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Primary Halide-Terminated Polyisobutylene: End-Quenching of Quasiliving Carbocationic Polymerization with *N*-(ω-Haloalkyl)pyrrole

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ABSTRACT: *N*-(ω-Haloalkyl)pyrroles (1-(2-chloroethyl)pyrrole, 1-(2-bromoethyl)pyrrole, and 1-(3-bromopropyl)pyrrole) were used to end-quench quasiliving isobutylene (IB) polymerizations initiated from 2-chloro-2,2,4-trimethylpentane (TMPCl)/$TiCl_4$ or 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)/$TiCl_4$ at −70 °C in hexane/CH_3Cl (60/40, v/v). Prechilled *N*-(ω-haloalkyl)pyrrole, either neat or in a solution of the reaction solvents, was charged to the polymerizations at full (>98%) IB conversion. In all cases, quantitative end-capping of about 0.03 M chain ends (CE) was achieved within 4 min using [*N*-(ω-haloalkyl)pyrrole] = 2[CE] and [$TiCl_4$] = 1.5[*N*-(ω-haloalkyl)pyrrole]. ^{1}H NMR analysis revealed mixed isomeric end groups in which polyisobutylene (PIB) was substituted at either C_2 or C_3 of the pyrrole ring. The isomer ratio C_2/C_3 was observed to be effected by the alkylene tether length. *N*-(2-Haloethyl)pyrroles yielded isomer ratios C_2/C_3 in the range 0.26/0.74 to 0.29/0.71; 1-(3-bromopropyl)pyrrole yielded C_2/C_3 in the range 0.38/0.62 to 0.40/0.60. GPC indicated the absence of coupled PIB, confirming exclusive monosubstitution on each pyrrole ring. Complete ^{1}H and ^{13}C NMR chemical shift assignments were made for both isomers produced from each of the three quenchers. ^{1}H NMR integration of PIB initiated from the difunctional aromatic initiator, *t*-Bu-*m*-DCC, showed two *N*-(ω-haloalkyl)pyrrole end groups per aromatic initiator residue.

Introduction

Polyisobutylenes (PIB) carrying functional end groups are useful intermediates toward a variety of products including fuel and lubricating oil additives,[1] low-moisture/gas-permeable architectural sealants,[2] and biomedical devices.[3−7] In the past, many functional end groups were introduced onto PIB through postpolymerization modification of *tert*-chloride end groups arising naturally from the carbocationic polymerization process;[8] however, these derivatizations were typically cumbersome, multistep processes often involving expensive reagents. More recently, research has been directed toward the more facile and efficient approach of in situ quenching. In this approach, functional end groups are introduced by direct reaction of nucleophilic reagents with quasiliving cationic PIB. Unfortunately, most nucleophiles are found to react with the overwhelmingly abundant Lewis acid, and the result is PIB with *tert*-chloride end groups. This is particularly the case for "hard" σ-nucleophiles such as nonhindered alcohols or amines.[9,10] To date, most successful quenching agents belong to the class of "soft" π-nucleophiles, including highly reactive aromatic substrates,[11−13] nonpolymerizing olefins such as 1,1-diphenylethylene[14] and 1,3-butadiene,[15,16] and olefins such as allyltrimethylsilane[10,17,18] and methallyltrimethylsilane,[19] which upon reaction with PIB carbenium ions undergo β-scission to eliminate a cationic fragment.

On the basis of recent literature reports, there is considerable interest in creating PIBs containing primary halide end groups, either directly through in situ quenching or by some combination of in situ quenching and postpolymerization modification. Primary halogen is readily displaced by nucleophiles such as amines, azide ion, etc., and is therefore a useful intermediate toward new products including block copolymers, macromonomers, and telechelic oligomers. For example, Binder et al.[20] reacted quasiliving PIB with the non-homopolymerizable olefin 1-(3-bromopropyl)-4-(1-phenylvinyl)benzene, to yield PIB with primary bromide end groups. This same group also reported an alternative synthetic route consisting of quenching quasiliving PIB with allyltrimethylsilane, followed by postpolymerization hydroboration−oxidation and subsequent bromination of the alcohol termini using carbon tetrabromide in the presence of triphenylphosphine (Appel reaction).[21] De and Faust reported that quasiliving PIB may be quenched with 1,3-butadiene to yield quantitative allyl chloride end groups (i.e., PIB−CH_2−CH=CH−CH_2−Cl) via monoaddition of the diene followed by immediate chlorination by collapse with the counteranion.[15,16] Since a primary bromide is generally more useful in nucleophilic substitution, Faust et al.[22] developed synthetic procedures to produce PIB−allyl bromide, including postpolymerization halogen exchange from PIB−allyl chloride[22] as well as the more complicated approach of wholesale replacement of the $TiCl_4$ polymerization catalyst with a totally brominated Lewis acid system produced from mixtures of trimethylaluminum and $TiBr_4$.[23] Subsequently, this group reported various end-functional PIB's derived by nucleophilic substitution at allylic halogen.[24] Ummadisetty and Kennedy reported the anti-Markovnikov addition of HBr to either commercial *exo*-olefin-terminated PIB (Glissopal 2300) or allyl-terminated PIB obtained through end-quenching with allyltrimethylsilane. The resulting primary bromide-terminated PIBs were subsequently fitted with hydroxyl, amino, and methacryloyl termini through further postpolymerization modification reactions. The authors reported that hydroxyl-terminated PIB (via allyl PIB) could be obtained using a multistep, one-pot synthesis.[25]

We recently reported that quasiliving cationic PIB reacts quantitatively with *N*-methylpyrrole to yield an isomeric mixture of 2- and 3-PIB-*N*-methylpyrroles, with no detectable

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Table 1. Experimental Conditions and Results of *N*-(ω-Haloalkyl)pyrrole End-Quenching of Quasiliving IB Polymerizations

exp	[IB] (M)	[TMPCl] (M)	[*t*-Bu-*m*-DCC] (M)	[26Lut] (M)	[$TiCl_4$] (M)	[PyCl]/[CE]	[PyBr]/[CE]	[PyPBr]/[CE]	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	quench time (min)	f^a	isomer ratio C_2/C_3
1	0.74	0.027		0.0037	0.083	2.0			1.76	1.05	20	1.0	0.26/0.74
2	0.62	0.038		0.0051	0.12		2.1		1.73	1.04	20	1.0	0.28/0.72
3	0.62	0.038		0.0031	0.12			2.0	1.38	1.05	60	1.0	0.39/0.61
4	0.62	0.038		0.0031	0.077			2.0	1.33	1.04	30	0.96	0.40/0.60
5	0.66	0.016		0.0032	0.048		2.1		2.85	1.02	30	1.0	0.28/0.72
6	0.65	0.016		0.0031	0.048	2.3			2.66	1.03	30	1.0	0.27/0.73
7	0.65	0.016		0.0031	0.048			2.0	2.90	1.03	30	1.0	0.40/0.60
8	0.62	0.033		0.0031	0.12			2.3	1.55	1.05	30	1.0	0.40/0.60
9	0.38		0.013	0.0053	0.080	2.0			2.61	1.03	30	2.0	0.27/0.73
10	0.38		0.013	0.0053	0.080		2.1		2.64	1.02	30	2.0	0.28/0.72
11	0.36		0.013	0.0032	0.080			2.0	2.12	1.02	30	2.0	0.38/0.62
12	0.59		0.014	0.0032	0.086		2.1		2.78	1.07	30	2.0	0.29/0.71

[a] Number-average functionality with respect to halogen.

disubstitution (coupled) products.[11] The alkyl substituent on nitrogen is critical because other substitution patterns on the pyrrole lead to different results. For example, unsubstituted pyrrole yields a mixture of mono- and disubstituted products,[26] and 2,5-dimethylpyrrole induces elimination, providing a convenient quenching method toward 100% *exo*-olefin PIB.[27] Herein, we show that the *N*-alkyl group, in addition to being critical to quantitative capping, can be exploited as an alkylene tether for the attachment of useful functional groups, including halogen.

Experimental Section

Materials. Hexanes (anhydrous, 95%), $TiCl_4$ (99.9%, packaged under N_2 in sure-seal bottles), 2,6-lutidine (26Lut) (redistilled, 99.5%), and chloroform-*d* (0.01% H_2O maximum) were purchased from Sigma-Aldrich Co. and used as received. *N*-(2-Bromoethyl)pyrrole (PyBr) and *N*-(2-chloroethyl)pyrrole (PyCl) were purchased from TCI America and distilled from calcium hydride. The gaseous reagents isobutylene (IB, BOC) and methyl chloride (CH_3Cl, Alexander Chemical Corp.) were passed at room temperature through columns packed with $CaSO_4$ and $CaSO_4$/4 Å molecular sieves, respectively, and then condensed at −70 °C within a N_2-atmosphere glovebox immediately prior to use. 2-Chloro-2,4,4-trimethylpentane (TMPCl)[28] and 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)[29] were synthesized according to the literature. *N*-(3-Bromopropyl)pyrrole (PyBrP) was synthesized by N-alkylation of pyrrolyl sodium salt with excess 1,3-dibromopropane in DMSO according to the literature[30] and purified by fractional distillation.

NMR Spectroscopy. NMR spectra were acquired using a Varian Mercury^{plus} 300 MHz NMR spectrometer. Samples were prepared by dissolving the polymer in chloroform-*d* (5−7%, w/v) and charging this solution to a 5 mm NMR tube. For quantitative integration of PIBs produced from an aromatic initiator, 32 transients were acquired using a pulse delay of 20 s. ^{13}C and ^{1}H resonances were correlated with gradient enhanced heteronuclear single-quantum coherence (gHSQC) spectroscopy, using the average of 16 transients for each of 2 × 512 increments and phase-sensitive detection in the F1 dimension.

Size Exclusion Chromatography (SEC). Molecular weights and polydispersities (PDI) of the polymeric materials were measured using a SEC system consisting of a Waters Alliance 2695 separations module, an online multiangle laser light scattering (MALLS) detector (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (Optilab rEX, Wyatt Technology Inc.) operating at 35 °C, an online differential viscometer (ViscoStar, Wyatt Technology, Inc.) operating at 35 °C, and two mixed E (pore size range $50-10^3$ Å, 3 μm bead size) PL gel (Polymer Laboratories Inc.) columns connected in series. Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were ca. 6−7 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 an assumed d*n*/d*c* value given by the following equation:[31]

$$\frac{dn}{dc} = 0.116\left(1 - \frac{108}{M_n}\right)\left(\frac{dL}{g}\right) \quad (1)$$

where M_n is the number-average molecular weight of the polymer sample being analyzed.

ATR-FTIR Spectroscopic Monitoring. A ReactIR 1000 reaction analysis system (ASI Applied Systems, Millersville, MD), previously described,[32,33] was integrated with an inert atmosphere glovebox (MBraun Labmaster 30) to obtain real-time FTIR spectra of the isobutylene polymerizations. Reaction conversion 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 IB.

Isobutylene Polymerization and *N*-(ω-Haloalkyl)pyrrole Quenching. Quasiliving polymerizations of IB with either TMPCl or *t*-Bu-*m*-DCC as initiator were carried out within a N_2 atmosphere glovebox, equipped with an integral, cryostated hexane/heptane bath according to the following representative procedure (Table 1, experiment 1). Into a round-bottom flask equipped with a mechanical stirrer, infrared probe, and thermocouple were added 100 mL of CH_3Cl, 150 mL of hexanes, and 0.116 mL (0.107 g, 1.0 mmol) of 2,6-lutidine. The mixture was allowed to equilibrate to −70 °C, and then 16.1 mL (11.2 g, 200 mmol) of IB was charged to the reactor. After thermal equilibration, 1.26 mL (1.10 g, 7.41 mmol) of TMPCl was added to the reactor. To begin the polymerization, 2.45 mL (4.24 g, 22.3 mmol) of $TiCl_4$ was charged to the reactor. Full monomer conversion (>98%) was achieved in 10 min, after which time a prechilled solution of PyCl, prepared by dissolving 1.72 mL of PyCl (1.94 g, 15.0 mmol) into 10 mL of hexane/CH_3Cl (60/40, v/v, −70 °C), was added to the polymerization. The color of the solution changed from slightly yellow to brown. PyCl was allowed to react with the living chain ends for 20 min. Finally, the reaction was quenched by addition of excess prechilled methanol. The contents of the reaction flask were allowed to warmed to room temperature, and the polymer in hexane was washed with methanol and then precipitated one time into methanol from hexane. The precipitate was collected by dissolution in hexane; the solution was washed with water, dried over $MgSO_4$, and concentrated on a rotary evaporator. Residual solvent was removed under vacuum at room temperature.

Results and Discussion

Synthesis of *N*-(ω-Haloalkyl)pyrrole-PIB. *N*-(ω-Haloalkyl)pyrroles (1-(2-bromoethyl)pyrrole, 1-(2-chloroethyl)pyrrole, and 1-(3-bromopropyl)pyrrole) were used to end-quench quasiliving isobutylene polymerizations initiated from TMPCl/

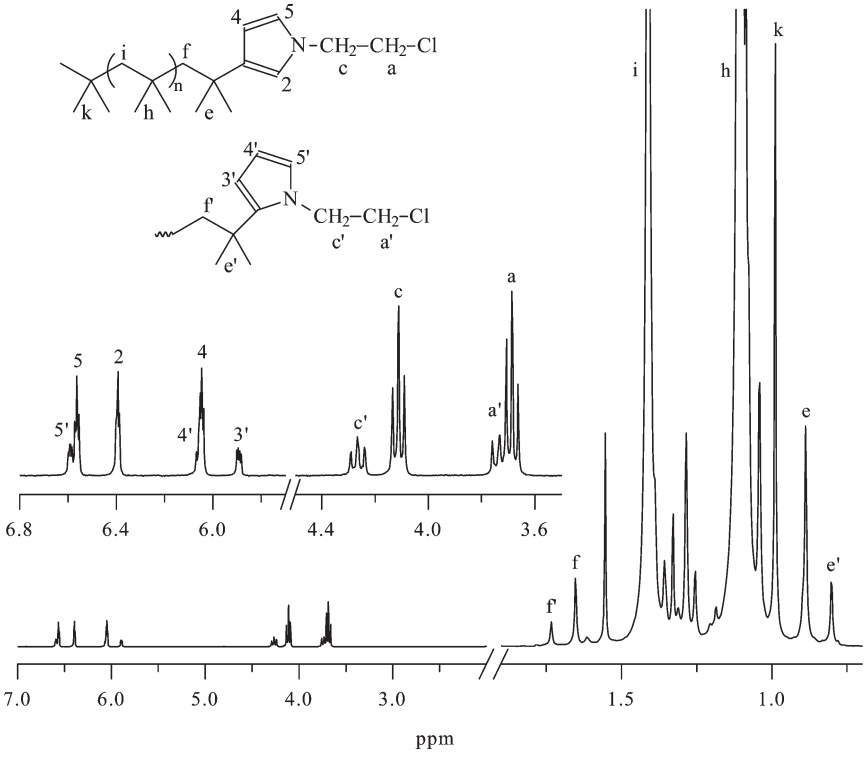

Figure 1. ^{1}H NMR spectrum of 1-(2-chloroethyl)pyrrole−PIB prepared with TMPCl, showing the major and minor isomers with PIB in the 3- and 2-positions of the pyrrole ring, respectively (Table 1, experiment 1).

$TiCl_4$ or *t*-Bu-*m*-DCC /$TiCl_4$ at −70 °C in hexane/CH_3Cl (60/40, v/v), as outlined in Table 1. Prechilled *N*-(*ω*-haloalkyl)pyrrole, either neat or in a solution of the reaction solvents, was charged to the polymerizations at full (>98%) IB conversion. The time of addition of the quencher in relation to monomer conversion was closely controlled using FTIR reaction monitoring[32,33] to avoid loss of *tert*-chloride end group functionality to unimolecular termination processes such as carbenium ion rearrangement[34] and *β*-proton elimination.[35] The quenching reactions were allowed to proceed for various times, at which point the catalyst was destroyed by the addition of excess prechilled methanol.

Low monomer-to-initiator ratios were used to produce low molecular weight materials amenable to end-group characterization using NMR. For TMPCl-initiated PIBs, integration of ^{1}H NMR spectra was used to determine the relative proportions of the various end groups as described previously.[11] For *t*-Bu-*m*-DCC-initiated PIB, the aromatic initiator residue provided an internal reference to which ^{1}H NMR peak integration of the various end groups could be compared. GPC was used to detect coupling of the PIB chains which would be evidenced by a shoulder in the chromatograph representing a molecular weight roughly twice that of the main peak.

Figure 1 shows the ^{1}H NMR spectrum of the reaction product of quasiliving PIB and 1-(2-chloroethyl)pyrrole (Table 1, experiment 1). The spectrum indicates quantitative end-functionalization via electrophilic aromatic substitution. Substitution is indicated by the absence of resonances associated with PIB *tert*-chloride end groups at 1.96 ppm (PIB−C**H**$_2$−C(CH$_3$)$_2$−Cl) and 1.68 ppm (PIB−CH$_2$−C(C**H**$_3$)$_2$−Cl). A new set of resonances appears at 1.65, 3.69, 4.11, 6.05, 6.40, and 6.56 ppm due to the product resulting from substitution at the 3-position of the pyrrole ring (major isomer). Substitution at the 2-position (minor isomer) is also apparent due to resonances at 1.73, 3.73, 4.27, 5.90, 6.07, and 6.59 ppm. Complete ^{1}H NMR chemical shift data are listed in Table A (Supporting Information).

Quantitative end-functionalization was also confirmed by ^{13}C NMR spectroscopy, by observing the disappearance of the resonances at 71.9 and 35.2 ppm, representing the quaternary and geminal dimethyl carbons, respectively, adjacent to the terminal *tert*-chloride group, and appearance of new peaks in both the aromatic and the aliphatic regions of the spectrum. ^{13}C NMR peak assignments for 1-(2-chloroethyl)pyrrole-PIB are shown in Figure 2. Complete ^{13}C NMR chemical shift data are listed in Table B (Supporting Information).

Alkyl bromides are generally more reactive than alkyl chlorides; consequently, 1-(2-bromoethyl)pyrrole was also evaluated as a quenching agent for quasiliving PIB. Figure 3 shows the ^{1}H NMR spectrum of the quenching product (Table 1, experiment 2). The spectrum indicates that quantitative end-functionalization was also obtained for the bromine-containing quencher, yielding an analogous mixture of 3- and 2-isomers. ^{1}H NMR chemical shift data are listed in Table C (Supporting Information).

The ^{13}C NMR spectrum of 1-(2-bromoethyl)pyrrole−PIB is shown in Figure 4. The spectrum is very similar to that of PIB−PyCl with one exception; the carbon adjacent to bromide in the 3 isomer (carbon "a" in Figure 4) could not be identified and was suspected to overlap with one of the major backbone carbon signals of PIB. To identify all the ^{13}C NMR assignments, the polymer was characterized by gHSQC (^{1}H, ^{13}C NMR single bond correlation) (Figure A, Supporting Information). Close examination of the gHSQC spectrum revealed that the protons adjacent to bromide in the 3 isomer, located at 3.53 ppm, are bonded to a carbon at 31.19 ppm and that its signal does indeed overlap with the large signal centered at 31.25 ppm due to the methyl carbons of the PIB backbone. Chemical shift data and ^{1}H−^{13}C correlations for the ethylene tethers of both isomers are listed in Table 2. Complete ^{13}C

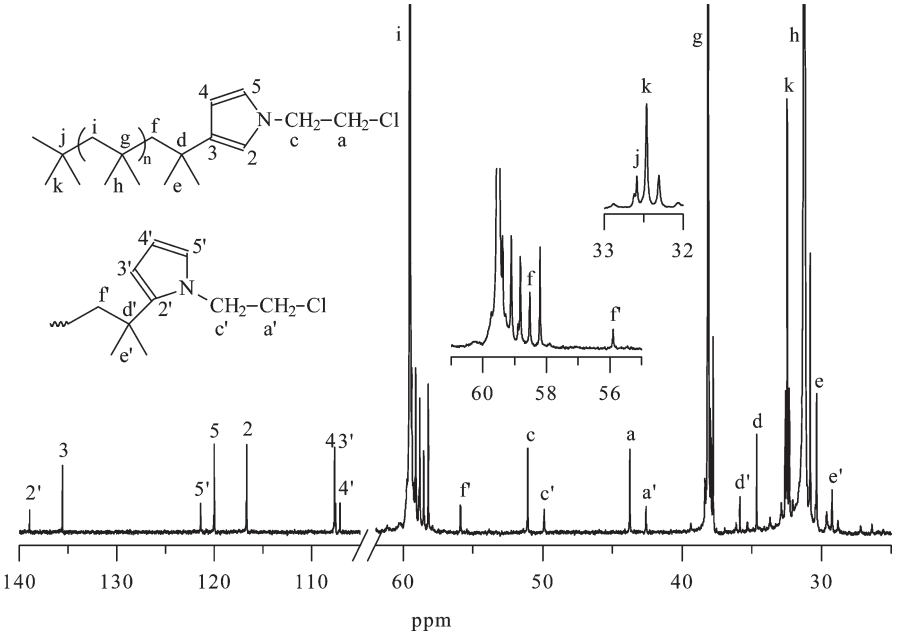

Figure 2. ^{13}C NMR spectrum of 1-(2-chloroethyl)pyrrole−PIB prepared with TMPCl (Table 1, experiment 1).

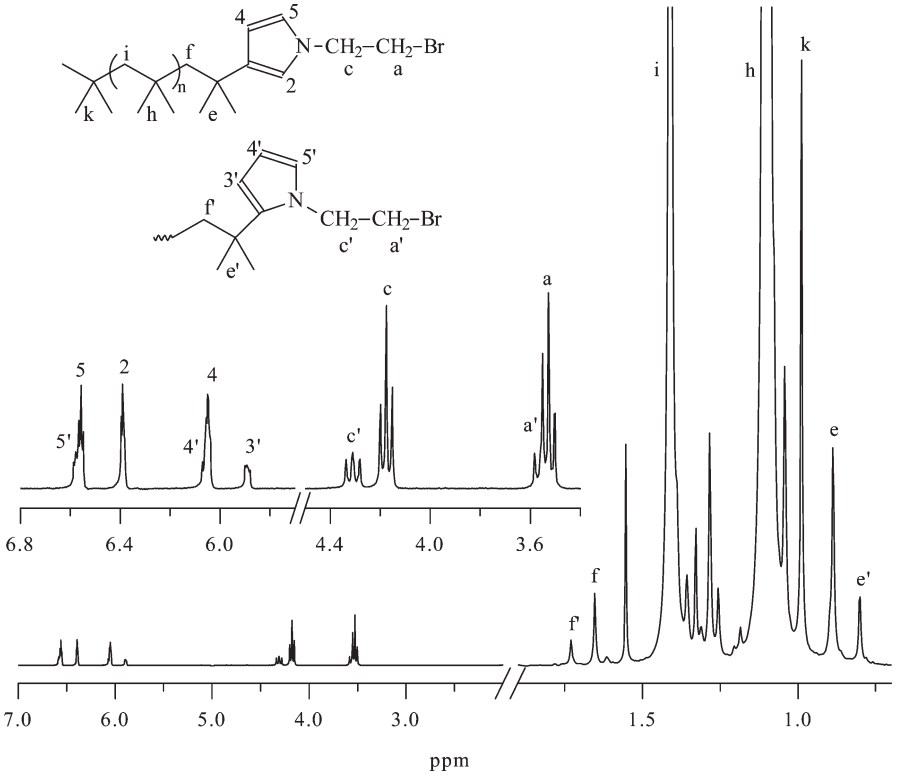

Figure 3. ^{1}H NMR spectrum of 1-(2-bromoethyl)pyrrole−PIB prepared with TMPCl, showing the major and minor isomers with PIB in the 3- and 2-positions of the pyrrole ring, respectively (Table 1, experiment 2).

NMR chemical shift data for *N*-(2-bromoethyl)pyrrole−PIB are listed in Table D (Supporting Information).

Figure 5 compares GPC traces of PIB's before (dotted line) and after (solid line) quenching with (a) 1-(2-chloroethyl)pyrrole and (b) 1-(2-bromoethyl)pyrrole. Except for a slight shift to lower elution volume due to addition of the 1-alkylpyrrole moiety, the GPC traces prior to and after quenching were nearly indistinguishable, indicating the absence of any coupling reactions or polymer degradation.

After obtaining positive quenching results with the 1-(2-haloethyl)pyrroles, we sought to determine whether alkylene tether length had any significant effect upon the quenching reaction. Thus, we synthesized 1-(3-bromopropyl)pyrrole, possessing a three-carbon tether, and explored its efficacy as a quencher. As shown in Table 1, it was also a very effective quencher, essentially identical to the haloethyl quenchers in terms of rate and extent of reaction. Figure 6 shows the ^{1}H NMR spectrum of a representative polymer (Table 1, experiment 3) with peak assignments. Addition of the capping

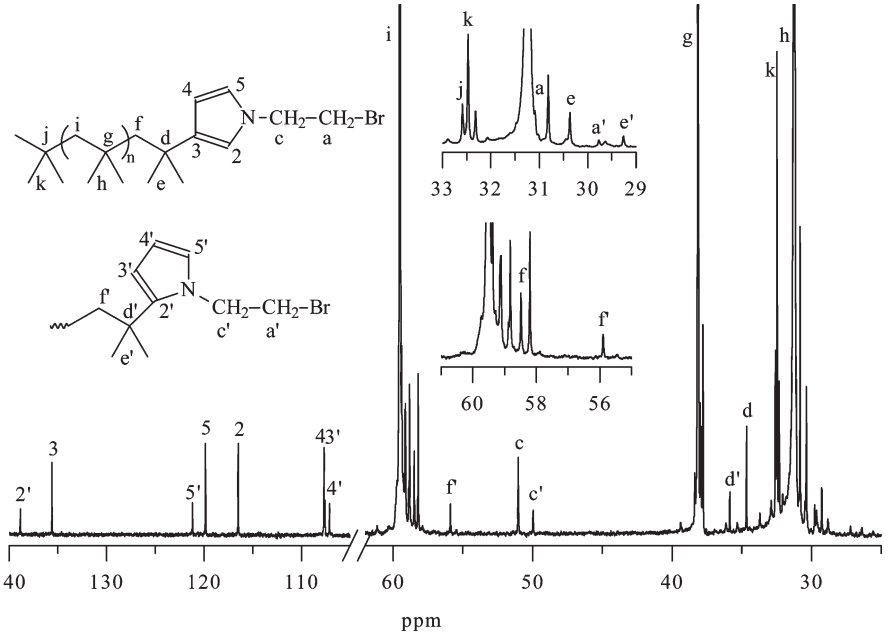

Figure 4. ^{13}C NMR spectrum of 1-(2-bromoethyl)pyrrole−PIB prepared with TMPCl (Table 1, experiment 2).

Table 2. ^{13}C and ^{1}H NMR Chemical Shifts for Alkylene Tether Carbons and Protons in 2- and 3-PIB−Pyrrole−CH_2−CH_2−Br

isomer	^{13}carbon (ppm)	proton (ppm)
3-PIB−Py−**CH_2**−CH_2−Br	51.07	4.18
2-PIB−Py−**CH_2**−CH_2−Br	49.96	4.31
3-PIB−Py−CH_2−**CH_2**−Br	31.19	3.53
2-PIB−Py−CH_2−**CH_2**−Br	29.76	3.58

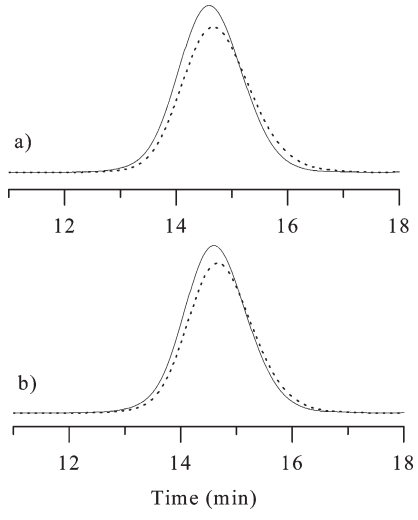

Figure 5. GPC traces of PIB before (dotted line) and after (solid line) quenching reaction with (a) 1-(2-chloroethyl)pyrrole (Table 1, experiment 1) and (b) 1-(2-bromoethyl)pyrrole (Table1, experiment 2).

agent was indicated by the disappearance of the resonances at 1.96 ppm (−PIB−C**H_2**−C$(CH_3)_2$−Cl) and 1.68 ppm (−PIB−CH_2−C$(CH_3)_2$−Cl) and the appearance of new resonances at 1.66, 2.21, 3.29, 3.99, 6.02, 6.38, and 6.55 ppm (3-isomer, major) and 1.76, 2.35, 3.50, 4.13, 5.88, 6.05, and 6.59 ppm (2-isomer, minor). Complete ^{1}H NMR chemical shift data for 1-(3-bromopropyl)pyrrole−PIB are listed in Table E (Supporting Information).

The ^{13}C NMR spectrum of 1-(3-bromopropyl)pyrrole−PIB (Table 1, experiment 8) is shown in Figure 7. To positively identify the carbons of the alkylene tether (PIB−pyrrole−**CH_2**−**CH_2**−**CH_2**−Br), the polymer was characterized by gHSQC (Figure B, Supporting Information); the resulting assignments for both isomers are shown in Table 3. Interestingly, the carbon bonded to bromine appears farther upfield than the central carbon of the tether; in contrast, the relative positions of the associated protons are exactly reversed; i.e., the protons of the central carbon appear farther upfield than the protons of the carbon bonded to bromine. Complete ^{13}C NMR chemical shift data for *N*-(3-bromopropyl)pyrrole−PIB are listed in Table F (Supporting Information).

Mechanism and Kinetics of End-Quenching. The proposed mechanism for end-quenching of quasiliving PIB with a *N*-(ω-haloalkyl)pyrrole is shown in Figure 8. This mechanism assumes that the pyrrole-based quencher (both unreacted and reacted) is complexed with the Lewis acid to some degree, governed by the equilibrium constant, K_{com}. We recognize that the position of the complexation equilibrium is different for unreacted and reacted quencher, and we simply employ K_{com} as a composite equilibrium constant for both complexations. Step 1 of the quenching reaction sequence is ionization of PIB *tert*-chloride to form a carbenium ion. The aforementioned complexation equilibrium reduces the effective $TiCl_4$ concentration available for ionization and hence reduces the carbenium ion concentration. Step 2 is the end-quenching reaction itself, via electrophilic aromatic substitution (EAS). Attack at C_2 is shown, since this is thought to be the kinetic product, with formation of the more stable (less sterically hindered) C_3 isomer occurring in a subsequent acid-catalyzed rearrangement reaction.[11,36] Step 3 is scavenging of the HCl condensate, which is expected to consume one net equivalent of $TiCl_4$ per equivalent of HCl scavenged, until the supply of proton acceptor molecules (purposefully added 2,6-lutidine or adventitious Lewis base) within the system is exhausted.

Assuming this mechanism, we may deduce that if quencher and $TiCl_4$ are supplied to the system at near-stoichiometric quantities, with no or little excess, the reaction will be of high total kinetic order, and the rate will become exceedingly slow at high conversions. For the quencher, the critical stoichiometry is relative to chain ends; for $TiCl_4$, it is relative to Lewis

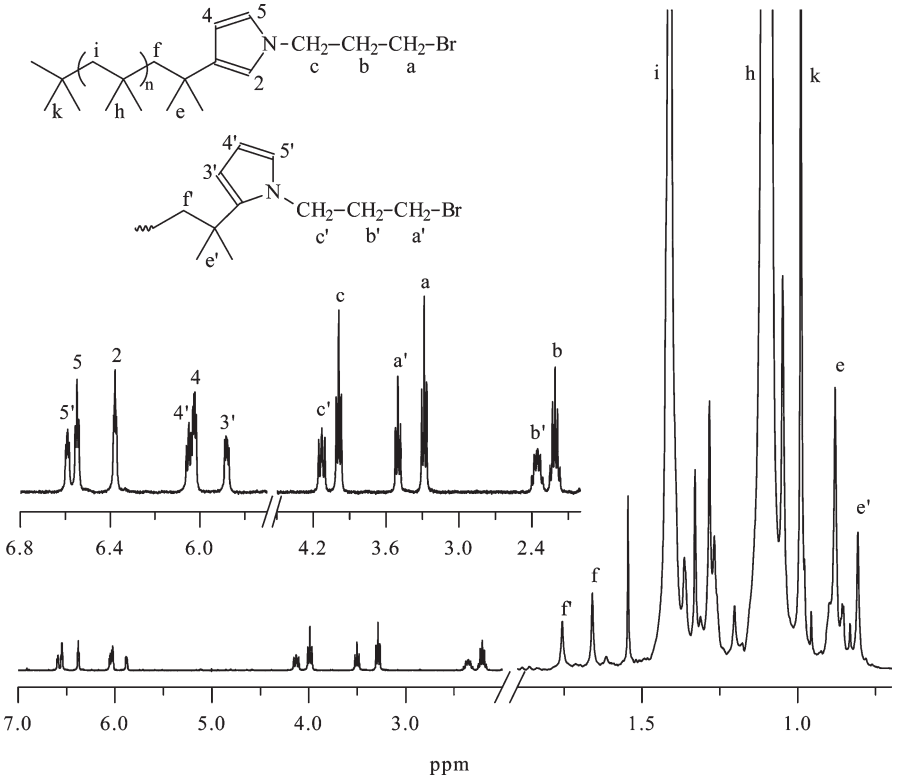

Figure 6. [1]H NMR spectrum of 1-(3-bromopropyl)pyrrole−PIB prepared with TMPCl, showing the major and minor isomers with PIB in the 3- and 2-positions of the pyrrole ring, respectively (Table 1, experiment 3).

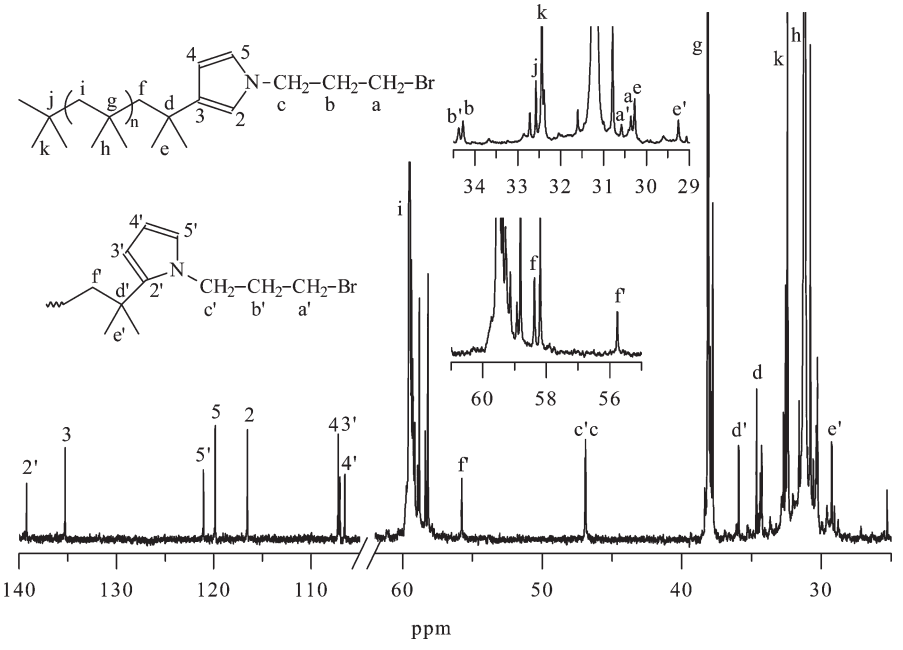

Figure 7. [13]C NMR spectrum of 1-(3-bromopropyl)pyrrole−PIB prepared with TMPCl (Table 1, experiment 8).

base and quencher. Thus, to achieve complete quenching within a reasonable time, one should provide Lewis acid sufficiently in excess of the total Lewis base concentration within the system, plus the appropriate fraction of the pyrrole quencher as dictated by K_{com}, so that fractional depletion of the free Lewis acid via step 3 is not too large.

The quenching reactions in Table 1 were conducted for at least 20 min, using a quencher/chain end (CE) molar ratio of about 2/1 and a $TiCl_4$/quencher molar ratio of about 1.5/1. Under these conditions, complete quenching generally required less than 4 min. However, in one case (Table 1, experiment 4) the $TiCl_4$/quencher molar ratio was reduced to 1/1, which resulted in incomplete quenching even after 30 min.

Most of the reactions in Table 1 were of small scale (<9 g product) and relatively dilute ([IB] ≤ 0.74 M), designed to provide analytical samples. No difficulties were encountered when batch size was increased; experiments

5 (monofunctional) and 12 (difunctional) were larger-scale preparations (≈75 g product), and these reactions proceeded smoothly with no compromise in quality of the final product. However, if the overall concentration of the reaction is increased, it becomes increasingly likely that the minimum [$TiCl_4$] required to obtain complete quenching at a reasonable rate will be higher than optimal for the prior quasiliving polymerization. In such cases, the [$TiCl_4$] used during polymerization should be optimized without reference to the subsequent quenching reaction. Then, upon introduction of the quencher, sufficient additional Lewis acid may be added to achieve complete quenching at an optimal rate. In a related sense, polymerization and quenching may be carried out in two separate reactions. *tert*-Chloride-terminated PIB may be formed and isolated using quasiliving polymerization, and then at some later time, the isolated polymer may be combined with the appropriate amount of *N*-(ω-haloalkyl) pyrrole quencher and the reaction activated by the addition of $TiCl_4$. The product obtained in this way is identical to that obtained using in situ quenching.

Structure of *N*-(ω-Haloalkyl)pyrrole−PIB. *N*-(ω-Haloalkyl)pyrrole quenching yielded a mixture of C_2 and C_3 isomers, consistent with our earlier results using *N*-methylpyrrole.[11] The isomer ratio was determined via ^{1}H NMR peak integration, and the results are listed in Table 1. For 1-(2-chloroethyl)pyrrole−PIB, the isomer ratio was determined by integrating the aliphatic PIB−Py−CH_2−CH_2−Cl triplets at 4.11 ppm (C_2-isomer) and 4.27 ppm (C_3-isomer) as well as the aromatic protons at 5.90 ppm (C_2-isomer) and 6.40 ppm (C_3-isomer). The results of these two measurements were averaged. Analogous peaks at 4.18 and 4.31 ppm and 5.90 and 6.40 ppm were used to quantify the isomer ratio for 1-(2-bromoethyl)pyrrole. For 1-(3-bromopropyl)pyrrole−PIB, the isomer ratio was determined by integrating the aliphatic triplets at 3.29 and 3.50 ppm and the aromatic protons at 5.88 and 6.38 ppm. The results showed that the quenchers possessing a two-carbon tether, 1-(2-chloroethyl)pyrrole and 1-(2-bromoethyl)pyrrole, behaved similarly, yielding a molar ratio C_2/C_3 in the range 0.26/0.74 to 0.29/0.71. However, results for 1-(3-bromopropyl)pyrrole showed that tether length does affect isomer ratio; a more closely balanced isomer ratio C_2/C_3 in the range 0.38/0.62 to 0.40/0.60 was consistently obtained with this quencher. In our previous paper,[11] we showed that *N*-methylpyrrole yields a nearly equal isomer distribution (C_2/C_3 = 0.46/0.54). In view of this, it appears that a halogen atom favors substitution at the 3-position, but its influence diminishes when it is placed farther from the pyrrole ring.

Table 3. ^{13}C and ^{1}H NMR Chemical Shifts for Alkylene Tether Carbons and Protons in 2- and 3-PIB−Pyrrole−CH_2−CH_2−CH_2−Br

isomer	^{13}carbon (ppm)	proton (ppm)
3-PIB−Py−CH_2−CH_2−**CH_2**−Br	30.36	3.29
2-PIB−Py−CH_2−CH_2−**CH_2**−Br	30.58	3.50
3-PIB−Py−CH_2−**CH_2**−CH_2−Br	34.27	2.21
2-PIB−Py−CH_2−**CH_2**−CH_2−Br	34.37	2.35
3-PIB−Py−**CH_2**−CH_2−CH_2−Br	46.89	3.99
2-PIB−Py−**CH_2**−CH_2−CH_2−Br	46.91	4.13

Difunctional *N*-(ω-Haloalkyl)pyrrole−PIB. *N*-(ω-haloalkyl)pyrroles (PyCl, PyBr, and PyBrP) were also used as quenchers for difunctional quasiliving PIB initiated from 1,3-di(2-chloro-2-propyl)-5-*tert*-butylbenzene (*t*-Bu-*m*-DCC). Reactions were carried out using hexane/CH_3Cl (60/40, v/v) cosolvents at −70 °C, as outlined in Table 1.

Because the aromatic initiator residue provides an internal reference for quantitative ^{1}H NMR analysis, peak integration could be used to directly determine if there were exactly two terminal 1-(3-bromopropyl)pyrrole moieties per aromatic initiator moiety as theoretically expected. A relatively long pulse delay (20 s) proved necessary to obtain accurate integration of the *N*-(ω-haloalkyl)pyrrole moieties. Standard pulse delays of 1−2 s were insufficient to obtain complete relaxation of the pyrrole ring protons, resulting in integrated areas for the alkylene tether protons that were too large relative to those of the pyrrole ring protons. This was observed for both the free quenchers and the quencher residues after end-capping. Figure 9 shows the ^{1}H NMR spectrum of a representative polymer end-capped with 1-(3-bromopropyl)pyrrole moieties (Table 1, experiment 11). A prequench control aliquot revealed that there were exactly two *tert*-chloride end groups per aromatic initiator residue. After 7 min reaction with 1-(3-bromopropyl)pyrrole, an aliquot from the reaction was subjected to ^{1}H NMR analysis. The resulting expanded spectrum with detailed peak integration data is shown in Figure 10. Resonances due to *tert*-chloride chain ends were not observed. The combined

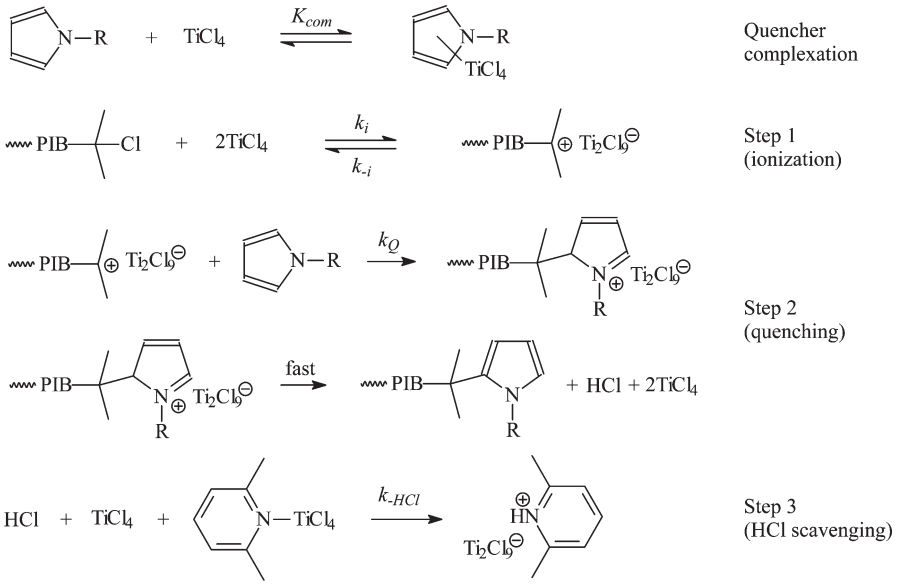

Figure 8. Mechanism of EAS quenching with a *N*-(ω-haloalkyl)pyrrole.

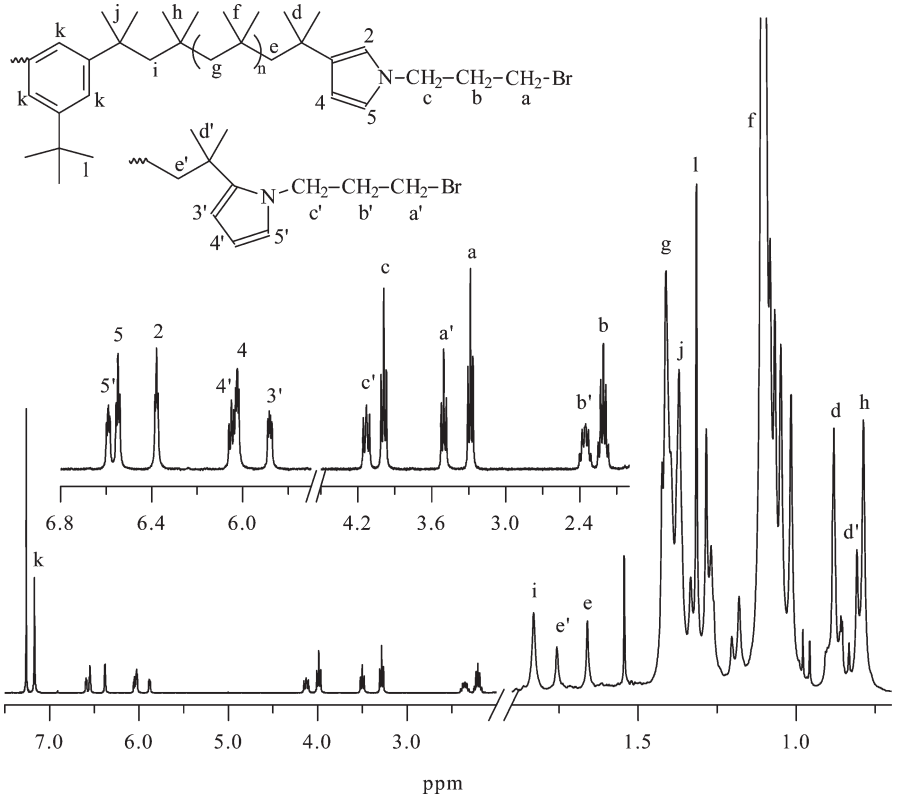

Figure 9. ^{1}H NMR spectrum of difunctional 1-(3-bromopropyl)pyrrole−PIB prepared with *t*-Bu-*m*-DCC (Table 1, experiment 11).

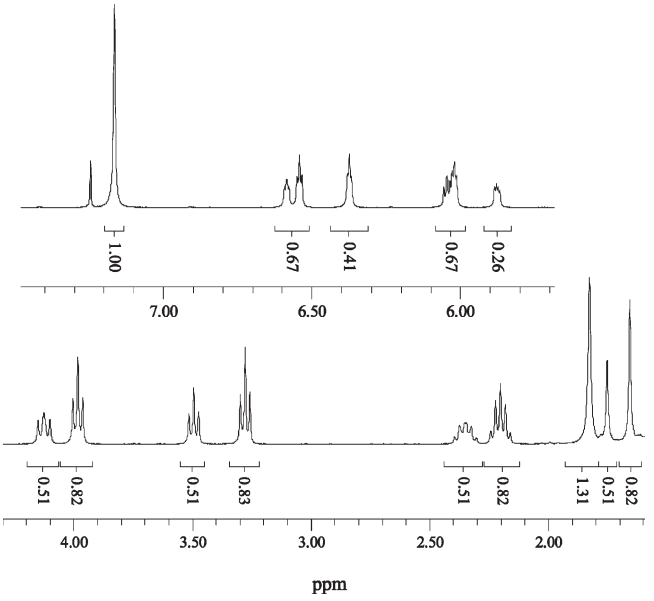

Figure 10. Expanded ^{1}H NMR spectrum of difunctional 1-(3-bromopropyl)pyrrole−PIB with peak integrations; peak assignments shown in Figure 9 (Table 1, experiment 11).

C_2- plus C_3-isomer peak area of each of the tether methylene protons (multiplets at 3.99 and 4.13, 3.29 and 3.50, and 2.21 and 2.35 ppm) was ~1.33 times that of the aromatic initiator proton resonance at 7.2 ppm, indicating quantitative bifunctionality. Likewise, the combined C_2- plus C_3-isomer peak area of the pyrrole ring protons (multiplets at 6.55 and 6.59, 6.02 and 6.05, and 5.88 and 6.38 ppm) were in all three cases 0.67 times that of the aromatic initiator resonance, further supporting perfect bifunctionality. GPC analysis of this polymer also revealed no coupling products (Figure 11).

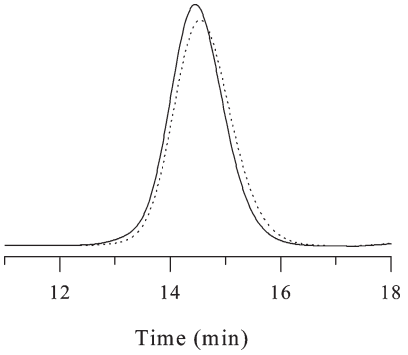

Figure 11. GPC traces of PIB before (dotted line) and after (solid line) reaction with 1-(3-bromopropyl)pyrrole (Table 1, experiment 11).

PyCl and PyBr were also used as quenchers for difunctional quasiliving PIB initiated from *t*-Bu-*m*-DCC. Figures C and D (Supporting Information) show the ^{1}H NMR spectra of the products. The GPC traces of the PIB prior to and after quenching for the quenching reactions carried out with 1-(2-chloroethyl)pyrrole and 1-(2-bromoethyl)pyrrole were essentially the same, indicating the absence of any coupling reactions or polymer degradation (Figure E, Supporting Information).

Conclusion

We have shown that *N*-(ω-haloalkyl)pyrroles are quantitative capping agents for quasiliving PIB chains activated by $TiCl_4$ in 60/40 hexane/CH_3Cl at −70 °C. The product of end-quenching is a mixture of 2- and 3-PIB-1-(ω-haloalkyl)pyrroles, consistent with our previous report concerning end-quenching with *N*-methylpyrrole.[11] For 1-(2-haloethyl)pyrroles the C_3 isomer was dominant: the C_2/C_3 molar ratio was in the range 0.26/0.74 to 0.29/0.71 for 1-(2-chloroethyl)pyrrole and

1-(2-bromoethyl)pyrrole. 1-(3-Bromopropyl)pyrrole quenching yielded a more balanced isomer ratio of C_2/C_3 in the range 0.38/0.62 to 0.40/0.60, closer to the nearly balanced ratio (0.46/0.54) obtained with *N*-methylpyrrole. Apparently, the halogen atom favors substitution at the 3-position, but its influence diminishes when it is placed farther from the pyrrole ring.

Kinetics of end-quenching with *N*-(ω-haloalkyl)pyrroles under these conditions are quite favorable. In all cases, quantitative end-capping of about 0.03 M chain ends (CE) was achieved within 4 min using [quencher] = 2[CE] and $[TiCl_4]$ = 1.5 [quencher]. Quenching slowed considerably when $[TiCl_4]$ = [quencher], suggesting that available Lewis acid is reduced through complexation with the pyrrole.

The *N*-(ω-haloalkyl)pyrrole−PIBs are interesting and potentially useful functional oligomers of uniform molecular weight and high purity that are easily synthesized in a one-step process. The terminal, primary halogens are readily displaced by nucleophiles, and this family of reactions is not effected by the presence of the neighboring electron-rich pyrrole ring. Therefore, the *N*-(ω-haloalkyl)pyrrole−PIBs represent useful intermediates toward new products including PIB-based block copolymers, macromonomers, telechelic oligomers, etc., which have potential commercial applications in many areas. Reaction of various nucleophiles, e.g., amines, azide, etc., with the halide-terminated PIBs will be the subject of future publications.

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Supporting Information Available: ^{1}H NMR spectra and GPC traces for difunctional 1-(2-chloroethyl)pyrrole−PIB and 1-(2-bromoethyl)pyrrole−PIB and tables of NMR chemical shift data for PIB-substituted *N*-(ω-haloalkyl)pyrroles. This material is available free of charge via the Internet at http://pubs.acs.org.

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