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Primary Hydroxy-Terminated Polyisobutylene via End-Quenching with a Protected *N*-(ω-Hydroxyalkyl)pyrrole

David L. Morgan and Robson F. Storey*

School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

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ABSTRACT: *N*-(2-*tert*-Butoxyethyl)pyrrole was used to end-quench $TiCl_4$-catalyzed quasiliving isobutylene polymerizations initiated from 2-chloro-2,2,4-trimethylpentane and 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene at −60 °C in 60/40 (v/v) hexane/methyl chloride. End-capping was near-quantitative except for the formation of < 5% *exo*-olefin chain ends, with alkylation occurring in both the C-3 (57%) and C-2 (38%) position on the pyrrole ring. Coupling was not observed for the monofunctional polymers; however, quenching of difunctional polymers resulted in small amounts of coupling due to dialkylation at the pyrrole ring. The terminal *tert*-butyl group of the *N*-(2-*tert*-butoxyethyl)pyrrole-capped polyisobutylene was rapidly and quantitatively removed *in situ* by addition of ethylaluminum dichloride and sulfuric acid to the reaction mixture. Furthermore, heating the reaction mixture to reflux (69 °C) forced alkylation by the residual *exo*-olefin chain ends and induced isomerization of the pyrrole-capped chain ends to yield exclusively [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole. The primary hydroxy-terminated polyisobutylenes showed excellent, unimpeded reactivity with carboxylic acid and isocyanates typically used in block copolymer synthesis.

Introduction

There has been significant interest in telechelic polyisobutylene (PIB) bearing primary hydroxyl groups,[1] and there is a need for a quantitative and efficient one-pot synthetic approach for obtaining the hydroxyl terminus. The traditional, multistep route to hydroxy-functional PIB has involved postpolymerization derivatization of telechelic PIB obtained through quasiliving polymerization processes or commercially available, high methyl vinylidene (*exo*-olefin) functional PIB.

Ivan, Kennedy, and Chang[2] were the first to synthesize telechelic primary hydroxy-functional PIB through a multistep process involving an *exo*-olefin-terminated intermediate. This was accomplished by preparing the *tert*-chloride-terminated polymer via the "inifer" technique, followed by regiospecific dehydrochlorination of the isolated product with potassium *tert*-butoxide[3] and finally hydroboration−oxidation of the *exo*-olefin end groups. Commercially available PIB with high *exo*-olefin content has also served as a substrate for hydroboration−oxidation;[4] however, on an industrial scale hydroformylation−hydrogenation of the olefin would be preferred.[5] An alternative route to hydroxyl functionality via olefinic PIB, with an even greater number of steps, involves epoxidation[6] followed by acid-catalyzed isomerization of the epoxide to an aldehyde and subsequent reduction of the aldehyde.[7] Kennedy et al.[8] have also demonstrated a somewhat more direct approach to hydroxyl functionality involving simultaneous dehydrochlorination and lithiation of telechelic *tert*-chloride PIB using *n*-butyllithium and potassium *tert*-butoxide, followed by oxyethylation of the macroanions with ethylene oxide.

Synthesis of hydroxy-telechelic PIB was simplified with the discovery of *in situ* functionalization/quenching techniques that provided a direct route to olefin chain ends. As shown by Kennedy et al.,[9,10] addition of allyltrimethylsilane to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization leads to quantitative formation of allyl end groups. Similarly, Ivan et al.[11] described quenching with methallyltrimethylsilane to obtain PIB with *exo*-olefin end groups. As an alternative, Storey et al.[12] have shown that deliberate addition of hindered amines to a $TiCl_4$-catalyzed isobutylene polymerization induces β-proton elimination at the chain end for quantitative *exo*-olefin formation.

An efficient method for transformation of olefinic termini to primary hydroxyl involves anti-Markovnikov hydrobromination and subsequent nucleophilic displacement reactions.[13] Kennedy et al.[14] achieved rapid hydrobromination of commercial, "highly reactive" PIB (Glissopal) and allyl-terminated PIB[9,10] by bubbling air through a solution of the polymer in boiling THF or hexane, followed by bubbling of HBr at 0 °C. The primary bromide termini formed from the allylic PIB were displaced by hydroxide after 8−12 h in a refluxing mixture of THF and 25−35 wt % 1-methyl-2-pyrrolidone. The same procedure was not as effective with the hydrobrominated *exo*-olefin PIB (Glissopal), which required displacement of the bromide by benzoate and then hydrolysis of the resulting ester with potassium hydroxide.

Synthetic routes not involving unsaturated PIB intermediates have also been reported. Puskas et al.[15] have worked with initiators containing latent hydroxyl groups masked as epoxides. Hydroxyl functionality at the initiation site was obtained by acid-induced ring-opening of the epoxide moiety. Quasiliving isobutylene polymerizations were demonstrated, but initiation efficiency remained low. For example, maximum initiation efficiencies of 40% where reported for α-methylstyrene epoxide, and apparently lower efficiencies were obtained for molecular weight targets under 4000 g/mol.[16] The low initiation efficiencies were caused by epoxide rearrangement (e.g., formation of aldehydes) and formation of polyethers,[17] the extent of such side reactions being determined by the initiator structure.[18] Knoll et al.[19] demonstrated the *in situ* synthesis of allyl chloride-terminated

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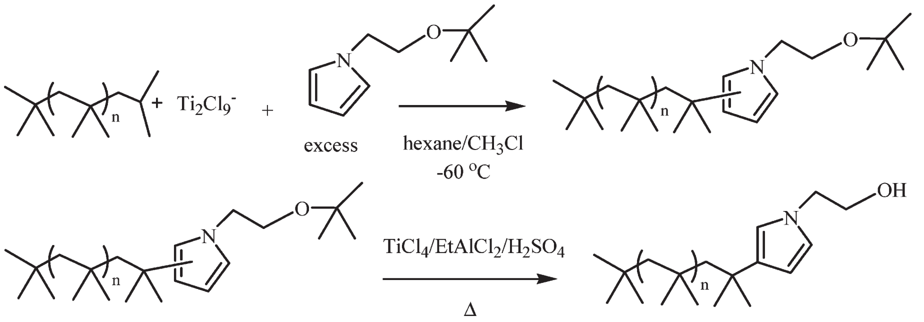
*Corresponding author. E-mail: robson.storey@usm.edu.

Scheme 1. Single-Pot Synthesis of Primary Hydroxy-Functional PIB from a $TiCl_4$-Catalyzed Quasiliving Isobutylene Polymerization by Direct Quenching with *N*-(2-*tert*-Butoxyethyl)pyrrole and Subsequent *In Situ* Cleavage of the Terminal *tert*-Butyl Ether



PIB by charging 1,3-butadiene to BCl_3-catalyzed isobutylene polymerizations. Later, Faust et al.[20] also obtained allyl chloride-terminated PIB by the 1,4-addition of butadiene to $TiCl_4$-catalyzed quasiliving PIB and subsequently achieved hydroxyl end groups by postpolymerization nucleophilic displacement of the terminal allyl chlorides by hydroxide in THF. These authors showed that reaction of a PIB allyl bromide with KOH in THF at 130 °C under pressure was significantly faster than reaction of the allyl chloride, the former requiring only 3 h vs 24 h for the latter; however, formation of the allyl bromide terminus required use of brominated alkylaluminum catalysts[21] or postpolymerization halide exchange.[22] Quenching to hydroxyl functionality by direct addition of 9-decen-1-ol to $TiCl_4$-catalyzed isobutylene polymerizations was reported by Chiba et al.[23] Surprisingly, hydroxyl functionality as high as 95% was obtained, but the process was complicated by reaction of the bare hydroxyls with $TiCl_4$ and competitive hydrochlorination of the 9-decen-1-ol α-olefin moiety.

As a further alternative, the traditional synthetic routes to low molecular weight PIB may be circumvented completely, and PIB macro-glycols can be obtained through ozonolysis and reduction of isobutylene−isoprene copolymers (e.g., butyl rubber).[24,25] Unfortunately, oxidative cleavage of isobutylene−diene copolymers may provide polydisperse oligomers with more or less than the desired functionality. For example, a hydroxyl functionality greater than two would arise upon ozonolysis and subsequent reduction of butyl rubber that contains significant levels of 1,2 or 3,4 isoprene enchainment.

We recently reported that quasiliving PIB reacts quantitatively with *N*-methylpyrrole to yield an isomeric mixture of 2- and 3-PIB-*N*-methylpyrroles, with no detectable disubstitution (coupled) products.[26] In addition, we have demonstrated that the *N*-alkyl group can be exploited as an alkylene tether for the attachment of more useful functional groups to PIB, such as primary halogen.[27] Herein, we report the *in situ* functionalization of PIB with pyrroles bearing a protected hydroxyl group attached via an *N*-alkylene tether as a means for single-pot synthesis of primary hydroxy-functional PIB (Scheme 1).

Experimental Section

Materials. Hexane (anhydrous, 95%), $TiCl_4$ (99.9%,), 2,6-lutidine (2,6Lut) (redistilled, 99.5%), ethylaluminum dichloride ($EtAlCl_2$) (97%), *tert*-butylacetic acid (98%), phenyl isocyanate (98%), butyl isocyanate (98%), 4,4′-methylenebis(phenyl isocyanate) (MDI) (98%), dimethyl sulfoxide (DMSO) (anhydrous, 99.9%), sodium hydride (95%), pyrrole (98%), 2-chloroethanol (99%), dibutyltin dilaurate (DBTDL) (95%), and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. Isobutylene from BOC Gases and methyl chloride from 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. 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, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The difunctional initiator, 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC), was synthesized as previously reported[28] and stored at 0 °C. Monofunctional *tert*-chloride-terminated PIB (2.0×10^3 g/mol) was prepared via BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[29] at −60 °C.

Instrumentation. NMR spectra of polymer samples (20−100 mg/mL in $CDCl_3$) were obtained using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^1H chemical shifts were referenced to tetramethylsilane (0 ppm), and all ^{13}C shifts were referenced to the residual $CDCl_3$ solvent resonance (77.01 ppm). NMR resonance assignments were made with the assistance of standard $^1H-^{13}C$ correlation experiments. Single bond $^1H-^{13}C$ connectivity was established using gradient-enhanced heteronuclear single-quantum coherence (gHSQC) spectra, and multiple bond connectivity was established using gradient-enhanced heteronuclear multiple bond coherence (gHMBC) spectra.

Number-average molecular weights ($\bar{M}_n$) and polydispersities (PDI = $\bar{M}_w/\bar{M}_n$) of the polymeric materials were estimated using 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 d*n*/d*c* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Real-time ATR-FTIR analysis was performed using a ReactIR 4000 (Mettler-Toledo) integrated with a N_2 atmosphere glovebox.[30] 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.

Synthesis of *N*-(2-*tert*-Butoxyethyl)pyrrole. *N*-(2-*tert*-Butoxyethyl)pyrrole was prepared in two steps. First, 2-(2-chloroethoxy)-2-methylpropane was synthesized by addition of isobutylene to 2-chloroethanol. Typically, 50 mL of 2-chloroethanol and 140 mL (2 equiv) of isobutylene were combined

Table 1. Experimental Conditions and Results of *N*-(2-*tert*-Butoxyethyl)pyrrole End-Quenching of $TiCl_4$-Catalyzed Quasiliving Isobutylene Polymerizations

				chain end composition						
						alkylated pyrrole		hydroxyl		
polymer	initiator	reaction event	mol wt $\bar{M}_n$ (PDI)	*tert*-Cl	*exo*-olefin	C-3	C-2	C-3	C-2	coupling
1[a]	TMPCl	polymerization (25 min, −60 °C)	1.9×10^3 (1.06)	1.0						
		alkylation (25 min, −60 °C)	2.2×10^3 (1.04)		0.05	0.57	0.38			
		deblocking (1.5 h, −60 → 0 °C)	2.0×10^3 (1.06)		0.03			0.60	0.37	
		isomerization (2.92 h, 0 → 69 °C)	2.0×10^3 (1.05)					0.98	0.02	
2[a]	*t*-Bu-*m*-DCC	polymerization (23 min, −60 °C)	2.7×10^3 (1.01)	1.0						
		alkylation (27 min, −60 °C)	3.0×10^3 (1.02)		0.05	0.55	0.38			0.02
		deblocking (1.5 h, −60 → 0 °C)								
		isomerization (3.83 h, 0 → 69 °C)	3.1×10^3 (1.05)					0.98		0.02
3[b]	TMPCl	polymerization (28 min, −60 °C)	2.0×10^3 (1.02)	1.0						
		alkylation (30 min, −60 °C)	2.3×10^3 (1.08)	0.42	0.04	0.17	0.17	0.04	0.02	0.14
4		chain extension of (2) with MDI	3.89×10^4 (2.06)							

[a] Polymerization/quench: 60/40 (v/v) hexane/methyl chloride, −60 °C, chain end concentration, [CE] = 0.02 M, [2,6Lut] = 0.005 M, $[TiCl_4]$ = [*N*-(2-*tert*-butoxyethyl)pyrrole] = 3[CE]. Deblocking/isomerization: additionally $[EtAlCl_2]$ = 5[CE], $[H_2SO_4]$ = 2[CE]. [b] Forced coupling: conditions same as polymer 1 except [*N*-(2-*tert*-butoxyethyl)pyrrole] = 0.5[CE].

at −25 °C under a N_2 atmosphere. While stirring vigorously, 10 mL (0.25 equiv) of concentrated H_2SO_4 was added to catalyze the reaction. After 30 min, the flask was removed from the cooling bath and allowed to warm to room temperature for 2 h as the excess isobutylene boiled off. The reaction mixture was immediately washed and neutralized with aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and filtered to yield 83 g (85%) of a colorless liquid. ^1H NMR ($CDCl_3$) δ: 1.21 (s, *tert*-butyl, 9H), 3.57 (t, $-CH_2Cl$, 2H), 3.61 (t, $-OCH_2-$, 2H). ^{13}C NMR ($CDCl_3$) δ: 27.3 ($(CH_3)_3C-$), 43.6 ($-CH_2Cl$), 62.4 ($-OCH_2-$), 73.5 ($(CH_3)_3C-$). The 2-(2-chloroethoxy)-2-methylpropane was then reacted with pyrrolyl sodium salt to form *N*-(2-*tert*-butoxyethyl)pyrrole. Typically, 34 mL of pyrrole in 50 mL of dimethyl sulfoxide (DMSO) was added dropwise to 12.9 g (1.1 equiv) of sodium hydride in 50 mL of DMSO under a N_2 atmosphere. After cessation of H_2 release, 70 g (1.05 equiv) of 2-(2-chloroethoxy)-2-methylpropane in 50 mL of DMSO was slowly added. After 3 h, the product was washed with water and extracted into methylene chloride. The resulting solution was dried over $MgSO_4$ and filtered, after which the solvent was removed under vacuum. Vacuum distillation of the crude product yielded 60 g (73%) of a colorless liquid, which was stored under N_2 in the absence of light. ^1H NMR ($CDCl_3$) δ: 1.22 (s, *tert*-butyl, 9H), 3.67 (t, $-CH_2O-$, 2H), 4.06 (t, NCH_2-, 2H), 6.2 (t, C-3-pyrrole, 2H), 6.78 (t, C-2-pyrrole, 2H). ^{13}C NMR ($CDCl_3$) δ: 27.3 ($(CH_3)_3C-$), 50.3 (NCH_2-), 62.2 ($-CH_2O-$), 73.3 ($(CH_3)_3C-$), 107.8 (C-3-pyrrole), 121.1 (C-2-pyrrole).

Polymerization and Quenching. Quasiliving isobutylene polymerizations from mono- and difunctional initiators and end-quenching of those polymerizations were carried out as follows (see Table 1, polymers 1 and 2): Within a N_2-atmosphere glovebox, 105 mL of hexane and 70 mL of methyl chloride were chilled to −60 °C and charged to a four-neck round-bottom flask equipped with an overhead stirrer, thermocouple, and ReactIR probe. To the 60/40 (v/v) mixture of hexane and methyl chloride were added 0.109 mL of 2,6-lutidine and either 0.65 mL of TMPCl (Table 1, polymer 1) or 0.537 g of *t*-Bu-*m*-DCC (Table 1, polymer 2) to yield a chain end concentration ([CE]) of 0.02 M. A final molecular weight of 2000 g/mol was targeted for the monofunctional PIB by charging the reactor with 9.8 mL of isobutylene, whereas a final molecular weight of 3000 g/mol was targeted for the difunctional PIB by charging the reactor with 7.0 mL of isobutylene. After thermal equilibration, the polymerizations were initiated with 1.23 mL (3 equiv per chain end) of $TiCl_4$. At complete monomer conversion, 3 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole was charged to the reactor, and the alkylation reaction was allowed to proceed for 25−30 min. Then, the reactor was charged with 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 to promote removal of the terminal *tert*-butyl blocking group residing on the pyrrole capping agent. After addition of the acids, the reaction flask was immediately removed from the cooling bath and allowed to warm to room temperature, which required ~4.5 h. The reaction flask was then placed on a heating mantle, fitted with a reflux condenser, and heated to reflux at 69 °C for 3−4 h. Finally, the catalysts were destroyed by addition of excess methanol. Impurities were removed by taking the polymer up in hexane and dripping the solution into excess methanol, causing polymer precipitation. After twice precipitating the polymer, residual solvents were removed under vacuum. Table 1 shows the molecular weights of the PIBs as well as the chain end composition for each stage of the reaction.

Chain end compositions were estimated by integration of ^1H NMR spectra. The amounts of C-2 and C-3 alkylated pyrrole (*tert*-butyl group intact) were quantified by integrating the resonances at 4.10 and 3.91 ppm due to the methylene units adjacent to the alkylated pyrrole nitrogen. When the *tert*-butyl group was displaced to provide hydroxyl functionality at the chain end, the relative amounts of the C-2 and C-3 alkylated pyrrole isomer were quantified by integration of the resonance at 4.15 ppm, due to the methylene unit adjacent to the C-2 alkylated pyrrole nitrogen, and the resonance at 3.81 ppm, due the terminal methylene unit adjacent to the hydroxyl on the C-3 alkylated pyrrole. The amount of *exo*-olefin was quantified by integration of the resonance at 2.00 ppm due to the terminal PIB methylene unit, and the amount of chain coupling via dialkylation of pyrrole was quantified by integration of the resonances at 6.28−6.35 ppm due to a single hydrogen on the dialkylated pyrrole ring. For those polymers exhibiting partial removal of the terminal *tert*-butyl group, the fraction of the *tert*-butyl groups remaining intact was estimated by integration of the resonances at 3.56 and 3.65 ppm due the methylene units on the C-2 and C-3 alkylated pyrroles adjacent to the *tert*-butoxy group. Initiation from *t*-Bu-*m*-DCC allowed conformation of chain end functionality by integration of the resonance at 7.17 ppm due to the initiator residue.

Kinetics of Quenching and Deprotection. Kinetics of the PIB−pyrrole alkylation reactions were investigated using 0.02 M solutions of monofunctional *tert*-chloride-terminated PIB. Into a 60/40 (v/v) mixture of hexane (120 mL) and methyl chloride (80 mL) at −60 °C were dissolved 7.8 g of 2000 g/mol *tert*-chloride-terminated PIB, 0.12 mL of 2,6-lutidine, and 0.44−3.63 mL (1.2−10 equiv) of *N*-(2-*tert*-butoxyethyl)pyrrole. The alkylation reactions were initiated by addition of 1.34 mL (3 equiv) of $TiCl_4$. Conversion of the chain ends was monitored by integration of ^1H NMR spectra of aliquots taken from the reactions.

A similar method was used to monitor the *in situ* removal of the terminal *tert*-butyl blocking group following completion of the *N*-(2-*tert*-butoxyethyl)pyrrole alkylation reaction. Into a 60/40 (v/v) mixture of hexane (105 mL) and methyl chloride (70 mL) at −60 °C were dissolved 6.9 g of 2000 g/mol *tert*-chloride-terminated PIB, 0.11 mL of 2,6-lutidine, and 1.9 mL (3 equiv) of *N*-(2-*tert*-butoxyethyl)pyrrole. The alkylation reaction was initiated with the addition of 1.19 mL (3 equiv) of $TiCl_4$. After 30 min of reaction time, additional acids were charged to the reactor, and it was immediately removed from the cooling bath to promote removal of the terminal *tert*-butyl group. After 4.5 h of warming at ambient temperature, most of the methyl chloride had volatilized. The remaining contents of the reactor were heated to reflux (69 °C) for an additional 3.5 h. As in previous reactions, changes in the chain end functionality were monitored by integration of ^1H NMR spectra of aliquots taken from the reactions.

Postpolymerization Reaction of Hydroxy-Functional PIB. Reaction of monohydroxy-functional PIB with monofunctional acid and isocyanates was carried out as follows: Under a N_2 atmosphere, vials were charged with 0.4 g samples of 2000 g/mol [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (Table 1, polymer 1) dissolved in 15 mL of toluene. The esterification reaction involved addition of 76 μL (3 equiv) of *tert*-butyl acetic acid along with 2 mg (0.1 equiv) of 4-(dimethylamino)pyridine and 46 μL (1.5 equiv) of *N,N'*-diisopropylcarbodiimide. The urethane-forming reactions involved addition of 68 μL (3 equiv) of butyl isocyanate or 65 μL (3 equiv) of phenyl isocyanate; both reactions were catalyzed by subsequent addition of 6 μL (0.05 equiv) of dibutyltin dilaurate (DBTDL). The reactions were allowed to proceed at room temperature for 4 h before concentrating the polymer solution and precipitating the polymers from toluene into methanol.

The α,ω-dihydroxypolyisobutylene (Table 1, polymer 2) was chain extended with 4,4'-methylenebis(phenyl isocyanate) (MDI). Under nitrogen, 1.2 g of α,ω-bis[*N*-(2-hydroxyethyl)-pyrrol-3-yl]polyisobutylene and 0.1 g (1.05 equiv per hydroxyl) of MDI were dissolved in 20 mL of toluene. The room temperature urethane-forming reaction was catalyzed by addition of 6 μL (0.5 wt %) DBTDL. The reaction was allowed to proceed for 12 h, after which time the polymer was precipitated into methanol. Residual solvents were removed under vacuum.

Results and Discussion

N-Alkyl-substituted pyrroles are highly susceptible to electrophilic attack by carbenium ions and therefore provide a convenient platform on which to pursue *in situ* functionalization of quasiliving PIB with terminal primary hydroxyl groups. Unfortunately, direct addition of compounds bearing an unprotected hydroxyl moiety to a $TiCl_4$-catalyzed quasiliving PIB typically results in rapid reaction of the hydroxyl with the Lewis acid present in the system, often rendering the catalyst and/or quencher unreactive toward the polymer chain ends.[10] Cognizant of this fact, we sought a suitable protecting group that could be placed on the *N*-alkyloxy tether of pyrrole and not only survive the acidic conditions of a $TiCl_4$-catalyzed isobutylene polymerization without interference but also be easily and efficiently removed *in situ* after pyrrole alkylation. Acyl protecting groups were considered unsatisfactory due to potentially debilitating complexation reactions that occur between carbonyl groups and $TiCl_4$.[31] Silyl protecting groups may be labile under acidic conditions; however, the substituents around silicon can be varied in bulk to increase stability.[32] Unfortunately, increasing steric bulk around silicon also makes subsequent removal difficult, often requiring fluoride-assisted hydrolysis.[33]

With these considerations in mind our choice for hydroxyl protection became a simple alkyl group, namely *tert*-butyl. *tert*-Butyl ethers are stable under a wide variety of conditions but can be cleaved under strongly acidic conditions.[33] Thus, an *N*-(2-*tert*-butoxyalkyl)pyrrole was synthesized by the following two-step procedure. First, the *tert*-butyl group was introduced onto 2-chloroethanol by acid-catalyzed addition of isobutylene. A pyrrolyl sodium salt was then used to displace the chloride, yielding *N*-(2-*tert*-butoxyethyl)pyrrole. An ethylene tether between pyrrole and the latent hydroxyl was chosen to minimize the incremental change in the PIB molecular weight after alkylation; however, longer alkylene tethers are expected to provide similar results.

Monofunctional Primary Hydroxy-Terminated Polyisobutylene. Figure 1 shows ^1H NMR spectra of aliquots (A, B, C) removed from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization initiated from TMPCl and quenched with 3 equiv per chain end of *N*-(2-*tert*-butoxyethyl)pyrrole (see Table 1, polymer 1). Figure 1A reveals the structure of the PIB immediately after the 25 min quenching reaction; ~95% of the PIB chains underwent electrophilic aromatic substitution (EAS), resulting in monoalkylation of the pyrrole ring at either the C-2 or C-3 position. The C-3 alkylated isomer exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, two triplets at 3.55 and 3.91 ppm due to the pyrrole *N*-alkylene tether, and resonances at 5.99, 6.41, and 6.55 ppm due to the pyrrole ring. The C-2 alkylated isomer exhibited a similar set of resonances: a singlet at 1.74 ppm due to the terminal PIB methylene unit, two triplets at 3.64 and 4.09 ppm due to the pyrrole *N*-alkylene tether, and resonances at 5.87, 6.02, and 6.64 ppm due to the pyrrole ring. The C-3 alkylated isomer was the major product representing 57% of the chain ends, and the C-2 alkylated isomer was the minor product representing 38% of the chain ends. The remaining 5% of the chain ends were *exo*-olefin as evidenced by the resonances at 1.78 ($-CH_2C(=CH_2)CH_3$), 2.00 ($-CH_2C(=CH_2)CH_3$), and 4.64/4.85 ppm ($-CH_2C(=CH_2)CH_3$). The *exo*-olefin functionality did not arise due to unimolecular β-proton expulsion (it was not present in a prequench aliquot) but is believed to be induced by the ether linkage of the quencher.[34] Similar pyrrole-based quenchers without ether linkages do not produce the *exo*-olefin chain ends as observed here.[26,27]

After the 25 min quenching reaction, 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 were charged to the reactor to assist in removal of the *tert*-butyl protecting group and promote further EAS reaction between the residual *exo*-olefin chain ends and residual quencher. At this time the reaction flask was also removed from the cooling bath to begin warming. After 1.5 h, the methyl chloride had boiled off, and the reaction had warmed to 0 °C. ^1H NMR analysis of an aliquot removed from the reactor at this time resulted in the spectrum shown in Figure 1B. This spectrum indicated that the *tert*-butyl groups were quantitatively displaced. This was

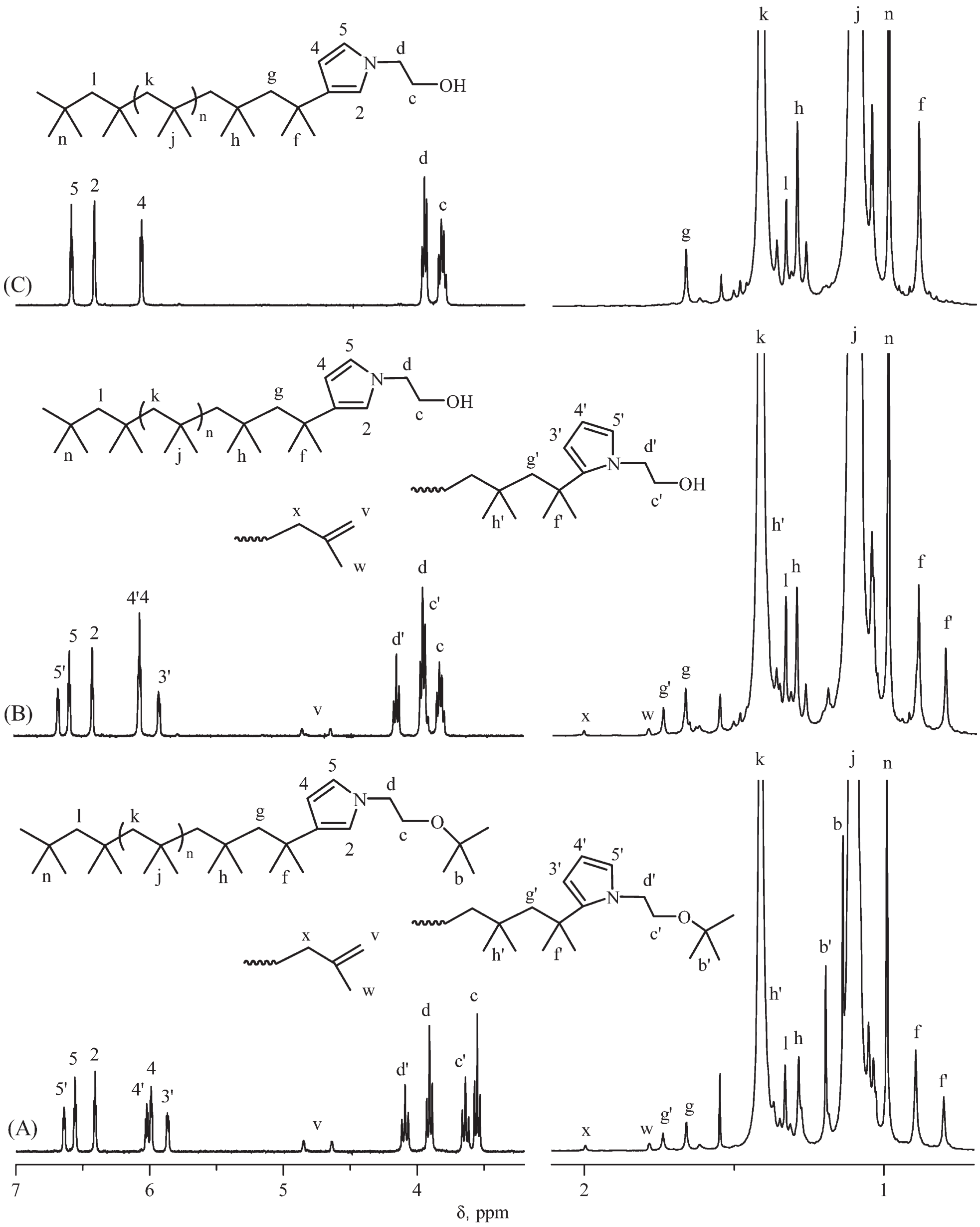


Figure 1. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of monofunctional polyisobutylene after (A) $TiCl_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole, (B) subsequent warming in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether, and (C) isomerization to [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (see Table 1, polymer 1).

seen most readily by a shift in the resonances of the methylene units of the *N*-alkylpyrrole tether. Two quartets appear at 3.81 and 3.94 ppm, due to the methylene units adjacent to the terminal hydroxyl of the C-3 and C-2 alkylated isomers, respectively. Figure 1B also shows that after warming the isomer ratio had slightly shifted toward the more thermodynamically stable C-3 isomer, and the percentage of chain ends bearing *exo*-olefin functionality was reduced by further EAS reactions.

The reduction of *exo*-olefin upon warming the reaction in the presence of the mixed acids was further exploited by heating the reaction mixture to reflux (69 °C) for ~3 h. ^{1}H NMR analysis of the final product after this time resulted in the spectrum shown in Figure 1C. Examination of this spectrum revealed that heating caused all residual *exo*-olefin to alkylate the pyrrole quencher, resulting in quantitative formation of primary hydroxyl chain ends. Furthermore, over 98% of the chain ends were shifted to the C-3 alkylated isomer. The final hydroxy-terminated PIB exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, resonances at 3.81 (quartet) and 3.95 ppm (triplet) due to the *N*-alkylene tether, and resonances at 6.06, 6.41, and 6.58 ppm due to the pyrrole ring.

Alkylation of pyrrole and subsequent deprotection was also confirmed by ^{13}C NMR. Figure 2A shows the spectrum of the PIB immediately after the 25 min quenching reaction. Resonances at 71.9 and 35.2 ppm, representing the ultimate quaternary and *gem*-dimethyl carbons of *tert*-chloride PIB,[35] respectively, were not present after the alkylation reaction and were replaced by a new set of resonances in both the aromatic and the aliphatic regions of the spectrum; the resonances of the pyrrole moiety occurred in pairs due to the C-2 and C-3 alkylated isomers. Figure 2B shows the spectrum of the final product. After refluxing the PIB alkylated pyrrole in the presence of the mixed acids for 3 h, resonances at 73.0 and 27.0 ppm due to the terminal *tert*-butyl

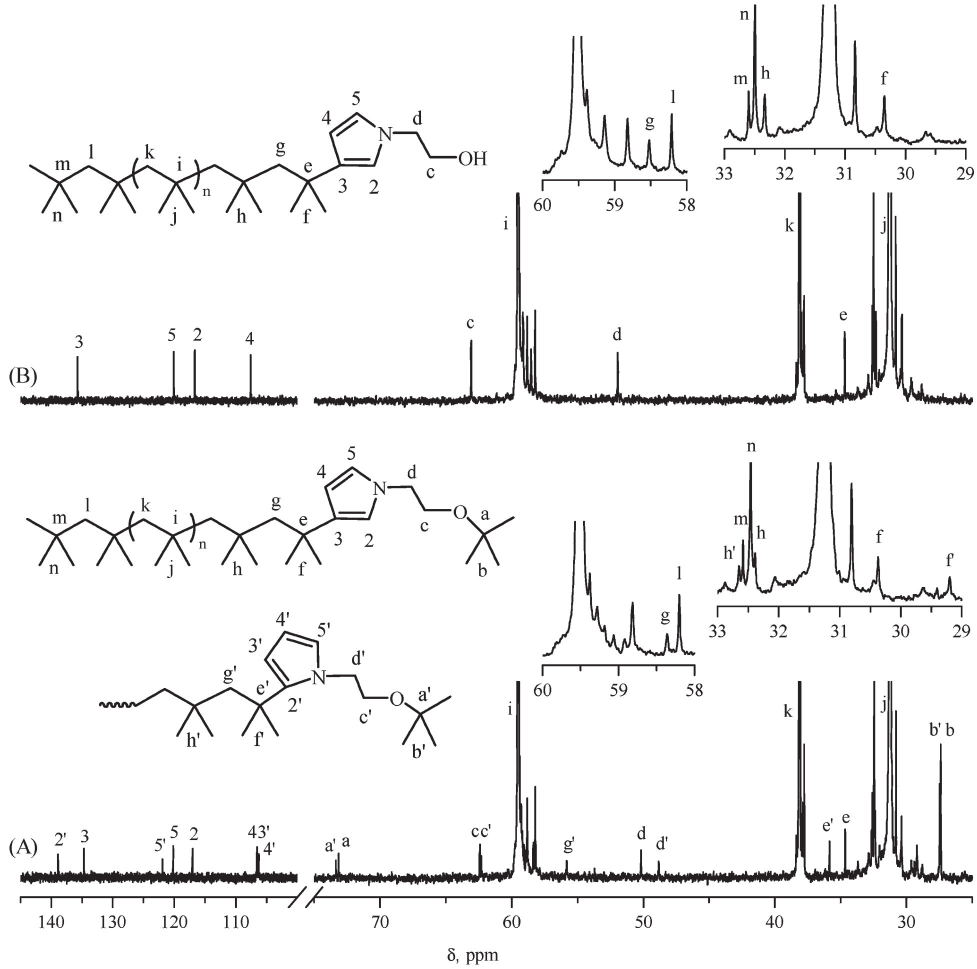


Figure 2. ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) spectra of monofunctional polyisobutylene after (A) $TiCl_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether and induce isomerization to [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (see Table 1, polymer 1).

protecting group disappeared indicating its removal. In addition, only resonances associated with the C-3 alkylated pyrrole were observed, further indicating nearly complete isomerization of the chain ends.

Difunctional Primary Hydroxy-Terminated Polyisobutylene. Figure 3 shows ^{1}H NMR spectra of PIB from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization initiated from *t*-Bu-*m*-DCC and quenched with 3 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole (see Table 1, polymer 2). As with the monofunctional PIB, the spectrum of Figure 3A reveals that both the C-2 and C-3 alkylated pyrroles were obtained after quenching for 27 min. The C-3 alkylated isomer was the major product representing 55% of the chain ends, and the C-2 alkylated isomer was the minor product representing 38% of the chain ends. Again, a small amount (5%) of *exo*-olefin was formed during the quenching reaction. The remaining 2% of the chain ends were involved in double alkylation of a single pyrrole ring (coupling), as discussed later.

After charging the reactor with 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4, it was allowed to warm to 0 °C and then heated to reflux (69 °C) for ~4 h. Figure 3B shows the ^{1}H NMR spectrum of the final α,ω-bis[*N*-(2-hydroxyethyl)-pyrrol-3-yl]polyisobutylene obtained after reflux with the mixed acids. The terminal *tert*-butyl groups were quantitatively displaced, and 98% of the chain ends shifted to the C-3 alkylated isomer. The spectrum exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, resonances at 3.81 (quartet) and 3.95 ppm (triplet) due to the *N*-alkylpyrrole tether, and resonances at 6.06, 6.41, and 6.58 ppm due to the pyrrole ring.

Figure 4 shows ^{13}C NMR spectra of difunctional PIB immediately after quenching (A) with *N*-(2-*tert*-butoxyethyl)pyrrole and after reflux (B) with the mixed acids. The 2- and 3-PIB alkylated pyrroles with *tert*-butyl protecting groups intact were observed after quenching, but after reflux with the mixed acids the resonances at 73.0 and 27.0 ppm due to the terminal *tert*-butyl protecting groups were absent, indicating removal. In addition, only resonances from the C-3 alkylated pyrrole were observed among the resonances for the aromatic initiator residue in Figure 4B, indicating near complete isomerization of the chain ends.

Close examination of the ^{1}H NMR spectrum of difunctional PIB alkylated pyrrole in Figure 3A reveals resonances at 6.28 and 5.70 ppm that were not observed with monofunctional PIB and that accounted for ~2% of the difunctional PIB chain ends. These resonances were assigned to pyrrole rings that had undergone double alkylation, resulting in coupling of two PIB chains. Figure 5 compares the GPC traces for mono- and difunctional PIB quenched with *N*-(2-*tert*-butoxyethyl)pyrrole under otherwise identical reaction conditions. Coupling was not detectable in the monofunctional PIB alkylated pyrrole sample, but the postquench trace for the difunctional PIB exhibited a shoulder centered at roughly twice the molecular weight of the main peak. Coupling occurred during the quenching reaction because it

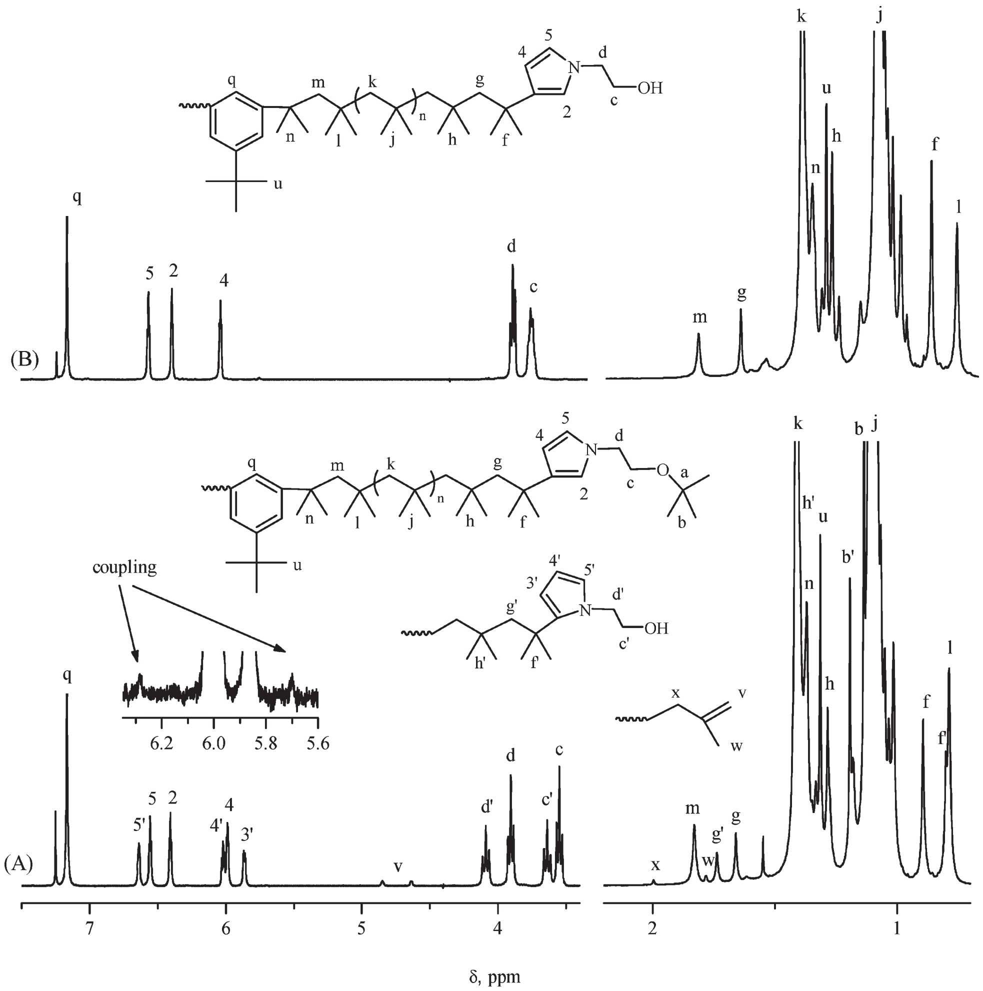


Figure 3. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of difunctional polyisobutylene after (A) $TiCl_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether and induce isomerization to α,ω-bis[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene (see Table 1, polymer 2).

was not observed in the prequench aliquot, and it increased slightly during the acid induced deprotection/isomerization at elevated temperatures.

To confirm that chain coupling occurred through the pyrrole ring, an isobutylene polymerization initiated from TMPCl was quenched with 0.5 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole to deliberately induce double alkylation (see Table 1, polymer 3). ^{1}H NMR analysis of the resulting PIB revealed that residual *tert*-chloride and *exo*-olefin were present as well as the expected 2- and 3-monoalkylated pyrrole isomers; a partial spectrum (aromatic region) of the resulting polymer is shown in Figure 6. The 2- and 3-monoalkylated pyrroles were represented by the major peaks at 5.99, 6.41, and 6.55 ppm (C-3) and 5.87, 6.02, and 6.64 ppm (C-2). In addition, a set of minor peaks offset slightly downfield from the major peaks indicated that a small fraction of the alkylated pyrroles had begun to lose the terminal *tert*-butyl group. Two additional, distinct resonances at 6.28 and 5.70 ppm were due to dialkylated *N*-(2-*tert*-butoxyethyl)pyrrole. Dialkylation appeared to occur exclusively in the C-2 and C-4 positions of the pyrrole ring. GPC traces for the pre- and postquench PIB of Figure 6 are shown in Figure 7. The postquench UV trace has a large shoulder of roughly twice the molecular weight of the main peak, indicating that coupling occurred through the UV-absorbing pyrrole ring.

Stokes[36] has shown that quasiliving PIB readily dialkylates unsubstituted pyrroles, but Storey et al. later demonstrated that *N*-substitution effectively prevents dialkylation.[26] It was concluded that steric constraints imposed by the *N*-substituent possibly prevent a second alkylation. For *N*-(2-*tert*-butoxyethyl)pyrrole steric constraints also exist, and dialkylation is largely prevented when excess *N*-(2-*tert*-butoxyethyl)pyrrole is present, especially for monofunctional PIB (see Figure 5). Coupling occurs to a greater extent with difunctional PIB and *N*-(2-*tert*-butoxyethyl)pyrrole, likely due to enhanced local concentration arising from aggregation of chains bearing at least one pyrrole moiety. The exact nature of the aggregation is not known, but it apparently involves interaction of the pyrrole moieties with $TiCl_4$. After one end of a difunctional PIB chain has alkylated pyrrole and subsequently aggregated with other PIB chains bearing pyrrole, the remaining *tert*-chloride end group is exposed to an elevated concentration of pyrrole that has already undergone one alkylation. During the deblocking stage of the reaction the difunctional hydroxy-terminated polymer actually precipitates from the reaction solvent due to formation of tri- and/or tetravalent metal alkoxide pseudo-cross-links. Once precipitated, the PIB chain ends are further restricted from accessing the free pyrrole in solution, hence further increasing the likelihood of chain coupling.

Non-$TiCl_4$ Catalysis. Since the inadvertent formation of *exo*-olefin termini (< 5%) and chain coupling with difunctional polymer were thought to arise due to interactions between *N*-(2-*tert*-butoxyethyl)pyrrole and $TiCl_4$, efforts were made to avoid the use of $TiCl_4$ during both the

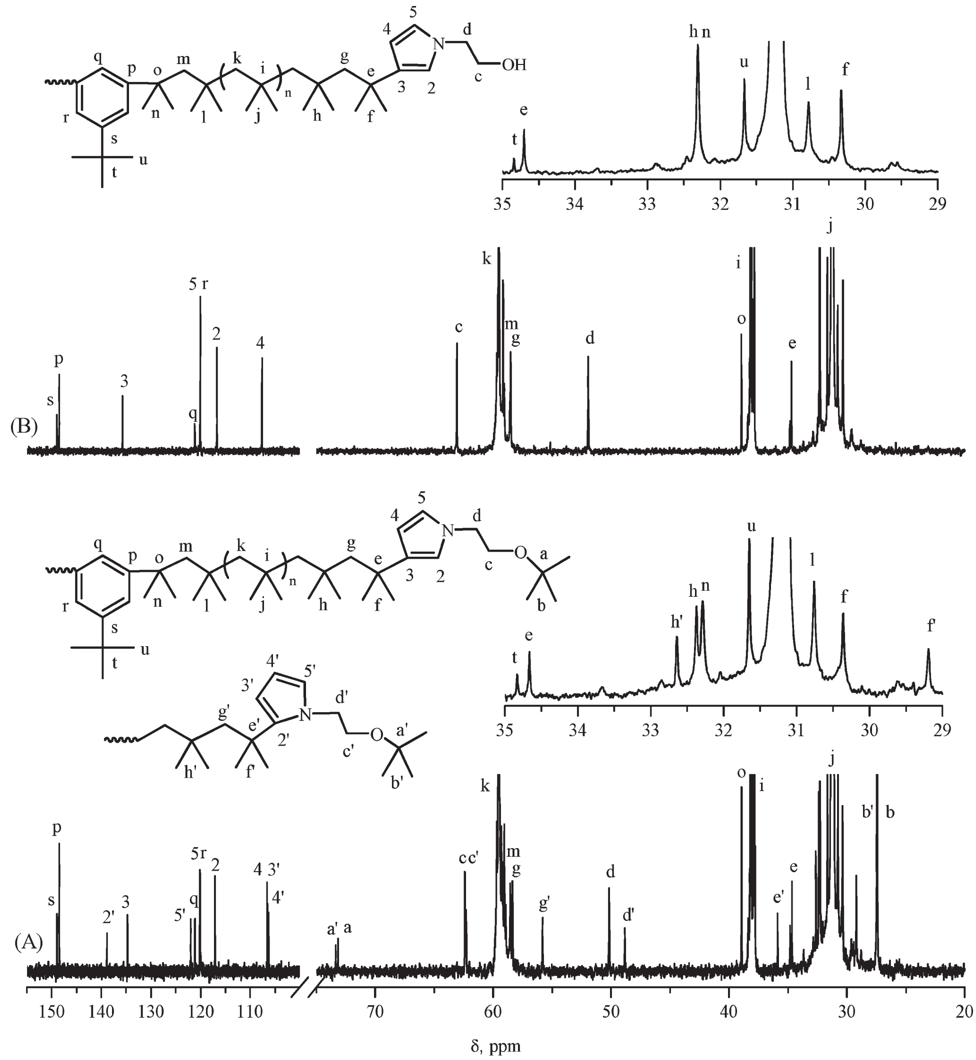


Figure 4. ^{13}C NMR (75 MHz, CDCl$_3$, 22 °C) spectra of difunctional polyisobutylene after (A) TiCl$_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of EtAlCl$_2$ and H$_2$SO$_4$ to cleave the terminal ether and induce isomerization to α,*ω*-bis[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene (see Table 1, polymer 2).

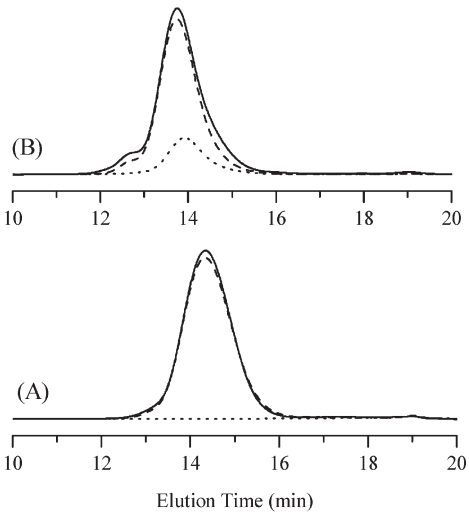


Figure 5. UV traces for GPC of (A) monofunctional PIB before quenching (dot), after quenching with *N*-(2-*tert*-butoxyethyl)pyrrole (dash), and after deblocking (solid), i.e., removal of the terminal *tert*-butyl group; and (B) difunctional PIB before quenching (dot), after quenching (dash), and after deblocking (solid).

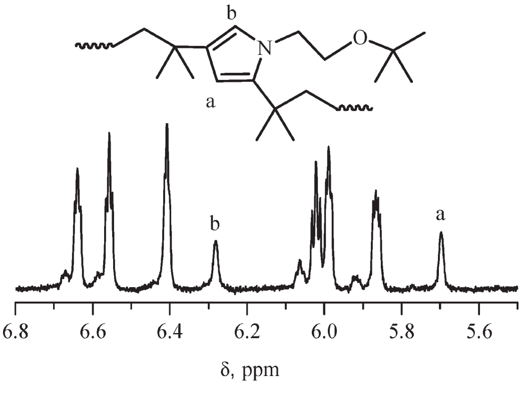


Figure 6. Partial ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C) spectrum showing the dialkylated pyrrole resonances of deliberately coupled PIB (Table 1, polymer 3). Unlabeled resonances are due to monoalkylated pyrrole isomers (see Figure 1).

polymerization and quenching reactions. EtAlCl$_2$ was capable of catalyzing both the alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and subsequent cleavage of the terminal *tert*-butyl ether to provide hydroxyl termini; unfortunately, it was too strong of a catalyst for controlled isobutylene

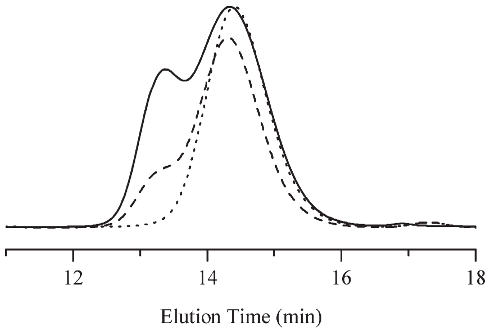


Figure 7. GPC traces (RI) for the PIB from Figure 6 before (dot) and after (dash) quenching with 0.5 equiv per chain end of *N*-(2-*tert*-butoxyethyl)pyrrole. Coupling through the pyrrole ring is indicated by the high molecular weight shoulder in the postquench UV trace (solid).

polymerization with the given 60/40 (v/v) hexane/methyl chloride solvent system. Even diethylaluminum chloride (Et_2AlCl) has been reported to require a highly nonpolar solvent system to yield "livingness".[37] Literature reports indicated that a better choice for alkylaluminum halide-catalyzed isobutylene polymerization may be dimethylaluminum chloride (Me_2AlCl).[38,39] However, we observed that Me_2AlCl-catalyzed isobutylene polymerizations from *t*-Bu-*m*-DCC in 60/40 (v/v) hexane/methyl chloride at −75 °C were plagued by both tri- and disubstituted olefin formation at the chain end as well as cycloalkylation at the initiation site after one isobutylene addition (indanyl ring formation) (see Supporting Information, Figure A). The use of boron trichloride (BCl_3) as a polymerization catalyst in methyl chloride[29] at −60 °C with subsequent addition of *N*-(2-*tert*-butoxyethyl)pyrrole and Me_2AlCl at full monomer conversion prevented olefin formation at the PIB chain end, but the mixed catalyst system was too strong, resulting in immediate cleavage of the *tert*-butyl ether quencher moiety and incomplete capping of the PIB.

Kinetics of Quenching and Deprotection. Figure 8A shows first-order kinetic plots for alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole by monofunctional *tert*-chloride PIB. The various plots represent *N*-(2-*tert*-butoxyethyl)pyrrole concentrations ranging from 1.2 to 10 times the chain end concentration of 0.02 M. For all concentrations the rates of alkylation were equal and independent of the quencher concentration, up to about 75% conversion of the chain ends. This zero-order dependence on quencher concentration indicated that the rate of quenching was limited by chain end ionization.[40] From run number measurements made under similar conditions at −60 °C, Thomas and Storey[41] calculated a value of k_i = 9.1 L^2 mol^{-2} s^{-1} for the rate constant for ionization of PIB chain ends. The initial first-order rate constant for alkylation in Figure 8A, divided by the square of the effective $TiCl_4$ concentration,[42] yielded a similar value of 8.4 L^2 mol^{-2} s^{-1}, thus supporting the conclusion that ionization was the rate-limiting step for the quenching reaction. Given the fact that increasing concentration of *N*-(2-*tert*-butoxyethyl)pyrrole in Figure 8A did not cause a measurable reduction in the initial rate of quenching suggests that the equilibrium constant, K_{com}, for complexation of $TiCl_4$ with *N*-(2-*tert*-butoxyethyl)pyrrole was small, or more precisely, K_{com} × [*N*-(2-*tert*-butoxyethyl)pyrrole] ≪ 1, assuming a 1:1 complex.

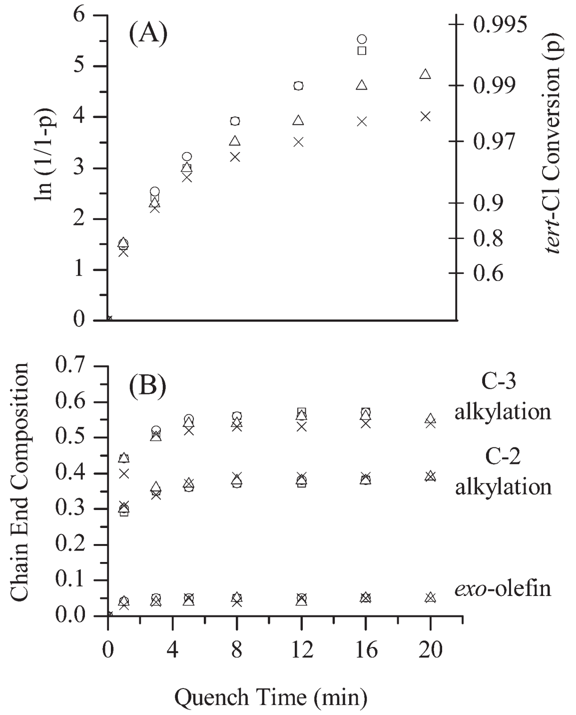


Figure 8. (A) Kinetics of *N*-(2-*tert*-butoxyethyl)pyrrole alkylation with monofunctional PIB (0.02 M) in 60/40 (v/v) hexane/methyl chloride at −60 °C with 2,6-lutidine (0.005 M) and 3 equiv of $TiCl_4$ using 1.2 (circle), 3 (square), 6 (triangle), and 10 equiv (×) of *N*-(2-*tert*-butoxyethyl)pyrrole. (B) The final chain end functionality remained approximately constant over the various quencher concentrations, with 57% C-3 alkylated pyrrole, 38% C-2 alkylated pyrrole, and 5% *exo*-olefin formation.

The first-order kinetic plots of Figure 8A are not linear but display downward curvature. The effect became more pronounced as the initial quencher concentration was increased. Since ionization was rate limiting at the start of reaction, it certainly was expected to remain rate limiting as chain ends were depleted by capping; hence, the observed downward curvature cannot be due to a shift in the rate-limiting step from ionization to capping. The observed curvature also cannot be ascribed to complexation between $TiCl_4$ and *N*-(2-*tert*-butoxyethyl)pyrrole, since initial rates were the same regardless of quencher concentration. Thus, the curvature almost certainly represents a retarding of the rate of ionization due to loss of $TiCl_4$. As alkylation of pyrrole proceeded, HCl was generated necessarily causing active $TiCl_4$ to salt out as inactive $Ti_2Cl_9^-$ counterions, effectively reducing the overall rate of ionization.

Figure 8B shows that the relative amounts of alkylated pyrrole isomers and concomitantly formed *exo*-olefin remained constant regardless of the ratio of quencher to chain ends. After alkylation the PIB chain ends were consistently comprised of 57% C-3 alkylated pyrrole, 38% C-2 alkylated pyrrole, and 5% *exo*-olefin. The observed isomer ratio is in the range previously found for *N*-methylpyrrole[26] (54% C-3 alkylation/46% C-2 alkylation) and *N*-(ω-haloalkyl)-pyrroles[27] (60−74% C-3 alkylation/26−40% C-2 alkylation, depending on alkylene tether length and identity of halogen).

Deprotection of the hydroxyl terminus via removal of the *tert*-butyl group (deblocking) can be induced with or without acids supplemental to the $TiCl_4$ used to catalyze the polymerization and alkylation reactions. Figure 9A shows the kinetics of deblocking in the presence of various acid combinations, including additional $TiCl_4$, $TiCl_4/H_2SO_4$, $EtAlCl_2$, and $EtAlCl_2/H_2SO_4$. In each case, the additional acids were charged to the reactor after the $TiCl_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole; the reactor was removed from the cold bath and allowed to warm to room temperature

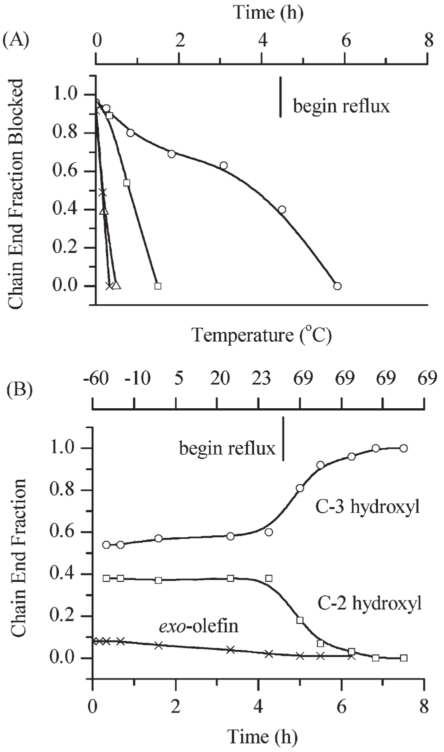


Figure 9. (A) Kinetics of deblocking *N*-(2-*tert*-butoxyethyl)pyrrole-capped PIB (terminal *tert*-butyl ether cleavage): additional 5 equiv of $TiCl_4$ (circle), 5 equiv of $TiCl_4$ and 2 equiv of H_2SO_4 (square), 5 equiv of $EtAlCl_2$ (triangle), or 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 (×). (B) Chain end composition during deblocking with 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 added: C-3 hydroxyl (circle), C-2 hydroxyl (square), *exo*-olefin (×).

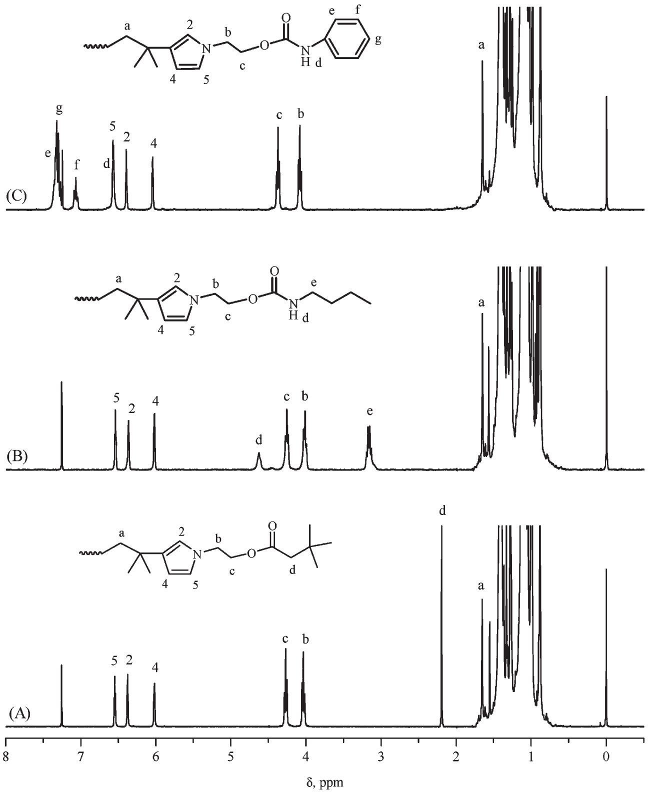


Figure 10. ^1H NMR (300 MHz, $CDCl_3$, 22 °C) spectra of polymers obtained after reaction of [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole with (A) *tert*-butyl acetic acid, (B) butyl isocyanate, and (C) phenyl isocyanate.

(requiring about 4.5 h, with evolution of methyl chloride) and then actively heated to hexane reflux (69 °C) for ~3.5 h. Simply allowing the reaction to warm to room temperature without supplemental acids, i.e., making use only of the $TiCl_4$ that was already present as the polymerization catalyst, resulted in very slow deblocking (not shown). Even with an additional 5 equiv of $TiCl_4$, deblocking was relatively slow and not complete by the time the reaction had reached room temperature; however, the rate increased as heat was applied and complete deblocking was achieved. The rate of deblocking by $TiCl_4$ also increased dramatically by addition of a protic acid, e.g., H_2SO_4. As shown, the $TiCl_4/H_2SO_4$ combination provided full deblocking before the reaction had warmed to 0 °C (about 90 min). The most rapid deblocking was achieved by the addition of a stronger Lewis acid, e.g., $EtAlCl_2$. Charging $EtAlCl_2$ to the reactor resulted in complete deprotection within about 30 min, and the combination of $EtAlCl_2$ and H_2SO_4 yielded even a slightly higher rate.

In addition to the rate of deblocking, the combination of acids used for deblocking was also found to affect the overall end group composition of the PIB. ^1H NMR analysis revealed that a major drawback of the use of $TiCl_4$ as the sole Lewis acid, with or without H_2SO_4, was that it failed to promote EAS reactions between *exo*-olefin PIB and excess quencher. In addition, $TiCl_4$ induced chain coupling through the pyrrole ring (particularly when used without H_2SO_4) at elevated temperatures (see Figures B and C, Supporting Information, for plots of chain end composition vs time for $TiCl_4$ and $TiCl_4/H_2SO_4$, respectively). Both of these issues negatively impact the overall functionality of the PIB; however, both were alleviated by addition of the stronger Lewis acid, $EtAlCl_2$. The use of $EtAlCl_2$ not only increased the rate of *tert*-butyl group removal but also prevented coupling (Figure D, Supporting Information). Moreover, as shown in Figure 9B, when the protic acid, H_2SO_4, was used in conjunction with $EtAlCl_2$, the residual *exo*-olefin was forced to alkylate pyrrole, resulting in quantitative hydroxyl functionality.

Figure 9B also illustrates isomerization of the PIB pyrrole chain ends that occurred during deblocking, principally at elevated temperature (69 °C). The C-2 alkylated pyrrole isomer was converted to the more thermodynamically stable C-3 alkylated pyrrole isomer. Isomerization occurred with all four acid combinations, but it was faster and more complete in the presence of $EtAlCl_2$. The final chain end composition in Figure 9B achieved by the addition of $EtAlCl_2/H_2SO_4$ was 98% C-3 hydroxyl and 2% C-2 hydroxyl, with no detectable *exo*-olefin or coupled products.

Postpolymerization Reactions on Hydroxy-Functional PIB. Difunctional hydroxy-terminated PIBs are particularly useful in the synthesis of segmented block copolymers. The aliphatic backbone of PIB exhibits outstanding thermal stability, oxidation and ozonolysis resistance, and barrier properties and has been incorporated as a soft segment in polyesters,[43] polyurethanes,[44,45] polyamides,[46] and polycarbonates.[47] Synthesis of these copolymers typically requires reaction of hydroxy-telechelic PIBs with polyfunctional isocyanates, carboxylic acids, or esters. To demonstrate that the currently discussed hydroxy-telechelic PIBs are sufficiently reactive toward such functionalities, model reactions with isocyanates and carboxylic acids were performed, and a chain extension reaction was preformed with an aromatic diisocyanate.

Figure 10 shows ^1H NMR spectra of the products from reaction of [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole with

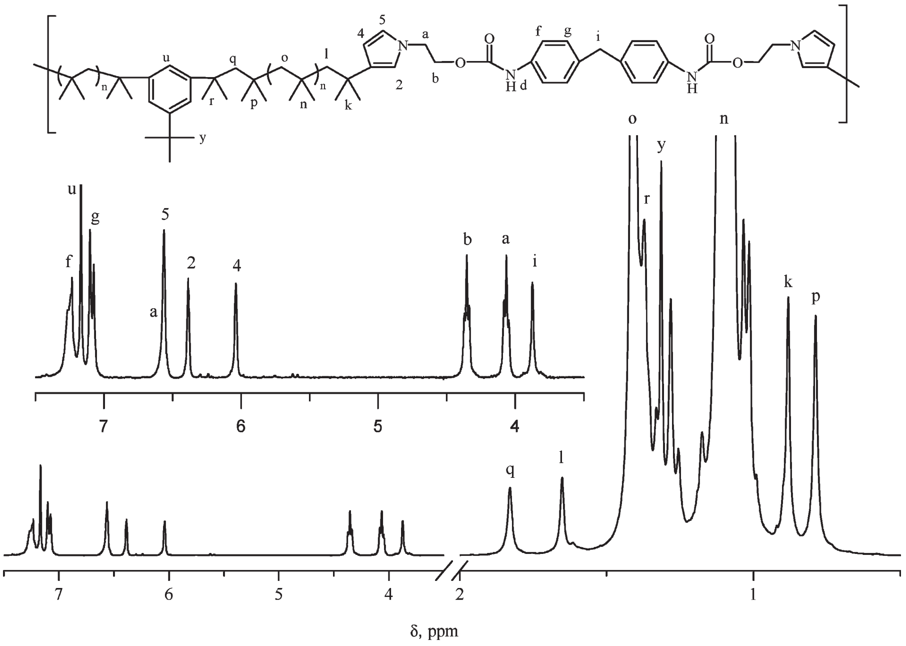


Figure 11. ^{1}H NMR (300 MHz, CDCl$_3$, 22 °C) spectrum of polymer obtained from chain extension of α,ω-bis[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene with 4,4′-methylenebis(phenyl isocyanate).

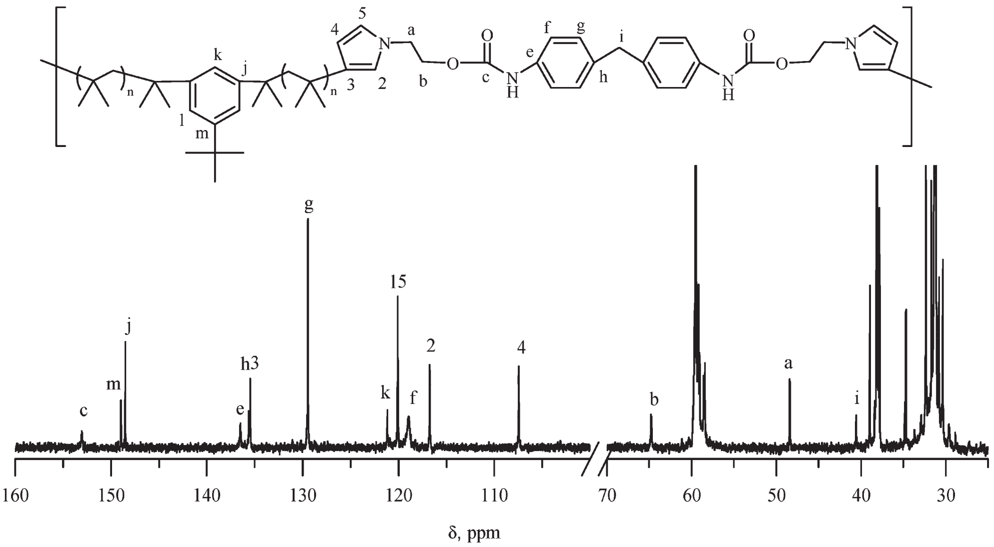


Figure 12. ^{13}C NMR (75 MHz, CDCl$_3$, 22 °C) spectrum of polymer obtained from chain extension of α,ω-bis[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene with 4,4′-methylenebis(phenyl isocyanate).

tert-butyl acetic acid (A), butyl isocyanate (B), and phenyl isocyanate (C). For all three cases, the catalyzed room temperature reactions were quantitative after 4 h. The resonances for the methylene protons adjacent to oxygen on the pyrrole moiety were shifted downfield from 3.81 ppm after formation of the electron withdrawing ester and urethane linkages. While it has been previously shown that isocyanates are capable of electrophilic addition to a pyrrole ring,[48] particularly in the C-2 position, reaction of isocyanate with the pyrrole ring was not observed here.

As further evidence of reactivity, the α,ω-dihydroxypolyisobutylene was chain extended in a dibutyltin dilaurate (DBTDL)-catalyzed urethane-forming reaction with 4,4′-methylenebis(phenyl isocyanate) (MDI) (see Table 1, polymer 4). Chain extension was confirmed in the ^{1}H NMR spectrum shown in Figure 11 by a downfield shift, from 3.81 to 4.35 ppm, of the resonance due to the ultimate methylene unit of the *N*-alkylene tether, adjacent to oxygen. The splitting pattern also changed, from a quartet to a triplet, consistent with loss of the hydroxyl proton. The aromatic resonances of the MDI residue were seen at 7−7.2 ppm as well as the bridge methylene protons at 3.88 ppm. Chain extension was also evident in the ^{13}C NMR spectrum of Figure 12, most notably due to the urethane carbonyl resonance at 153.0 ppm. The number-average molecular weight determined from GPC after chain extension was 3.89×10^4 g/mol with a polydispersity of 2.06 (see Supporting Information, Figure E).

Conclusion

We have shown that direct addition of excess *N*-(2-*tert*-butoxyethyl)pyrrole to a TiCl$_4$-catalyzed quasiliving isobutylene polymerization in 60/40 (v/v) hexane/methyl chloride at −60 °C resulted in rapid alkylation of the pyrrole ring and concomitant formation of < 5% *exo*-olefin-terminated PIB. By heating the reaction mixture after quenching/alkylation in the presence of $EtAlCl_2$ and a protic acid, such as H_2SO_4, the terminal *tert*-butyl groups were successfully and expeditiously removed *in situ*. The deblocking treatment also induced alkylation of pyrrole by the residual *exo*-olefin chain ends to yield quantitative hydroxy-functional PIB. The resulting primary hydroxy-terminated PIBs showed excellent reactivity with acids and isocyanates and may serve as building blockings for copolymer synthesis.

Acknowledgment. This research was generously supported by Chevron Oronite Co., LLC.

Supporting Information Available: ^1H NMR spectrum of PIB from a polymerization/quenching reaction catalyzed by Me_2AlCl, plots of chain end composition during deblocking with acid combinations other than $TiCl_4/EtAlCl_2/H_2SO_4$, and GPC traces of the PIB−polyurethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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