N-Methylpyrrole-Terminated Polyisobutylene through End-Quenching of Quasiliving Carbocationic Polymerization

Robson F. Storey,*,† Casey D. Stokes,† and James J. Harrison‡

School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, and Chevron Oronite Company, LLC, Richmond, California 94802-0627

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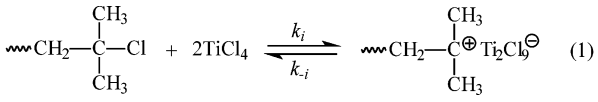
ABSTRACT: Quasiliving isobutylene polymerization initiated by 2-chloro-2,4,4-trimethylpentane/$TiCl_4$/2,6-dimethylpyridine in 60/40 *n*-hexane/methyl chloride at −70 °C was allowed to reach 98+% monomer conversion and then reacted with *N*-methylpyrrole. All polyisobutylene (PIB) chains alkylated the *N*-methylpyrrole ring to form a mixture of 46% 2-PIB−*N*-methylpyrrole and 54% 3-PIB−*N*-methylpyrrole. GPC indicated the absence of coupled PIB, confirming that exclusively monosubstitution had occurred. Complete ^1H and ^{13}C NMR chemical shift assignments were made for both isomers. The product was converted exclusively to mixed 2- and 3-PIB−*N*-methylpyrrolidine by catalytic hydrogenation using PtO_2 in glacial acetic acid. Quantitative ^1H NMR integration of PIB initiated from the difunctional aromatic initiator, 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene, showed exactly two *N*-methylpyrrole end groups per aromatic initiator residue. Quantitative reaction of PIB chains with *N*-methylpyrrole could not be obtained with BCl_3 systems. In methyl chloride diluent at −45 °C, <10% *N*-methylpyrrole capping was obtained after 70 min; in 1,2-dichloroethane at −10 °C, 77% of the PIB chains reacted with *N*-methylpyrrole after 15 min, and no further reaction was observed up to 18 h. In both BCl_3 systems, GPC analysis showed the product to be unimodal, indicating the absence of coupling through dialkylation of *N*-methylpyrrole.

Introduction

A tremendous advantage of living and/or quasiliving polymerization is the potential for in-situ functionalization of the active chain ends with an appropriate quenching agent. Polyisobutylenes (PIB) carrying terminal functionality are important materials with applications in fuel and lubrication additives, low-permeability sealants and glazing compounds, and soft segments for polyurethane elastomers. Quasiliving carbocationic polymerization of isobutylene (IB) holds great potential for new functional materials, but it also presents special problems with regard to end-quenching. Under the most common conditions for isobutylene (IB) quasiliving polymerization, $TiCl_4$ activates dormant *tert*-chloride chain ends in the following equilibrium:



(1)

The value of k_i/k_{-i} is typically about 10^{-7} M^{-2};[1] therefore, at a typical $[TiCl_4]$ of 10^{-2} M, the ratio $[PIB^+TiCl_9^-]/[PIB\text{-}Cl]$ is on the order of 10^{-11}. If a nucleophilic quenching agent is not overwhelmingly more reactive toward the chain-end carbenium ions, it will be consumed in reaction with the far more abundant Lewis acid, and the result will be PIB chains with *tert*-chloride end groups. Without exception, this has been the result when the quenching agent is a hard, protic nucleophile such as methanol or ammonia.[2,3]

Certain "soft" or π nuclephiles, however, react preferentially with the carbenium ions and thus yield structures other than *tert*-chloride. For example, Kennedy et al.[4,5] showed that $TiCl_4$-co-initiated, quasiliving PIB could be quenched with allyltrimethylsilane to produce allyl end groups. Mayr et al. have made use of the analogous reaction involving methallyltrimethylsilane.[6] Hadjikyriacou and Faust demonstrated that 2-alkylfurans can be used to quench quasiliving PIB, co-initiated with either $TiCl_4$ or BCl_3, to yield the mono-addition product.[7] They further showed that the resulting allylic carbenium ion may be either quenched with methanol to induce proton elimination and rearomatization or trapped with tributyltin hydride to yield the nonaromatic, 2,5-disubstituted addition product. The authors also noted that the 2-alkyl substituent was necessary to prevent oligomerization of the furan and possibly chain coupling through dialkylation. Ivan and De Jong[8] have published a patent application claiming that a broad range of aromatic ring systems, including both unsubstituted and substituted pyrroles, furans, and thiophenes can be used to functionalize quasiliving PIB through end quenching. However, many of their claims seem unreasonable, and some are directly contradicted by published findings of Faust et al.[7] and one of us.[9] In all of these examples, the mechanism of chain quenching with soft nucleophiles is electrophilic addition of the carbenium ion to the π electron system of the quencher, followed by elimination to form the substitution product.

PIB-based fuel and/or lubricating additives consist of low molecular weight, monofunctional PIB tails carrying polar headgroups. For example, the most common lubricant dispersants consist of polar oligo(iminoethylene) segments ($\bar{X}_n = 5$, typically) connected to an oil-soluble PIB segment ($\bar{X}_n \cong 40$, typically) through a succinimide linkage.[10] These materials are manufactured using three separate reactions, including the initial polymerization of IB. An in situ quenching process whereby quasiliving PIB is functionalized with a polar, nitrogen-containing moiety, in a single reaction, could lead to competitive materials with tremendous economic advantages.

† The University of Southern Mississippi.
‡ Chevron Oronite Company.

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Table 1. Conditions Used for End-Quenching with *N*-Methylpyrrole (NMPy)[a]

reaction	1	2[b]	3	4	5	6	7	8	9
Lewis acid	$TiCl_4$					BCl_3			
solvent	*n*-hexane/CH_3Cl 60/40			CH_3Cl		1,2-dichloroethane			
temperature (°C)	−70			−45		−10			
initiator	TMPCl[c]		bDCC[d]	TMPCl					
[isobutylene] (M)	0.50	2.0	0.50	0.60	0.60	0.60	2.0	2.0	2.0
[initiator] ($M \times 10^2$)	1.4	14.3	0.70	2.4	2.4	3.3	6.0	6.0	8.3
[Lewis acid] (M)	0.083	0.43	0.083	0.50	0.25	0.33	0.18	0.30	0.83
NMPy/TMPCl (mol/mol)	1.05	2.0	1.1	2.0	2.0	5	3	3	3
NMPy rxn time (min)	15	12	3	70	65	1080	30	25	49
prequench PIB-Cl (%)[e]	96		100	97	44	85	76	63	36
postquench PIB-Cl (%)[f]	94			93	26				
PIB−NMPy (%)	96	100	100	<10	40	77	5−10	0	7

[a] [2,6-Dimethylpyridine] = 1.0×10^{-2} M in all cases. [b] Preparative-scale reaction (~140 g). [c] TMPCl = 2-chloro-2,4,4-trimethylpentane. [d] bDCC = 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene. [e] Percent polyisobutylene *tert*-chloride chain ends remaining at time of *N*-methylpyrrole introduction (the balance was principally *exo*/*endo* olefin). [f] Percent polyisobutylene *tert*-chloride chain ends in control reaction at time of termination by MeOH.

Pyrrole contains nitrogen and is more highly reactive toward electrophilic substitution reactions than either furan or thiophene;[11,12] however, we observed that it yielded a mixture of mono- and dialklated (coupled) products when used as a quenching for quasiliving PIB.[9] In this paper, we show that quasiliving PIB chains ($TiCl_4$-activated) react quantitatively with *N*-methylpyrrole (NMPy) to yield *N*-methylpyrrole-terminated PIB (100% monosubstituted) with potential uses in fuel and lubricant additives.

Experimental Section

Materials. *N*-Methylpyrrole (NMPy, 99%), 2,6-dimethylpyridine (2,6-DMP, 99+%, redistilled), 1,2-dichloroethane (DCE, 99%), and *n*-hexane (Hex, 99+%) were purchased from Sigma-Aldrich Co. and freshly distilled from calcium hydride before use. Methanol (MeOH, 99+%) and titanium tetrachloride ($TiCl_4$, 99.9%, packaged in SureSeal bottles under nitrogen) were purchased and used as received from Sigma-Aldrich Co. Platinum(IV) oxide (PtO_2, Adams Catalyst) was purchased and used as received from Sigma-Aldrich Corp. Glacial acetic acid (trace metal grade) was purchased and used as received from Fisher Chemical Co. Hydrogen (H_2, gas) was used as received from the Chevron Richmond Refinery. IB and MeCl (BOC gases) were dried by passing the gases through a column packed with $CaSO_4$ and $CaSO_4$/molecular sieves, respectively, and were then condensed at the specified reaction temperature immediately prior to use. 2-Chloro-2,4,4-trimethylpentane[13] (TMPCl) and 5-*tert*-butyl-1,3-di(2-chloro-2-propyl)benzene[14] (bDCC) were synthesized as described previously.

Isobutylene Polymerization and *N*-Methylpyrrole Quenching. Polymerizations were carried out within a glovebox, equipped with an integral, cryostated heptane bath. Linear monofunctional PIBs were synthesized via quasiliving carbocationic polymerization techniques employing TMPCl as initiator, either $TiCl_4$ or BCl_3 as co-initiator, and 2,6-DMP as Lewis base additive. Linear difunctional PIB was synthesized using bDCC/$TiCl_4$/2,6-DMP in Hex/MeCl 60/40 (v/v) at −70 °C. In some cases a master batch reaction mixture was divided into multiple tubes to provide identical quenching and control polymerizations. In other cases a single batch reaction was employed (no control). For single batch reactions, IB conversion was monitored using in situ remote-probe FTIR-ATR, as previously described.[15−17] For master batch mixtures, TMPCl, solvent, 2,6-DMP, and IB were mixed thoroughly and allowed to thermally equilibrate for 15 min prior to initiation with either $TiCl_4$ or BCl_3. Upon initiation, the polymerization solution was immediately divided into 30 mL aliquots (via a prechilled 50 mL graduated cylinder) and placed in 50 mL test tubes equipped with threaded caps. At the appropriate reaction time (i.e., 98% IB conversion, determined from prior kinetic measurements) the polymerizations were quenched with either 10 mL of prechilled MeOH (control) or a solution of *N*-methylpyrrole.

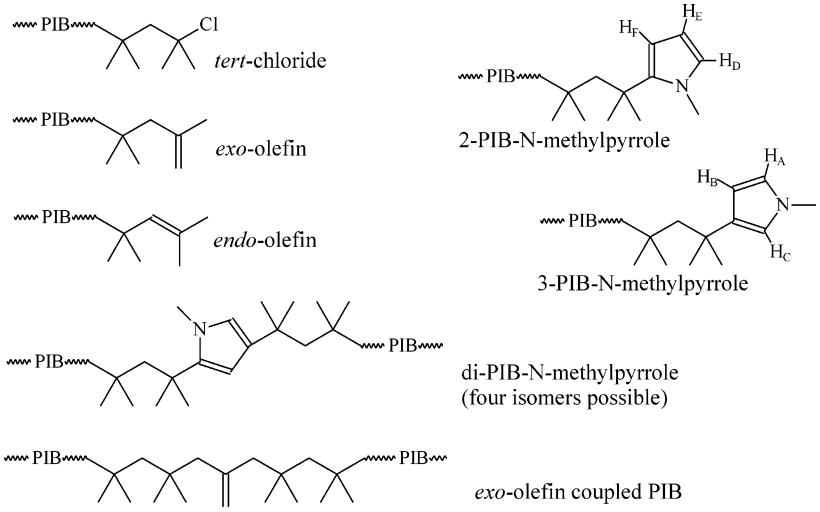
A typical master batch reaction was conducted as follows: a chilled 500 mL four-neck round-bottom flask was charged with 9.60×10^{-3} mol (1.43 g) of TMPCl, 368 mL of DCE, 4.0×10^{-3} mol (0.47 mL) of 2,6-DMP, and 0.240 mol (21.5 mL) of chilled IB (−10 °C). After thermal equilibration, 0.10 mol (8.4 mL) of chilled, neat BCl_3 (−10 °C) was added. A portion of this reaction mixture was immediately divided into three 50 mL test tubes (30 mL aliquots), which were identified as (1) reaction, (2) prequench control, and (3) postquench control. The mixtures were allowed to polymerize for 30 min (98% monomer conversion), at which point 1.5×10^{-3} mol (0.12 g) of *N*-methylpyrrole, dissolved in 5.0 mL of DCE, was charged to the reaction tube, and 10 mL of chilled MeOH was charged to the prequench control tube. After 65 min further reaction, the reaction and postquench tubes each received a charge of 10 mL of chilled MeOH.

Terminated reaction mixtures were allowed to warm to room temperature, and low boiling components were volatilized. A volume of hexane (2−3 mL) was added to each sample to dissolve the PIBs, and then the polymers were precipitated into MeOH. Finally, the isolated PIBs were shaken vigorously with fresh MeOH to remove any remaining salts and dried by vacuum stripping. Samples prepared for GPC and NMR characterization were dried in a vacuum oven maintained at 40 °C for at least 24 h prior to analysis.

A preparative-scale, single batch reaction (reaction 2, Table 1) was carried out as follows: a 2 L round-bottom flask equipped with an overhead mechanical stirrer and temperature probe was charged with 460 mL of hexane, 307 mL of MeCl, 161 mL (2.0 mol) of IB, 21.24 g (0.143 mol) of TMPCl, and 1.16 mL (1.0×10^{-2} mol) of 2,6-DMP. The solution was mixed until it reached thermal equilibrium (−70 °C), at which time 47 mL of neat $TiCl_4$ (0.43 mol) was charged. The polymerization was allowed to proceed for 3 min, and then a prechilled solution containing 25.4 mL of *N*-methylpyrrole (0.286 mol) and 25 mL of MeCl was charged to the reactor. After 12 min, the reaction was terminated by the addition of 200 mL of MeOH (prechilled). The terminated reaction mixture was allowed to warm to room temperature, and low boiling components were volatilized. The organic phase was extracted several times with a dilute (7 wt %) aqueous HCl solution and then with distilled water (repeatedly, until the extract was neutral in pH) to remove inorganic material from the product. The organic phase was then dried overnight over $MgSO_4$ and vacuum stripped to yield 133.44 g of PIB (95% yield).

Catalytic Hydrogenation of 2- and 3-PIB−*N*-Methylpyrrole. Preparation of 2- and 3-PIB−*N*-methylpyrrolidine was carried out using the following procedure. A 500 mL glass hydrogenation vessel was charged with 0.41 g of PtO_2 catalyst and 120 g of glacial acetic acid. Then 9.11 g (7.6 mmol) of a 46/54 mixture of 2- and 3-PIB−*N*-methylpyrrole (M_n = 1200 g/mol) was added. The reaction vessel was then attached to a Parr hydrogenator, and 50 psig hydrogen pressure was applied. The reaction was hydrogenated at 25−30 °C for 64 h. Then the reaction mixture was filtered, and the glacial acetic

Scheme 1. Possible End Groups for Polyisobutylene (PIB) Quenched with *N*-Methylpyrrole under Conditions Listed in Table 1



acid was removed in vacuo. A total of 5.59 g (61%) of crude product was obtained. Then the product was dissolved in about 50 mL of toluene and was washed twice with 1% KOH in water and then twice with water. An emulsion formed, which was diluted with about 50 mL of toluene and then washed six times with water. The product was then dried over anhydrous $MgSO_4$. The product from this reaction, the 2- and 3-PIB−*N*-methylpyrrolidine, was characterized by positive ion electrospray ionization mass spectrometry ESI-MS. The ESI-MS gave peaks at *m/z* of 366, 422, 478, 534, 590, 646, 702, etc., which are characteristic of the ammonium salt of the desired product. The product was also characterized by ^{1}H, ^{13}C, APT, DEPT, HETCOR, and COSY NMR spectroscopy. The NMR analysis indicated that the aromatic ring of the 2- and 3-PIB−*N*-methylpyrrole had been completely reduced to form a mixture of the 2- and 3-PIB−*N*-methylpyrrolidine.

NMR Spectroscopy. NMR spectra were acquired using a Varian Gemini 300 MHz NMR spectrophotometer with VNMR software. Samples were prepared by dissolving 0.1 g of polymer in 1 mL of $CDCl_3$ and placing this in a 5 mm NMR tube. ^{1}H, ^{13}C, APT, and HETCOR experiments were run using standard pulse sequences supplied by Varian. Quantitative ^{13}C NMR spectra were run in a 10 mm probe using 1.0 g of polymer dissolved in 3 mL of $CDCl_3$ containing 0.05 M $Cr(acac)_3$ as described previously.[18]

Size Exclusion Chromatography (SEC). Size exclusion chromatography experiments were performed to determine the molecular weights and polydispersities (PDI) of the polymeric materials. The SEC system consisted of a Waters Alliance 2690 separations module, an on-line multiangle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 690 nm (MiniDAWN, Wyatt Technology Inc.), a tunable UV absorbance detector operating at 265 nm (Waters model 484), an interferometric refractometer (Optilab DSP, Wyatt Technology Inc.) operating at 35 °C and 690 nm, and one of two sets of PLgel (Polymer Laboratories Inc.) SEC columns. One set consisted of two mixed E columns (pore size range 50−10^3 Å, 3 μm bead size) and the other of two mixed D columns (pore size range 50−10^4 Å, 5 μm bead size); each set was attached in a separate switchable loop with only one of the two sets active during data acquisition. The 3 μm particle size columns were useful for samples that did not contain molecules above ca. 30 000 g/mol; the 5 μm particle size columns were useful in separating molecules between ca. 30 000 and 2 000 000 g/mol. 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 a d*n*/d*c* value calculated from the signal response of the Optilab DSP and assuming 100% mass recovery from the columns.

Electrospray Ionization Mass Spectrometry. Samples (0.1 mg) were dissolved in 1 mL of THF/water (3/1, v/v). The mass spectrometer was a Finnigan TSQ7000. The samples were introduced into the mass spectrometer via a syringe pump at 8 μL/min. The mass spectrometer was scanned from 10 to 2000 amu in 2 s. The spectra were acquired in profile mode and were the result of spectra accumulation for 2 min.

Results and Discussion

N-Methylpyrrole was used as a quenching agent for quasiliving isobutylene polymerization. Several sets of conditions, listed in Table 1, were used to compare the effects of catalyst, solvent, and temperature on in situ functionalization. Polymerizations were initiated using TMPCl and, in one case, bDCC at low [M]/[I] ratios to produce low molecular weight materials amenable to NMR characterization. A solution of prechilled *N*-methylpyrrole was added to the polymerization charges at 98% IB conversion. The quenching reaction was allowed to proceed for various times depending on conditions (see Table 1), at which time the catalyst was destroyed by the addition of prechilled methanol.

The time of addition of *N*-methylpyrrole in relation to monomer conversion was closely controlled to avoid loss of *tert*-chloride end group functionality to unimolecular termination processes such as carbenium ion rearrangement[19] and β-proton elimination.[20] For reactions 1−4 in Table 1, these nonliving processes should be negligible, but for reactions 5−9 (higher temperature) they might not be. Therefore, in general, the statistically significant end groups on the PIB product molecules were expected to be limited to those shown in Scheme 1. For TMPCl-initiated PIBs, integration of ^{1}H NMR spectra was used to determine the relative proportions of the various end groups, assuming that the end groups in Scheme 1 represent the total of all end groups. For bDCC-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. Dual detector (RI and UV) GPC was used to detect coupling of PIB chains. β-Proton elimination can lead to chain coupling due to addition of carbenium ions to resulting *exo*-olefin end groups ("*exo*-olefin coupling"). For TMPCl-initiated PIBs, this reaction produces a UV-invisible peak (observed only in the RI response) on the

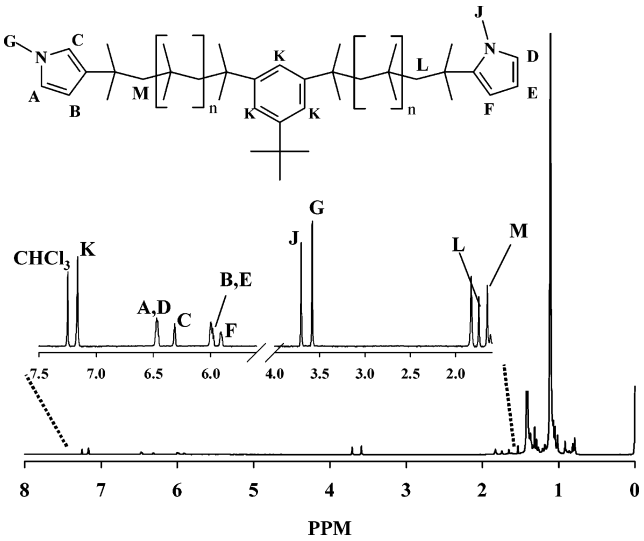


Figure 1. ^{1}H NMR spectrum of $TiCl_4$-activated quasiliving PIB quenched with *N*-methylpyrrole (reaction 3, Table 1).

low elution volume side of the main polymer peak. Coupling through dialkylation of *N*-methylpyrrole produces a similar peak that is visible in both the RI and UV traces. Dialkylation coupling was not observed under any of the conditions of Table 1.

$TiCl_4$-Co-Initiated Systems. Figure 1 shows the ^{1}H NMR spectrum of the product that results when $TiCl_4$-co-initiated quasiliving PIB is quenched with *N*-methylpyrrole (reaction 3 in Table 1). It is immediately apparent that no *tert*-chloride end groups are present in the sample due to the absence of characteristic peaks at 1.68 and 1.96 ppm, associated with the methylene and *gem*-dimethyl protons, respectively, adjacent to the terminal chlorine atom. The spectrum is also void of any resonances in the range 4.5−5.2 ppm, thus indicating no *exo*- and *endo*-olefinic end groups. Four multiplets appear in the aromatic region at 6.5, 6.3, 6.0, and 5.9 ppm, and two prominent singlets of roughly equal intensity are observed at 3.71 and 3.59 ppm. As will be discussed in detail in the next section, these resonances are consistent with the aromatic ring protons and the *N*-methyl protons, respectively, of terminal *N*-methylpyrrole moieties. Further evidence of the presence of the *N*-methylpyrrole end groups is provided by the appearance of new singlets at 1.65 and 1.74 ppm, assigned to the ultimate PIB methylene protons adjacent to the *N*-methylpyrrole moieties.

Figure 2 compares GPC traces of a typical *N*-methylpyrrole-quenched PIB (reaction 2, Table 1) with an aliquot removed from the same reactor prior to the introduction of *N*-methypyrrole. The traces show that the final product is identical to the prequench control aliquot from the standpoint of molecular weight and molecular weight distribution, and there is no evidence of coupled PIB due either to *exo*-olefin coupling or dialkylation of *N*-methylpyrrole.

The sample shown in Figure 1 is a difunctional PIB sample produced using the aromatic initiator, bDCC. Because the aromatic initiator residue provides an internal reference for quantitative ^{1}H NMR analysis, it could be directly determined by peak integration whether there were exactly two terminal *N*-methylpyrrole moieties per aromatic initiator moiety as theoretically expected. A prequench control aliquot revealed that there were exactly two *tert*-chloride end groups per

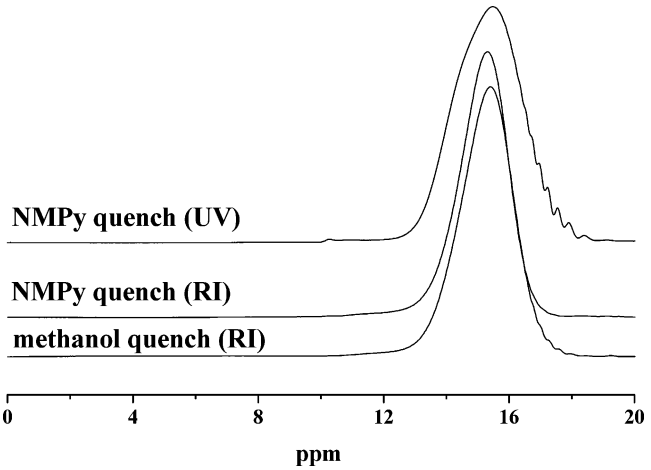


Figure 2. GPC traces of $TiCl_4$-activated quasiliving PIB quenched with *N*-methylpyrrole vs methanol (reaction 2, Table 1). RI = refractive index detector; UV = ultraviolet detector.

aromatic initiator residue with no indication of olefin end groups and no *exo*-olefin coupling. After 3 min reaction with *N*-methylpyrrole, ^{1}H NMR analysis revealed that the combined peak area of the *N*-methyl singlets at 3.71 and 3.59 ppm was exactly twice that of the aromatic proton resonance at 7.2 ppm, indicating perfect bifunctionality; in addition, there were no detectable resonances due to *tert*-chloride or *exo*- or *endo*-olefinic end groups. GPC analysis of this polymer also revealed no coupling of either type. The target degree of polymerization, $\bar{X}_n$, for this sample was 71; integration of the PIB backbone methylene protons and *gem*-dimethyl protons relative to the aromatic initiator protons yielded calculated $\bar{X}_n$ of 72 and 70, respectively.

On the basis of the foregoing ^{1}H NMR and GPC evidence, we concluded that $TiCl_4$-activated quasiliving PIB chains are cleanly and rapidly end-capped by *N*-methylpyrrole to form the 2- and 3-monosubstitution products in roughly equivalent amounts (see Scheme 1). We found that *N*-methylpyrrole quenching works equally well in analytical- and preparative-scale reactions and that a large excess of *N*-methylpyrrole relative to chain ends is not necessary; a 5−10% excess is sufficient. Large scale synthesis (140 g, reaction 2, Table 1) gave 95% isolated yield (see Experimental Section) of mixed 2- and 3-PIB−*N*-methylpyrrole with 100% of the chains carrying the desired functionality. Detailed structural characterization supporting this conclusion is presented in the following section.

Structure of PIB−*N*-Methylpyrrole. Several groups of authors have reported the synthesis of 2- and 3-substituted pyrroles.[21−23] It is possible that the 3-isomer is formed as a result of acid catalyzed rearrangement of the 2-isomer.[23] Of particular relevance to this work, Iovel et al.[21] have reported the ^{1}H NMR spectrum of 2- and 3-*tert*-butyl-*N*-methylpyrrole. On the basis of the data of Iovel et al., we assigned the four multiplets at 6.5, 6.3, 6.0, and 5.9 ppm to the protons on the pyrrole rings of 2- and 3-PIB−*N*-methylpyrrole isomers (Scheme 1). The two N−CH_3 singlets at 3.59 ppm (major isomer) and 3.71 ppm (minor isomer) were assigned to the 3-PIB−*N*-methylpyrrole (major) and 2-PIB−*N*-methylpyrrole (minor) isomers. The integrated ratio of major to minor isomers was found to be 1.18.

Expansion and resolution enhancement of the aromatic region (5.8−6.6 ppm) of the spectrum shows a wealth of splitting (Figure 3). Each ring proton appears

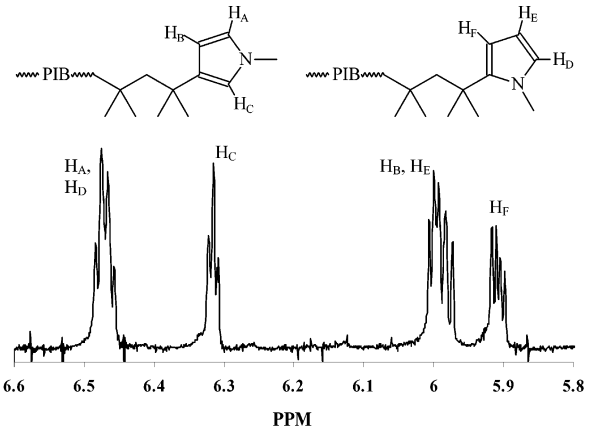


Figure 3. Aromatic region of ^{1}H NMR spectrum for the mixture of 2- and 3-PIB−*N*-methylpyrrole.

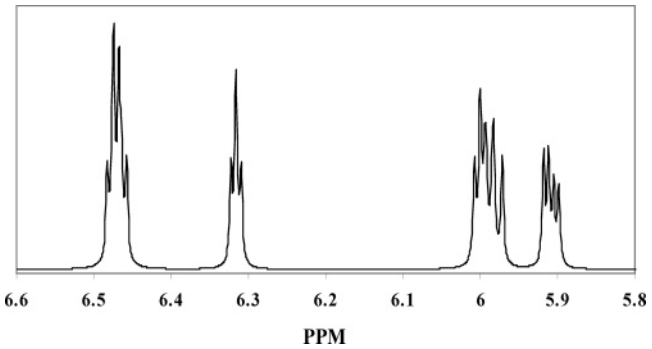


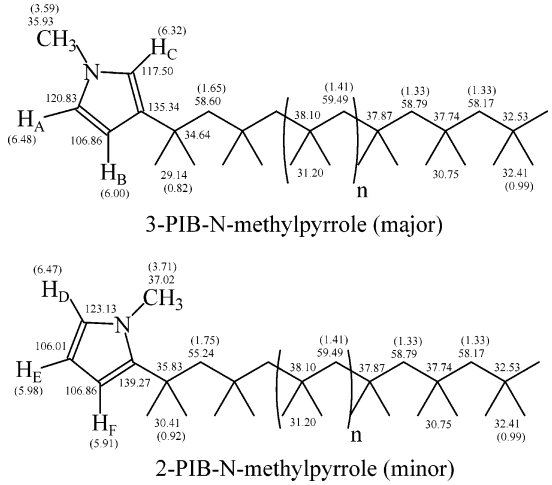
Figure 4. Simulated ^{1}H NMR spectrum (aromatic region) for the mixture of 2- and 3-PIB−*N*-methylpyrrole. Major/minor isomer ratio: 1.0. Chemical shifts (ppm): $H_A = 6.48$; $H_B = 6.00$; $H_C = 6.32$; $H_D = 6.47$; $H_E = 5.98$; $H_F = 5.91$. Coupling constants: $J_{A,B} = 2.5$; $J_{A,C} = 1.9$; $J_{B,C} = 2.0$; $J_{D,E} = 3.0$; $J_{D,F} = 2.0$; $J_{E,F} = 3.8$.

as a doublet of doublets, since each is coupled to two other protons on the ring. The multiplets at 6.5 and 6.0 ppm each represent two protons, one from each isomer, with similar but distinct chemical shifts. Therefore, each of these multiplets represents two separate doublets of doublets, superimposed upon each other. This region of the spectrum was simulated as shown in Figure 4, using the chemical shifts and coupling constants listed in the figure caption. For this simulation we used a major/minor isomer ratio of 1.0. The fit was excellent.

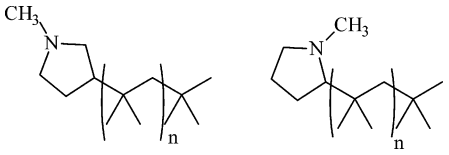
The ^{13}C and ^{1}H−^{13}C heteronuclear correlation (HETCOR) NMR spectra for the 2- and 3-PIB−*N*-methylpyrrole were also obtained (see Supporting Information). Scheme 2 shows the detailed ^{13}C NMR chemical shift assignments for 2- and 3-PIB−*N*-methylpyrrole based on the correlations thus obtained. Assignment of the ^{13}C chemical shifts for the PIB chain starting at the *tert*-butyl headgroup was made using the data in ref 18. These assignments were consistent with all the data obtained in this study. Close examination of the HETCOR spectrum showed that H_A was bound to a carbon at 120.83, H_B to a carbon at 106.86, H_C to a carbon at 117.50, H_D to a carbon at 123.13, H_E to a carbon at 106.01, and H_F to a carbon at 106.86. For the *N*-methyl group, the 3.71 ppm methyl protons of the 2-isomer were bonded to the carbon at 37.02 ppm and the 3.59 ppm methyl protons of the 3-isomer were bonded to the carbon at 35.93 ppm.

Integration of the ^{1}H and quantitative ^{13}C NMR spectra of the 2- and 3-PIB−*N*-methylpyrrole mixture

Scheme 2. ^{1}H and ^{13}C NMR Chemical Shift Data (ppm) for 2- and 3-PIB−*N*-Methylpyrrole



Scheme 3. Structure of 2- and 3-PIB−*N*-Methylpyrrolidines Obtained via Hydrogenation of PIB−*N*-Methylpyrrole Isomers



was consistent with our assignment of the major and minor isomers.

Catalytic Hydrogenation of 2- and 3-PIB−*N*-Methylpyrrole. To provide additional support for the structures assigned to the PIB−*N*-methylpyrroles and to provide potentially useful *tert*-aliphatic amine derivatives, we hydrogenated the pyrrole aromatic rings to form a mixture of the 2- and 3-PIB−*N*-methylpyrrolidines, as shown in Scheme 3. This was accomplished using PtO_2 in glacial acetic acid at room temperature for 64 h with 50 psig H_2 pressure. The positive ion electrospray ionization mass spectrum (ESI-MS) of the mixture of PIB−*N*-methylpyrrolidines is shown in Figure 5. The spectrum consists of a series of parent ions located at $m/z = 366, 422, \ldots$ separated by 56 mass units. This is consistent with the protonated structures in Scheme 2, where $n = 4, 5, \ldots$.

The ^{1}H NMR spectrum of the 2- and 3-PIB−*N*-methylpyrrolidine (Supporting Information) revealed, as expected, complete absence of the aromatic protons, which are characteristic of the starting 2- and 3-PIB−*N*-methylpyrrole. Instead, we observed a spectrum that was characterized by two singlets at 2.42 and 2.33 ppm assigned to the N−CH_3 protons of the two isomeric 2- and 3-PIB−*N*-methylpyrrolidines. Characteristic peaks due to the PIB substituent group were also observed at 1.41 ppm (CH_2, singlet) and at 1.11 ppm (CH_3, singlet). A number of complex multiplets were observed at room temperature for ring CH_2 and CH protons in the region of 1.5−4.0 ppm. Additional ^{1}H NMR experiments at temperatures from 20 to 120 °C confirmed that a dynamic exchange process, which we attribute to inversion about the nitrogen atom in the 2- and 3-PIB−*N*-methylpyrrolidine rings,[24] occurs (Scheme 4).

The ^{13}C, APT, DEPT, and HETCOR NMR spectra (Supporting Information) were also obtained for the 2- and 3-PIB−*N*-methylpyrrolidine, and a partial assignment of the spectra was made. The ^{13}C signals located

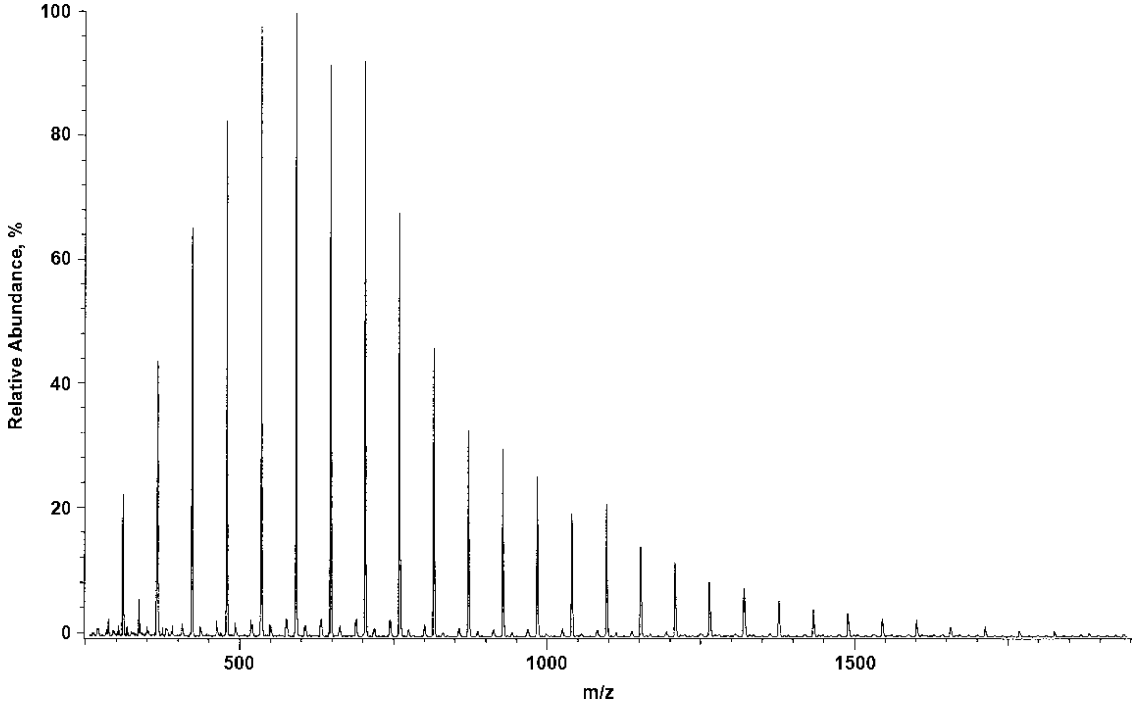
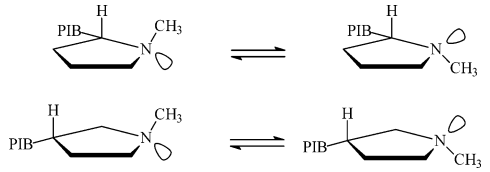


Figure 5. Positive ion electrospray ionization mass spectrum of 2- and 3-PIB−*N*-methylpyrrolidine (see Scheme 3).

Scheme 4. Inversion about the Nitrogen Atom in the 2- and 3-PIB−*N*-Methylpyrrolidine Rings



at 77.78 and 51.00 ppm were assigned to the methine carbons of the pyrrolidine ring for the 2- and 3-isomer, respectively. These carbons are both bonded to methine protons centered at 2.17 ppm (complex multiplet) in the ^{1}H NMR spectrum. The ^{13}C methyl carbons located at 46.78 and 42.51 ppm, which are bonded to the methyl protons at 2.42 and 2.33 ppm, respectively, were assigned to the $N-CH_3$ carbons. The methylene carbons in the pyrrolidine ring for the 2- and 3-PIB−*N*-methylpyrrolidine isomers were assigned to the signals at 28.27, 26.66, and 24.89 ppm in the ^{13}C NMR spectrum. A summary of the peak assignments for PIB−*N*-methylpyrrolidine is listed in the Supporting Information.

BCl_3-Co-Initiated Systems. Quasiliving IB polymerizations co-initiated by BCl_3 were quenched at 98% IB conversion using *N*-methylpyrrole under various conditions, as reported in Table 1 (reactions 4−9). Longer quenching times were used to account for the lower carbenium ion concentrations typical of BCl_3 systems. In pure MeCl solvent at −45 °C (reaction 4, Table 1) less than 10% of the PIB chains had alkylated *N*-methylpyrrole after 70 min; the balance of the PIB carried *tert*-chloride end groups. GPC analysis showed that a slight amount of *exo*-olefin coupling was present in the sample prior to introduction of *N*-methylpyrrole.

Several high-temperature BCl_3 systems (reactions 5−9, Table 1) were also investigated. Reaction 5 was conducted using DCE solvent at −10 °C, and *N*-methylpyrrole quenching was carried out for 65 min after essentially complete IB conversion. In this case, 40% of the PIB chains gave the desired product. The low yield of the desired product in reaction 5 was caused by loss of *tert*-chloride end group functionality, due to β-elimination, during the IB polymerization prior to introduction of the *N*-methylpyrrole (prequench PIB-Cl only 44%); a slight amount of *exo*-olefin coupling was also present in the prequench sample, consistent with the presence of olefins. Since this was a relatively high-temperature reaction, persistence of *tert*-chloride end groups depended greatly on proper timing of introduction of the quencher. Since this was a tube reaction, and monomer conversion could not be monitored, the polymerization reaction time prior to quenching may have been too long. Reaction 6 in Table 1 was formulated similarly to reaction 5, except that the initiator concentration was higher and a larger NMPy/chain end ratio was employed for quenching. Reaction 6 was conducted in a single batch reactor, and IB conversion was accurately monitored using in situ remote-probe FTIR-ATR. In this case, the prequench PIB-Cl content was much higher (better retention of quasiliving chain ends), and the yield of PIB−NMPy after 15 min quenching was 77%. Interestingly, reaction 6 was allowed to further react with NMPy for 18 h, and during this time the yield of PIB−NMP remained at 77%. GPC analysis revealed no coupling of PIB chains in either the prequench aliquot or the final product. It is also noteworthy that, of the *tert*-chloride chain ends remaining at the time of quencher addition, the fraction that was successfully end-capped was the same for reactions 5 and 6, i.e., 91%. Reactions 7−9 all gave disappointing results; this was probably due to the relatively high hydrocarbon content of the reaction medium (2 M IB repeat units), which is known to decrease the ionization equilibrium constant in BCl_3-co-initiated systems.[16] The ratio of 3- to 2-PIB−*N*-methylpyrrole isomers for BCl_3 systems was found to be consistently 1.2, the same as that obtained with $TiCl_4$.

Although quantitative end-capping of PIB with *N*-methylpyrrole could not be obtained with BCl_3, higher solvent polarity and higher temperature clearly help to

increase the yield. The synergistic interplay of these two factors is reasonable in the case of BCl_3-co-initiated systems. Rate of alkylation of *N*-methylpyrrole should be proportional to the concentration of carbenium ions. The ionization equilibrium shown in eq 1 is fairly strongly exothermic in the forward direction for the case of $TiCl_4$ in a moderately nonpolar cosolvent system;[14,20] however, for BCl_3 in the more polar, chlorinated hydrocarbon solvent, it is only weakly exothermic or possibly slightly endothermic.[25] It is therefore reasonable that the rate of quenching would increase with increasing temperature.

Conclusion

We have shown that *N*-methylpyrrole is a quantitative capping agent for quasiliving PIB chains activated by $TiCl_4$ in 60/40 hexanes/MeCl at −70 °C. The product is an approximately equimolar mixture of 2- and 3-PIB−*N*-methylpyrrole. The nearly equal proportions of 2- and 3-substituted products are consistent with the known reactivity characteristics of pyrrole and the steric constraints that are particular to *N*-methylpyrrole. In comparison to thiophene, and particularly furan, which are considerably more reactive at C_2, the two positions of pyrrole are closer matched in reactivity toward electrophiles;[25] selectivity should further diminish with increasing reactivity of the attacking electrophile. The PIB carbenium ion is strongly electrophilic, and it is bulky. Thus, it is not surprising that the combination of low selectivity and greater steric compression at C_2, due to the 1-methyl substituent, would drive the production of a greater proportion of 3-isomer than might be predicted simply on the basis of resonance delocalization of the positive charge in the intermediate carbocation. It is somewhat unexpected that dialkylation does not occur to any detectable extent with *N*-methylpyrrole, since dialkylation does occur when the identical reaction is carried out with pyrrole itself. We conclude that either steric constraints prevent a second substitution or, perhaps, the intermediate carbocation from the first addition is persistent, i.e., slow to rearomatize through elimination, effectively preventing a second substitution. The latter scenario is known to occur when 2-alkylfuran is used as a quenching agent for PIB under similar conditions.[7]

We were unable to identify conditions that yielded quantitative end-capping by *N*-methylpyrrole in BCl_3-co-initiated systems. Less than 10% capping was achieved in 70 min using MeCl solvent at −45 °C. Higher temperature was expected to improve the yield of PIB−NMP in BCl_3 systems, and indeed 77% of NMP end groups was achieved using DCE solvent at −10 °C. Extended reaction time up to 18 h did not improve this yield. Solvent polarity seems critical for BCl_3 systems since higher monomer/polymer repeat unit concentration tended to depress yield of the end-capped product.

The PIB-substituted *N*-methylpyrroles represent interesting functional oligomers of uniform molecular weight and high purity that are easily synthesized in a one-step, one-pot process. The terminal *N*-methylpyrrole groups are readily modified by hydrogenation to create 2- and 3-PIB−*N*-methylpyrrolidines. These materials have potential commercial applications as fuel and lubricant additives.[26]

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Supporting Information Available: ^{13}C NMR, HETCOR NMR, ^1H NMR, APT NMR, and DEPT NMR spectra of 2- and 3-PIB−*N*-methylpyrrolidine and table of partial chemical shift assignment for 2- and 3-PIB−*N*-methylpyrrolidine. This material is available free of charge via the Internet at http://pubs.acs.org.

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