primary halide functional PIB obtained via *in situ* alkylation of *ω*-halo-alkoxybenzene.

(2-Chloroethoxy)benzene. Primary halide functional PIB was readily obtained by quenching quasiliving PIB with (*ω*-haloalkoxy)benzenes. For example, direct addition of 3 equiv per chain end of (2-chloroethoxy)benzene to a $TiCl_4$-catalyzed isobutylene polymerization at −70 °C in a 40/60 (v/v) hexane/methyl chloride solvent system resulted in alkylation of (2-chloroethoxy)benzene, as shown by the ^1H NMR spectrum in Figure 6A. A resonance for the ultimate PIB methylene unit adjacent to (2-chloroethoxy)benzene appeared at 1.79 ppm, and resonances at 3.79 (triplet), 4.21 (triplet), 6.83 (doublet), and 7.27 ppm (doublet) were due to the alkylated (2-chloroethoxy)benzene. Evidence of (2-chloroethoxy)benzene alkylation is also given by the ^{13}C NMR spectrum of Figure 7A. Resonances at 71.9 and 35.2 ppm, representing the ultimate quaternary and *gem*-dimethyl carbons of *tert*-chloride PIB, respectively, were not present after the alkylation reaction. A new set of resonances appeared in both the aromatic region and at 41.8 and 68.0 ppm due methylene carbons of the (2-chloroethoxy)benzene moieties.

Primary halide offers a wealth of opportunity for facile nucleophilic substitution reactions useful in conversion to other functionalities.[84] With a two-carbon tether between the halide and oxygen an easy transformation to a reactive macromer can be achieved by dehydrohalogenation. The primary chloride functional PIB was converted to a vinyl

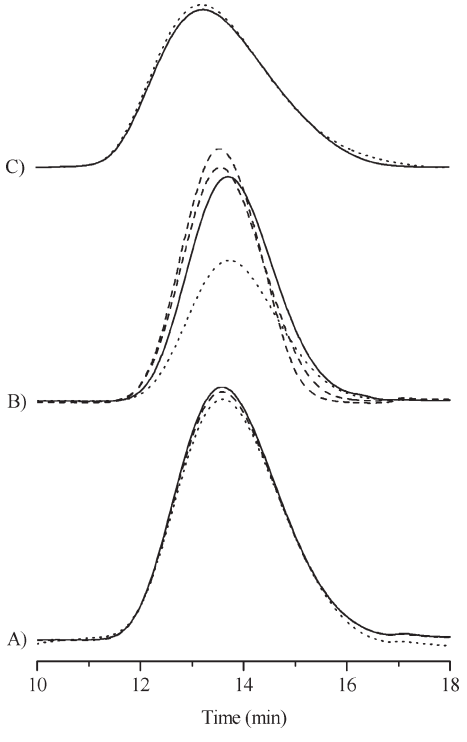

Figure 8. GPC differential refractive index traces of PIB obtained from $TiCl_4$-catalyzed quasiliving isobutylene polymerizations quenched with (A) (2-chloroethoxy)benzene and (B) (3-bromopropoxy)benzene: prequench (dotted); postquench (solid); and after conversion of the primary halide to vinyl ether (A only) and hydroxyl via benzoate hydrolysis (B only) (dashed) (Table 1, entries 5 and 6). (C) Olefin-terminated PIB (mixed olefin isomers: *exo*/*endo* = 5.4 mol/mol) was also used to alkylate (3-bromopropoxy)benzene under conditions for $TiCl_4$-catalyzed quasiliving isobutylene polymerization: prequench (dotted); postquench (solid).

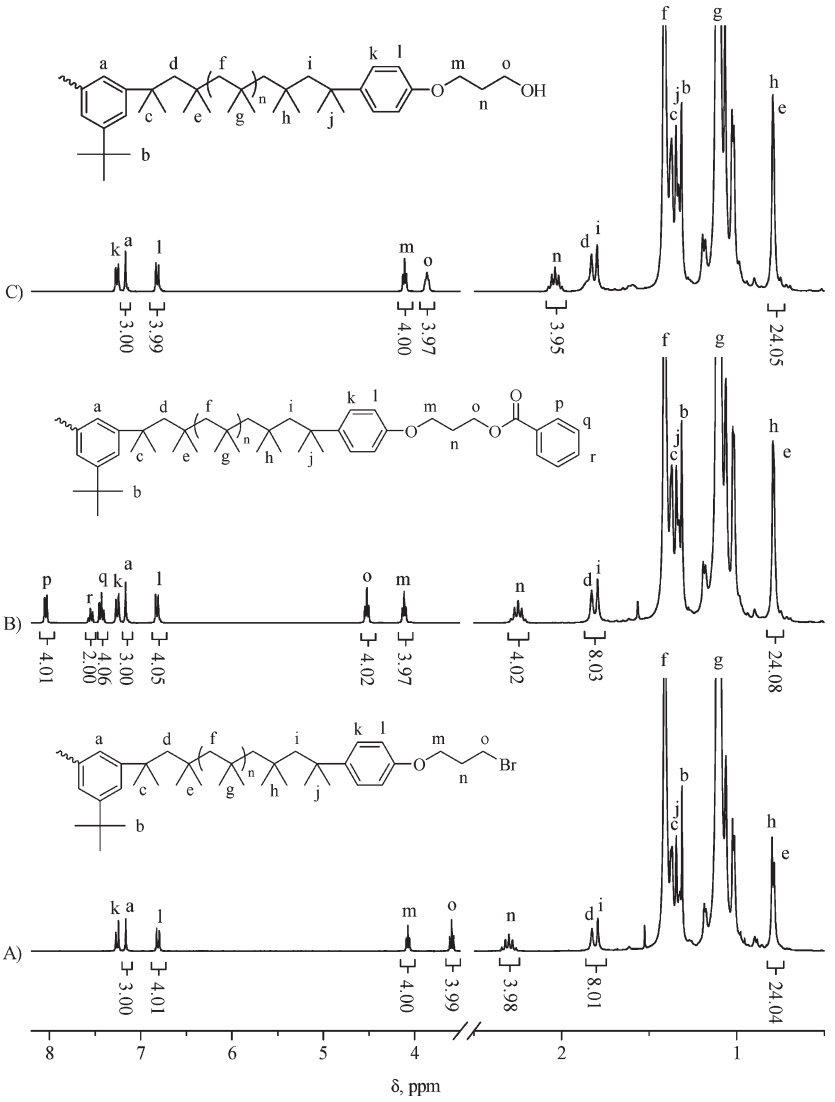

Figure 9. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis[4-(3-bromopropoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with (3-bromopropoxy)benzene, (B) α,ω-bis[4-(3-benzoyloxypropoxy)phenyl]polyisobutylene obtained by displacement of the primary bromide with benzoate, and (C) α,ω-bis[4-(3-hydroxypropoxy)phenyl]polyisobutylene obtained by subsequent hydrolysis (Table 1, entry 6).

ether macromer by reaction with excess potassium *tert*-butoxide in a refluxing mixture of 50/50 (v/v) heptane/DMF. Under the conditions used, dehydrochlorination was complete in less than 1 h. As shown in the ^{1}H NMR spectrum in Figure 6B, the resonances at 3.79 and 4.21 ppm due to the (2-chloroethoxy)benzene methylene units are replaced by three doublet-of-doublets centered at 4.37, 4.72, and 6.63 ppm due to the terminal vinyl ether. The ^{13}C NMR spectrum of Figure 5B indicates formation of the vinyl ether by appearance of resonances at 94.3 and 148.6 ppm. The GPC traces in Figure 8A show that no chain coupling occurred during the alkylation reaction, and no changes in molecular weight distribution were observed after dehydrochlorination to the PIB−vinyl ether macromer.

(3-Bromopropoxy)benzene. A primary bromide end group offers even easier transformation to other functionalities via nucleophilic substitution. Our previous publication demonstrated quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with (3-bromopropoxy)benzene and subsequent transformation of the primary bromide terminus to azide and primary amine.[85] An additional transformation of interest is to primary hydroxyl. Figures 9A and 10A show ^{1}H and ^{13}C NMR spectra, respectively, of primary bromide telechelic PIB obtained by directly charging an excess (2.5 equiv per chain end) of (3-bromopropoxy)benzene to $TiCl_4$-catalyzed quasiliving polyisobutylene in 40/60 (v/v) hexane/methyl chloride at −70 °C. Evidence of (3-bromopropoxy)-benzene alkylation is given in the ^{1}H NMR spectrum by the resonance for the ultimate PIB methylene unit adjacent to (3-bromopropoxy)benzene at 1.79 ppm, and by resonances at 3.60 (triplet), 2.30 (quintet), 4.07 (triplet), 6.83 (doublet), and 7.27 ppm (doublet), due to the (3-bromopropoxy)benzene moiety. After alkylation, the ^{13}C NMR spectrum exhibited new resonances in the aromatic region and at 30.1, 32.5, and 65.2 ppm due to methylene carbons of the (3-bromopropoxy)-benzene moiety.

Conversion to primary hydroxyl was achieved by displacement of bromide with excess sodium benzoate and subsequent hydrolysis of the newly formed ester linkage.[86] The conversion was done in two steps in a solvent mixture of 50/50 (v/v) heptane/DMF, which in such proportions are immiscible at room temperature but become monophasic upon heating above 70 °C. The thermomorphic behavior of this solvent system allows for polar reactants to be mixed and

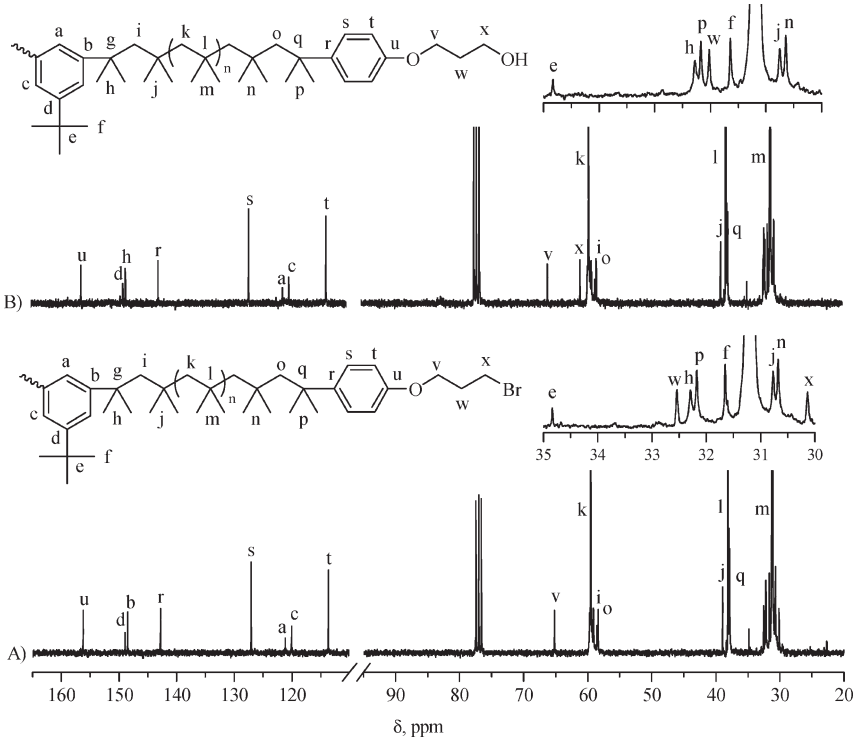

Figure 10. ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis[4-(3-bromopropoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with (3-bromopropoxy)benzene and (B) α,ω-bis[4-(3-hydroxypropoxy)phenyl]polyisobutylene obtained by displacement of the primary bromide by benzoate and subsequent hydrolysis (Table 1, entry 6).

reacted with polyisobutylene at high temperatures, while allowing facile purification of the polymer upon cooling due to its high phase selectivity for heptane.[87] Sodium benzoate and the primary bromide-terminated PIB were refluxed in 50/50 (v/v) DMF/heptane for 4 h. After cooling and phase separation, the benzyl ester-terminated polymer was isolated in the heptane layer. The ^1H NMR spectrum in Figure 9B shows the presence of the phenyl ester by multiplets at 7.43, 7.55, and 8.04 ppm, and the resonance for the terminal tether methylene unit has shifted downfield from 3.60 to 4.52 ppm due the electron-withdrawing ester linkage. The PIB in heptane was then mixed with an equal volume of DMF containing sodium hydroxide and heated to reflux for 12 h. After cooling and phase separation, the primary hydroxyl-terminated polymer was isolated in the heptane layer. Figure 9C shows a ^1H NMR spectrum of the purified PIB in which the resonance for the methylene unit adjacent to the terminal hydroxyl appears at 3.87 ppm. Primary hydroxyl functionality is also evidenced in the ^{13}C NMR spectrum of Figure 10B by the resonance at 60.9 ppm due the carbon adjacent to the hydroxyl. The GPC traces of Figure 8B indicated no changes in molecular weight during nucleophilic displacement of the bromide and hydrolysis of the ester.

3-Phenoxypropyldimethylchlorosilane. Functionalization of PIB with Si−Cl and Si−H termini was first achieved by Kennedy et al.[88] via hydrosilylation of *exo*-olefin-terminated PIB. Later, silicon functional initiators were developed,[89] and subsequent work has shown that silyl chlorides can survive conditions of $TiCl_4$-catalyzed quasiliving isobutylene polymerization.[29−31] These approaches to silicon functional PIBs require either multiple steps or initiators that are not commercially available. With the alkoxybenzene quencher, 3-phenoxypropyldimethylchlorosilane, we were able to obtain silicon functional PIB in a single step. Figure 11 shows a ^1H NMR spectrum of silicon functional PIB obtained by direct addition of 3-phenoxypropyldimethylchlorosilane to $TiCl_4$-catalyzed quasiliving PIB in 60/40 (v/v) hexane/methyl chloride at −70 °C. As evidenced by the methyl resonance at 3.44 ppm, the highly reactive silyl chloride end groups were converted to silyl methoxy end groups after destroying the catalyst with excess methanol. The GPC traces shown in Figure 12 indicated that a small amount of chain coupling occurred. However, coupling was due to mutual reaction of the silyl end groups during work-up, rather than dialkylation of the 3-phenoxypropyldimethylchlorosilane.

Trimethyl(3-phenoxy-1-propynyl)silane. There has been recent interest in alkyne-terminated PIB for use in Huisgen 1,3-dipolar cycloaddition ("click") reactions, which provide a facile route for the synthesis of block copolymers,[90,91] cyclic PIBs,[92] and supramolecular gels.[93] Alkyne functionality on an alkoxybenzene presents difficulty due the activity of the triple bond in polymerization. When phenyl propargyl ether was added directly to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization, a significant amount of chain coupling occurred. To prevent coupling, a trimethylsilyl blocking group was added, which was sufficient to prevent carbocation addition across the triple bond. As indicated by the resonance at 0.17 ppm in the ^1H NMR spectrum of Figure 13A, ∼90% of the trimethylsilyl groups remained intact after termination of the polymerization. Upon treatment with TBAF, the alkyne proton triplet at 2.49 ppm became evident as shown in the ^1H NMR spectrum of Figure 13B. The GPC traces in Figure 12B indicate no chain coupling during polymerization, quenching, and deblocking.

Phenoxyalkanol and Phenoxyalkylamine. Direct addition of molecules with unprotected hydroxyl groups to reaction media containing strong Lewis acids such as $TiCl_4$ generally leads to decomposition of the Lewis acid (formation of titanates) and cessation of catalyst activity. Thus, most literature reports indicate that when a $TiCl_4$-catalyzed quasiliving isobutylene polymerization is charged with a hard nucleophile such as hydroxyl, *tert*-chloride chain ends are

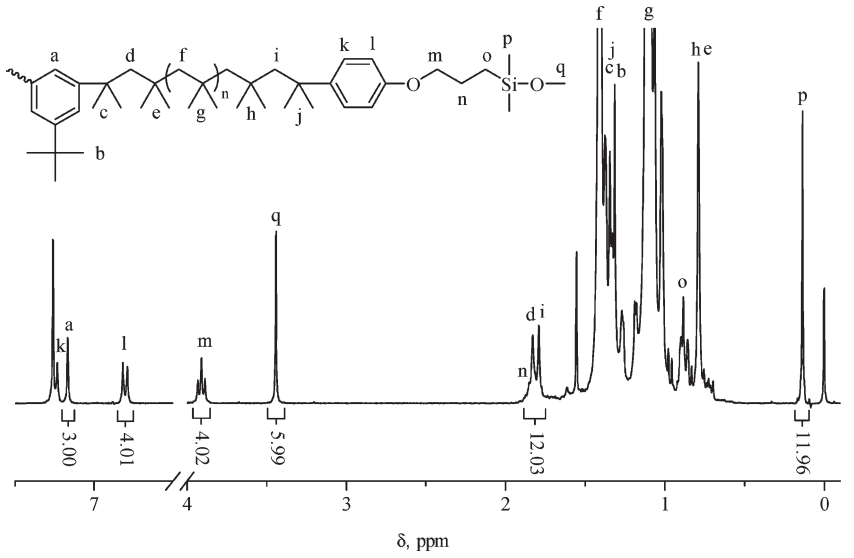

Figure 11. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectrum of α,ω-bis[4-(3-methoxydimethylsilylpropoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 3-phenoxypropyldimethylchlorosilane and subsequent reaction with methanol (Table 1, entry 7).

returned.[94] However, the successful use of low concentrations of unprotected hydroxyl groups on initiators[27] and capping agents[95] has been reported, but with complications. To alleviate such problems, the hydroxyl group may be protected and unmasked only after the $TiCl_4$ catalyst has performed its service.[96] Rather than seek a suitable blocking group for a phenoxyalkanol, our approach involved direct addition of an unmodified phenoxyalkanol to the quasiliving PIB. The rationale for such an approach was that the site of alkylation, i.e., the phenyl ring, could be spatially separated from the functionality of interest, i.e., the hydroxyl. If sufficient $TiCl_4$ remained in the reaction after titanate formation, then the alkylation could be successfully carried out, albeit with a higher demand for $TiCl_4$.

Our initial attempts with the simplest phenoxyalkanol having a two-carbon tether, 2-phenoxyethanol, proved unsuccessful. Subsequent systematic experimentation showed that with tether lengths of two and three carbons interaction with $TiCl_4$ was detrimental to the desired alkylation; however, phenoxyalkanols with carbon tethers of four or greater were alkylated by $TiCl_4$-catalyzed quasiliving PIB. Figure 14 illustrates the effect of the $TiCl_4$ concentration during alkylation of 4-phenoxy-1-butanol. The alkylation reaction proceeds rapidly at first and then slows, and higher levels of $TiCl_4$ provide higher capping efficiencies for a given reaction time. However, analysis of the data in Figure 14A,B shows that the disappearance of *tert*-chloride functionality is more rapid than the appearance of hydroxyl functionality, particularly at high [$TiCl_4$]. This indicates accumulation of a slowly reacting intermediate, which we propose to be isomerized chain ends resulting from carbenium ion rearrangement.[97] When the ratio of $TiCl_4$ to 4-phenoxy-1-butanol was 2.5 or higher, over 60% of the chain ends were capped within 30 min; however, 30−40% of the chain ends had also become rearranged. Despite the loss of *tert*-chloride functionality, alkylation slowly continued, and the hydroxyl functionality increased over time as shown in Figure 14B. In this latter stage of reaction, we propose that alkylation occurs through isomerized tertiary and possibly secondary chloride structures that arise from $TiCl_4$-catalyzed rearrangement. Longer tether lengths were investigated to determine the effect of increased separation between the titanate and the site of alkylation. As shown in Figure 15, increasing the tether

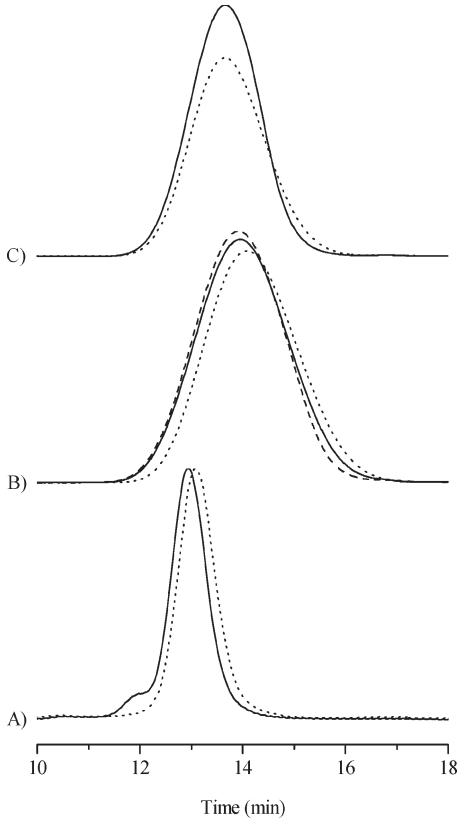

Figure 12. GPC differential refractive index traces of PIB obtained from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization quenched with (A) 3-phenoxypropyldimethylchlorosilane, (B) trimethyl(3-phenoxy-1-propynyl)silane, and (C) 4-phenoxy-1-butanol: prequench (dotted); postquench (solid), and after deprotection of the alkyne moiety (dashed, B only) (Table 1, entries 7−9).

length to six and eight carbons did provide increased hydroxyl functionality for a given reaction time. However, the phenoxyalkanols with longer tethers were marginally better since the same result could be achieved with 4-phenoxybutanol using longer reaction time or more $TiCl_4$.

To achieve near-quantitative hydroxyl functionality via direct quenching, the alkylation of 4-phenoxy-1-butanol was

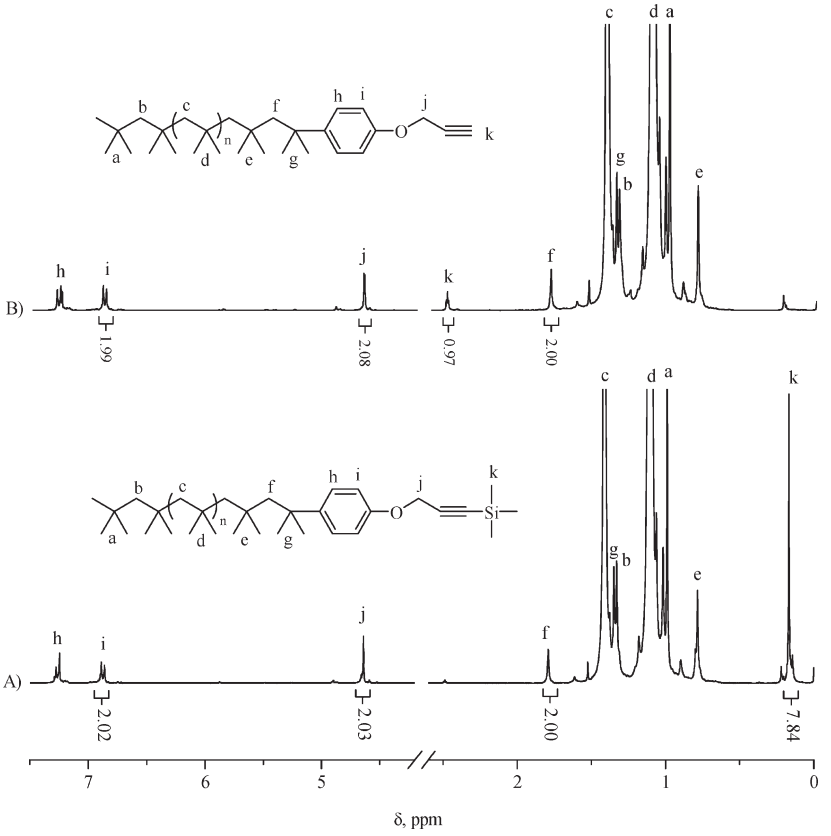

Figure 13. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of (A) 1-(3-trimethylsilyl-2-propynyloxy)-4-polyisobutylbenzene and (B) 1-(propargyloxy)-4-polyisobutylbenzene obtained by direct addition of trimethyl(3-phenoxy-1-propynyl)silane to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent postpolymerization removal of the trimethylsilyl blocking group (Table 1, entry 8).

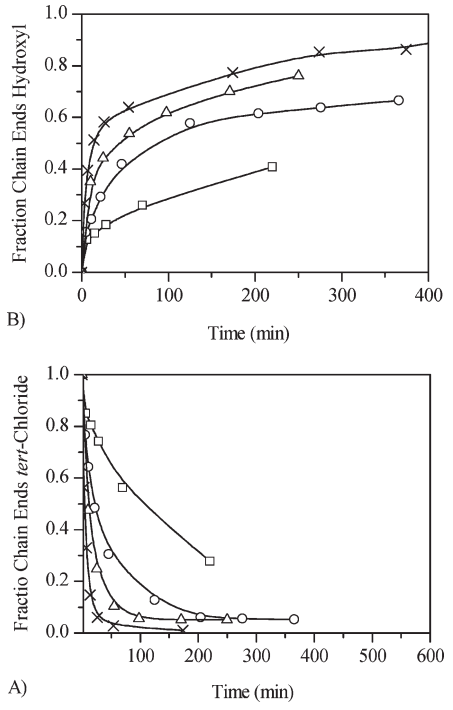

Figure 14. Fraction of chain ends bearing (A) *tert*-chloride and (B) hydroxyl functionality as a function of time for various concentrations of $TiCl_4$ after direct addition of 4-phenoxy-1-butanol to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations. Polymerization/quench at −70 °C in 40/60 (v/v) hexane/methyl chloride, [2,6-lutidine] = 0.005 M, [*t*-Bu-*m*-DCC] = 0.025 M, [isobutylene] = 1.1 M, [$TiCl_4$] = 0.015 M (polymerization), [4-phenoxy-1-butanol] = 0.125 M, and [$TiCl_4$] = 0.165 (□), 0.19 (○), 0.215 (Δ), and 0.315 M (×) during quench.

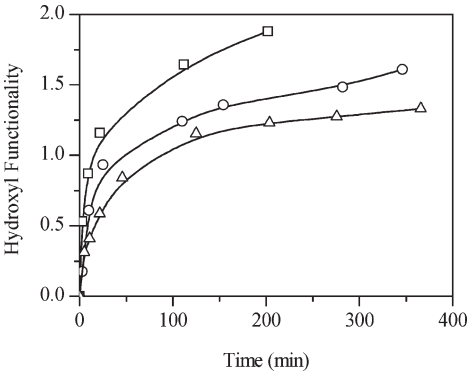

Figure 15. Number-average hydroxyl functionality of quasiliving PIB quenched with 4-phenoxy-1-butanol (Δ), 6-phenoxy-1-hexanol (○), and 8-phenoxy-1-octanol (□). Polymerization/quench at −70 °C in 40/60 (v/v) hexane/methyl chloride, [2,6-lutidine] = 0.005 M, [*t*-Bu-*m*-DCC] = 0.025 M, [isobutylene] = 1.1 M, [$TiCl_4$] = 0.015 M (polymerization), [quencher] = 0.125 M, and [$TiCl_4$] = 0.19 M during quench.

allowed to proceed for 8 h in the presence of a large excess of $TiCl_4$ as described in Figures 16A. The terminal methylene unit adjacent to the hydroxyl end group was observed at 3.72 ppm (triplet) in the ^{1}H NMR spectrum of Figure 16A and at 62.6 ppm in the ^{13}C NMR spectrum of Figure 17A. The GPC traces in Figure 12C indicate that no coupling or degradation occurred during the 8 h alkylation reaction.

Arguably the more difficult direct functionalization via alkoxybenzene quenching would be with amine because of anticipated reactivity toward both $TiCl_4$ and PIB carbenium ions. To prevent proton abstraction from the carbenium ion chain end, the amine either must be sufficiently hindered to prevent approach to the chain end or sufficiently unhindered

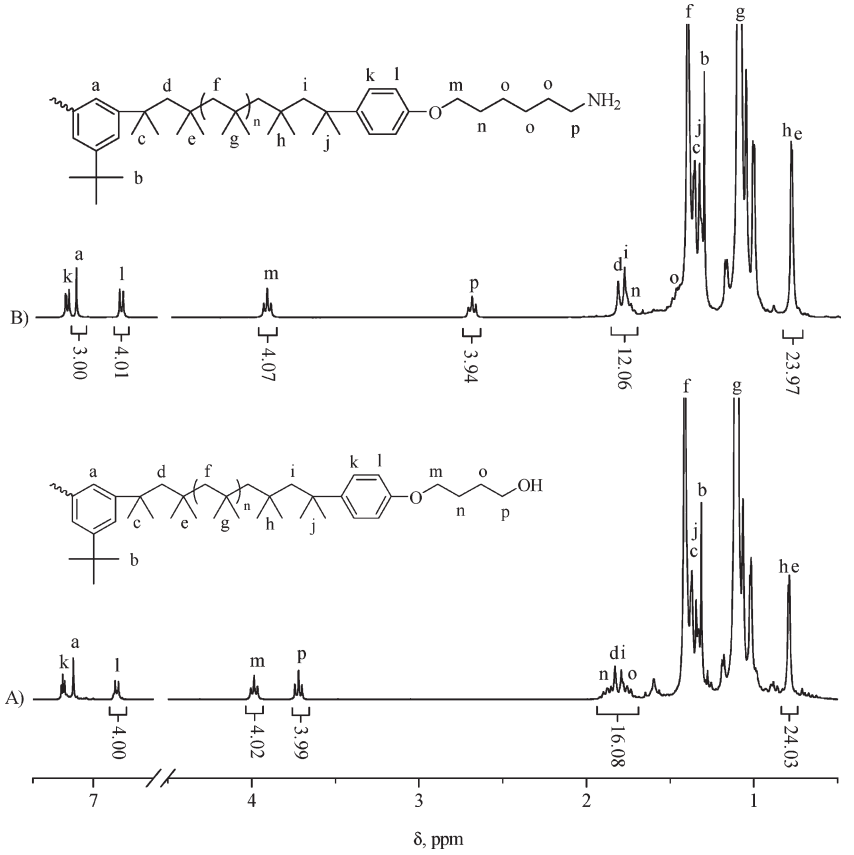

Figure 16. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis[4-(4-hydroxybutoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 4-phenoxy-1-butanol and (B) α,ω-bis[4-(6-aminohexoxy)phenyl]polyisobutylene obtained by quenching with 6-phenoxyhexylamine (Table 1, entries 9 and 10).

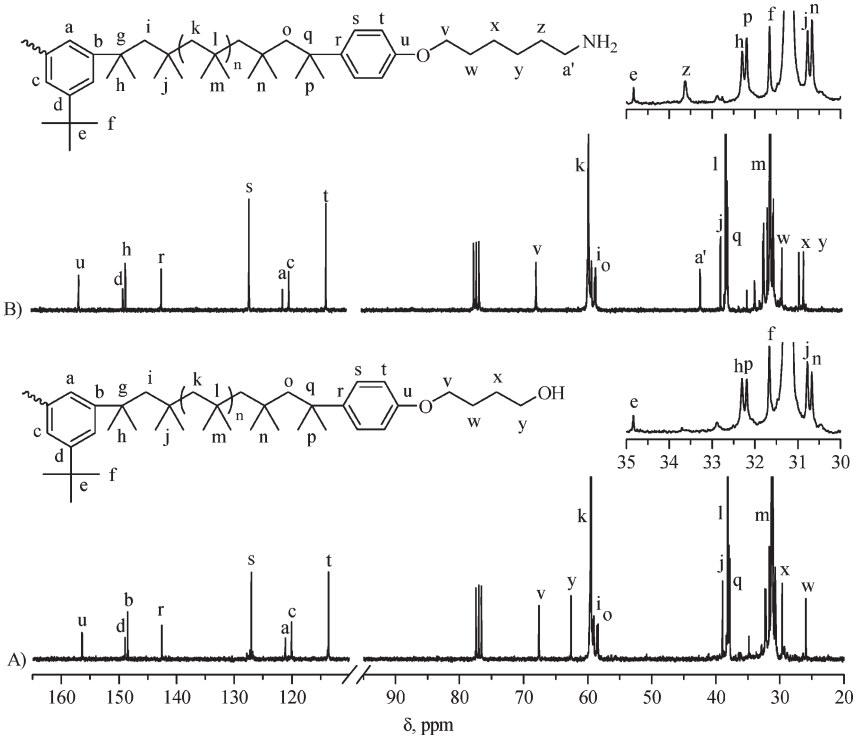

Figure 17. ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) spectra of (A) α,ω-bis[4-(4-hydroxybutoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 4-phenoxy-1-butanol and (B) α,ω-bis[4-(6-aminohexoxy)phenyl]polyisobutylene obtained by quenching with 6-phenoxyhexylamine (Table 1, entries 9 and 10).

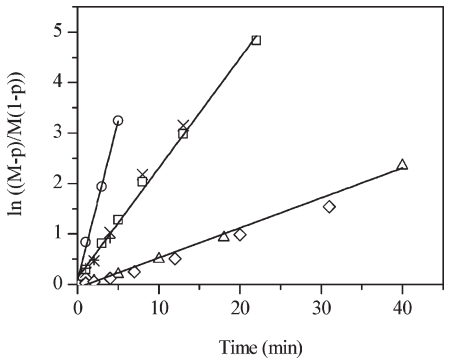

Figure 18. Second-order kinetic plot for $TiCl_4$-catalyzed alkylation of butyl phenyl ether (○), (3-bromopropoxy)benzene (×), anisole (□), allyl phenyl ether (+), (2-bromoethoxy)benzene (Δ), and (2-chloroethoxy)-benzene (◇) by quasiliving PIB. Polymerization/quench was conducted at −70 °C in 40/60 (v/v) hexane/methyl chloride, with [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [IB] = 1.58 M, [$TiCl_4$] = 0.015 M (polymerization), [quencher] = 0.1 M, and [$TiCl_4$] = 0.09 M (quench).

so that its nucleophilicity is mitigated through quantitative complexation with $TiCl_4$. When the completely unhindered amine, 6-phenoxyhexylamine, was charged to a quasiliving isobutylene polymerization, with excess $TiCl_4$ to account for complexation, alkylation proceeded as with 4-phenoxybutanol, and over 65% of the chains were capped within the first 20 min. The rate of alkylation then slowed significantly, likely due to depletion of $TiCl_4$ via formation of $Ti_2Cl_9^-$ ions, which are formed when the amino tethers are protonated by the HCl generated from the alkylation reaction. After 9 h, near-quantitative primary amine functionality was obtained. The ^1H NMR spectrum of the product in Figure 16B shows a triplet at 2.70 ppm characteristic of the terminal methylene unit adjacent to the amine, and the ^{13}C NMR spectrum in Figure 17B shows a resonance at 42.1 ppm, also characteristic of the terminal methylene unit adjacent to the amine. In both the ^{13}C and ^1H NMR spectra there is no evidence of olefin formation.

Alkylation Kinetics. The rate of alkoxybenzene alkylation by $TiCl_4$-catalyzed quasiliving PIB (quenching) may be described by the following second-order rate equation

$$\frac{dp}{dt} = k_c K_{eq}[TiCl_4]^2[PIBCl]_0(1-p)(M-p) \qquad (1)$$

where p is conversion of *tert*-chloride chain ends, k_c is the rate constant for alkylation, $[PIBCl]_0$ is initial chain end concentration, $[TiCl_4]$ is the effective concentration of $TiCl_4$ available for participation in the ionization equilibrium, M = $[alkoxybenzene]_0/[PIBCl]_0$ is the ratio of the initial alkoxybenzene concentration to the initial *tert*-chloride chain end concentration, and K_{eq} is the ionization equilibrium constant. If $[TiCl_4]$ is in large excess relative to basic additives such as 2,6-lutidine, then the formation of onium salts through HCl scavenging does not significantly diminish $[TiCl_4]$, and eq 1 may be integrated to yield

$$\ln\left(\frac{M-p}{M(1-p)}\right) = k_c K_{eq}[TiCl_4]^2[PIBCl]_0(M-1)t \qquad (2)$$

Figure 18 shows data for the alkylation of several alkoxybenzenes by $TiCl_4$-catalyzed quasiliving PIB at −70 °C in 40/60 (v/v) hexane/methyl chloride, plotted according to eq 2. From the plots it is clear that the rate of alkylation is heavily dependent on the identity of the alkyloxy tether. The fastest rate of alkylation was for butyl phenyl ether, and

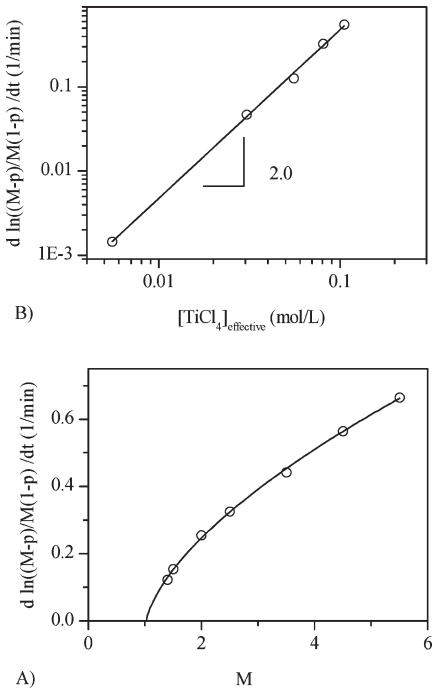

Figure 19. Plots of the apparent second-order rate constant (k_cK_{eq}-$[TiCl_4]_{effective}^2[PIBCl]_0$) for $TiCl_4$-catalyzed alkylation of anisole by quasiliving PIB as a function of (A) the anisole concentration as M = $[anisole]_0/[TMPCl]$ and (B) the effective $TiCl_4$ concentration, defined as $[TiCl_4]_{effective}$ = $[TiCl_4]$ - 2[2,6-lutidine]. Polymerization/quench at −70 °C in 40/60 (v/v) hexane/methyl chloride, [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [isobutylene] = 1.58 M, [$TiCl_4$] = 0.015 M (polymerization), [anisole] = 0.125 M (B only), and [$TiCl_4$] = 0.09 M (quench, A only).

under the conditions described in Figure 18, near-quantitative capping of the chain ends could be achieved in ∼10 min. For anisole, (3-bromopropoxy)benzene, and allyl phenyl ether, the rate of alkylation was more than 2.5 times slower than for butyl phenyl ether. When electron-withdrawing halides become closer to the phenyl ring as with (2-bromoethoxy)benzene and (2-choroethoxy)benzene, the reactivity was further decreased by a factor of 5. Though longer alkyl tethers help to minimize electronic and steric interference with the alkylation reactions, as well as promote solubility, they come at the expense of increased mass at the PIB chain end.

Second-order kinetics for anisole alkylation were further studied as a function of both M and the effective $TiCl_4$ concentration, defined as $[TiCl_4]_{effective}$ = $[TiCl_4]$ − 2[2,6-lutidine]. This definition of $[TiCl_4]_{effective}$ accounts for the fact that all of the 2,6-lutidine in the system is converted to onium salts ($C_8H_{10}N^+Ti_2Cl_9^-$) early in the reaction. Figure 19A is a plot of the slope obtained from eq 2 as a function of M; Figure 19B is a ln−ln plot of the slope obtained from eq 2 as a function of $[TiCl_4]_{effective}$. The kinetic model represented by eq 2 does not account for diminution in $TiCl_4$ activity as a result of interaction between the alkoxybenzene and $TiCl_4$. However, the effect of interaction is clearly manifested in Figure 19A by the initially declining slope as M rises from 1 to about 1.6. This represents the range of M for which [anisole] < $[TiCl_4]_{effective}$, and therefore, increasing [anisole] reduces $TiCl_4$ activity. For values of M greater than 1.6, [anisole] > $[TiCl_4]_{effective}$. Within this regime of anisole concentrations, the anisole−$TiCl_4$ interaction is saturated, and additional anisole causes no further decline in the slope or decrease in $TiCl_4$ activity. Figure 19B shows that the alkylation of anisole has a second-order dependence on the effective

$TiCl_4$ concentration, reflecting the well-known second-order dependency of ionization on $[TiCl_4]_{effective}$.[98]

Figure 20 demonstrates that the rate of alkylation increases with decreasing temperature. This phenomenon is due to the apparent negative activation energy associated with the $TiCl_4$-catalyzed ionization of the *tert*-chloride chain ends. Activation energies for the apparent rate constant k_cK_{eq} calculated from the slopes of the data in Figure 20 were −7.0 and −6.6 kcal/mol for the hexane/methyl chloride and toluene/dichloromethane solvent systems, respectively.

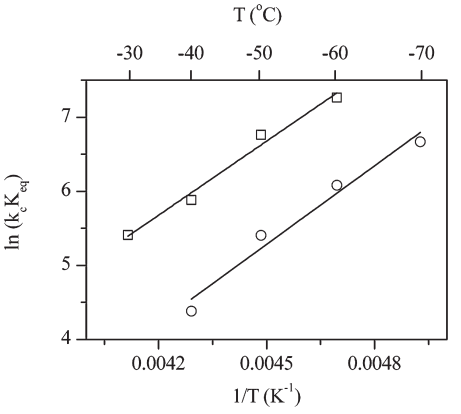

Figure 20. van't Hoff plots for $TiCl_4$-catalyzed alkylation of anisole by quasiliving PIB using 40/60 (v/v) hexane/methyl chloride (○) and 50/50 (v/v) toluene/methylene chloride (□) solvent systems. Polymerization/quench at −70 to −40 °C, [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [isobutylene] = 1.58 M, $[TiCl_4]$ = 0.015 M (polymerization), [anisole] = 0.1 M, and $[TiCl_4]$ = 0.09 M (quench).

Alkylation with Olefinic PIB. For all of the $TiCl_4$-catalyzed isobutylene polymerizations and *in situ* alkylation reactions discussed to this point, yield of the desired alkylated PIB was never diminished because of the presence of terminal unsaturations, even under conditions where olefin-terminated PIB would likely be formed via *β*-proton expulsion or abstraction, i.e., above −40 °C.[99] Even when small fractions of olefin termini were observed in a prequench aliquot, they disappeared over the course of the alkylation (quenching) reaction. Though it is not surprising that a PIB olefin terminus serves as an alkylating agent, this observation is technologically important because it signifies that quantitative functionalization with an alkoxybenzene is still attainable even under conditions where the prior polymerization is less than perfectly living and termination has occurred. To definitively illustrate alkylation via olefinic PIB, a sample of monofunctional, olefin-terminated PIB (mixed olefin isomers: *exo*/*endo* = 5.4 mol/mol) was reacted with (3-bromopropoxy)benzene under conditions similar to those used in the quasiliving polymerization of isobutylene, i.e., $TiCl_4$ catalysis at −70 °C in 40/60 (v/v) hexane/methyl chloride. As shown by the ^{1}H NMR spectra of Figure 21, both the *exo*- and *endo*-olefin were rapidly hydrochlorinated in the presence of $TiCl_4$. Within the first 5 min of the reaction, no *exo*-olefin remained and ∼10% of chains exhibited *endo*-olefin termini. Within 3.5 h all of the *exo*- and *endo*-olefin chain ends were capped with (3-bromopropoxy)benzene as indicated by the disappearance of resonances at 1.69 and 1.96 ppm due to the ultimate *gem*-dimethyl and methylene units of *tert*-chloride PIB as well as the disappearance of the resonances at 1.78, 2.0, 4.64, and 4.84 ppm due to the *exo*-olefin and 1.62, 1.66, and 5.15 ppm due to *endo*-olefin.

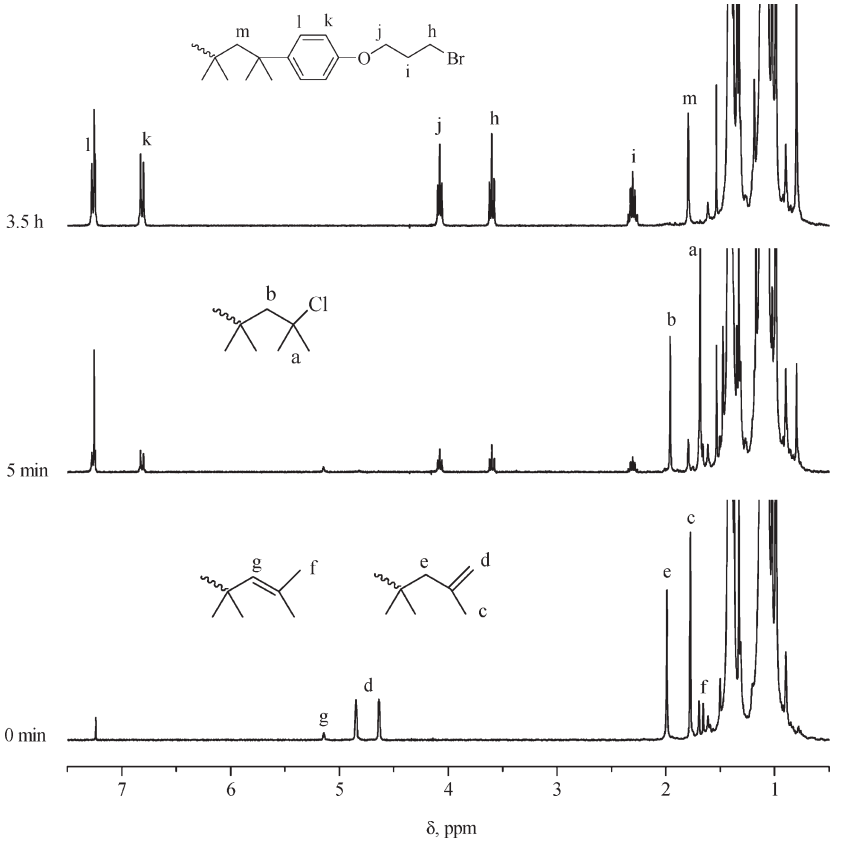

Figure 21. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of olefin-terminated PIB (mixed olefin isomers: *exo*/*endo* = 5.4 mol/mol) as a function of time during the $TiCl_4$-catalyzed alkylation of (3-bromopropoxy)benzene. Alkylation was conducted at −70 °C in 40/60 (v/v) hexane/methyl chloride; [PIB] = 0.01 M, [(3-bromopropoxy)benzene] = 0.03 M, and $[TiCl_4]$ = 0.06 M.

The remaining resonances after 3.5 h at 1.79, 2.30, 3.60, 4.07, 6.83, and 7.27 ppm were due to the (3-bromopropoxy)-benzene-capped chain ends. The GPC traces (Figure 8C) of the olefin-terminated PIB precursor and final product showed no significant differences; the molecular weight (polydispersity) before and after the alkylation reaction were 3.1×10^3 (1.35) and 3.3×10^3 g/mol (1.30), respectively. The reaction as described in Figure 21 was performed in the absence of a basic additive; however, in the presence of an additive typically used to enhance "livingness" of the isobutylene polymerization, e.g., 2,6-lutidine, both hydrochlorination and subsequent alkylation by olefin-terminated PIB were greatly inhibited. This was expected; the base serves as a proton trap, and the olefin cannot be protonated to form a carbenium ion. When quenching an isobutylene polymerization at higher temperatures (>−40 °C), where the end groups are mixed *tert*-chloride and olefin, alkylation by the former produces HCl concentrations in far excess of the basic additive for moderately high chain end concentrations, i.e., >0.01 M, and alkylation via olefin end groups is uninhibited.

Conclusions

We have shown that direct addition of alkoxybenzenes to $TiCl_4$-catalyzed quasiliving isobutylene polymerization provides a versatile method for chain end functionalization. Alkylation of simple alkyl phenols such as anisole and isopropoxybenzene with subsequent *in situ* deprotection allowed synthesis of phenolic PIB. The alkylation reactions were also tolerant of primary halide, silyl chloride, and protected alkyne functionality, allowing placement of these functionalities on the PIB chain end in a single step. Using suitably long alkyl tethers made possible alkylation of alkoxybenzenes bearing functionalities that interact strongly with $TiCl_4$, namely primary hydroxyl and amine. The $TiCl_4$/alkoxybenzene combination at low temperature provided rapid alkylation of mixed *endo*-/*exo*-olefin-terminated PIB.

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Supporting Information Available: ^{13}C NMR spectrum of 1-(3-bromopropoxy)-4-polyisobutylbenzene obtained by alkylation of 3-bromopropoxybenzene by olefin-terminated PIB (mixed olefin isomers: *exo*/*endo* = 5.4 mol/mol), catalyzed by $TiCl_4$. −70 °C; 40/60 (v/v) hexane/methyl chloride; [PIB$_=$] = 0.01 M, [(3-bromopropoxy)benzene] = 0.03 M, [$TiCl_4$] = 0.06 M (Figure A). This material is available free of charge via the Internet at http://pubs.acs.org.

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