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End-Quenching of Quasiliving Carbocationic Isobutylene Polymerization with Hindered Bases: Quantitative Formation of *exo*-Olefin-Terminated Polyisobutylene

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ABSTRACT: Polyisobutylenes possessing exclusively *exo*-olefin end groups were created by end-quenching $TiCl_4$-catalyzed quasiliving isobutylene (IB) polymerizations with a hindered base at −60 to −40 °C. Polymerizations were initiated from either 2-chloro-2,4,4-trimethylpentane (TMPCl) or 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene, in 60/40 hexane/methyl chloride in the presence of 2,6-dimethylpyridine, allowed to reach 98+% isobutylene conversion, and then reacted with either 2,5-dimethylpyrrole, 1,2,2,6,6-pentamethylpiperidine, or 2-*tert*-butylpyridine for various times ranging from 10 to 170 min. Typical reaction molar concentrations were $[IB] = 0.5$, $[TMPCl] = 0.014$, $[26Lut] = 0.010$, $[TiCl_4] = 0.083$, and $[\text{hindered base}] = 0.02-0.04$ M. In some cases, minor amounts of coupled PIB were produced through reaction of carbenium ions with *exo*-olefin. Coupling was suppressed by higher temperature and lower chain end concentration. 2,5-Dimethylpyrrole was the most effective quencher under the conditions studied, yielding the most rapid quenching and exhibiting the least tendency toward coupling.

Introduction

For low-molecular-weight polyisobutylenes (PIB), many important end-group functionalization reactions proceed through the intermediacy of a terminal double bond.[1,2] For example, *exo*-olefin (i.e., isobutenyl or methyl vinylidene)-terminated PIB is a key intermediate toward hydroxyl-,[3] phenol-,[4] epoxide-,[5] and sulfonic acid[6]-terminated PIB. A notable commercial intermediate, critical toward the synthesis of low-molecular-weight dispersants for lubricating oils,[7] is PIB-succinic anhydride (PIBSA), formed by the thermal, paracyclic ene reaction of *exo*-olefin-terminated PIB with maleic anhydride.[8]

PIBs carrying one terminal olefinic end group have been produced commercially for many years using chain-transfer-dominated polymerization processes.[9] These products often contain complex mixtures of various olefinic isomers,[10−12] but those containing a high proportion of the more reactive *exo*-olefin isomer are favored because of their higher reactivity in postpolymerization functionalization reactions.[13] Difunctional *exo*-olefin-terminated PIB synthesis was first reported by Kennedy et al. in 1979.[14] This two-step process involved first the synthesis of *tert*-chloride-terminated PIB via the inifer method[15] using a difunctional initiator-transfer agent, 1,4-bis(2-chloro-2-propyl)benzene (*p*-DCC), and co-initiator BCl_3 in MeCl at −50 °C. After polymer cleanup and isolation, the second step involved refluxing the *tert*-chloride-terminated PIB with excess potassium *tert*-butoxide in THF for roughly 20 h. This method was reported by the authors to yield exclusively *exo*-olefin-terminated PIB, although later investigations[16,17] have revealed that the product is actually contaminated with low percentages of *endo*-olefin.

More recently, olefinic end groups have been introduced into PIB by end-quenching of quasiliving isobutylene (IB) polymerizations. Wilczek and Kennedy[18] produced allyl-terminated PIB by reactivating isolated *tert*-chloride-terminated PIB, produced using *p*-DCC/BCl_3, with $TiCl_4$ in the presence of allyltrimethylsilane (ATMS). In a subsequent variation, a 1−3 M excess (relative to *tert*-chloride chain ends) of ATMS and $TiCl_4$ were simultaneously added in situ to the BCl_3-co-initiated IB polymerization, resulting in allyl-terminated chain ends. The first direct end-capping of a quasiliving IB polymerization using ATMS was reported by Ivan and Kennedy.[19] Several years later, Roth and Mayr showed that methallyltrimethylsilane (MATMS) can be reacted with isolated, *tert*-chloride-terminated isobutylene oligomers in the presence of $TiCl_4$ to produce *exo*-olefin-terminated oligomers in high yield.[20] Shortly thereafter, Nielsen et al. introduced MATMS directly into quasiliving IB polymerizations;[21] however, only a two-step process involving reinitiation of isolated, *tert*-chloride-terminated PIB by $TiCl_4$ was reported to yield *exo*-olefin-terminated PIB free of side products (principally chain-coupled PIB).

Over the years, various researchers[22−26] have proposed that hindered bases, particularly 2,6-di-*tert*-butylpyridine (D*t*BP), can abstract β-protons from carbenium ion chain ends during isobutylene polymerization, despite the common view that these so-called proton traps are too sterically hindered to react with carbenium ions. Recently, Faust and co-workers[27] offered a different interpretation of this phenomenon, attributing β-proton abstraction to the presence of impurities within D*t*BP, in their case a cyclic imine base, which they postulated to be sterically too hindered to quantitatively complex with $TiCl_4$ but sufficiently sterically unhindered to still allow approach to the carbocation. Faust and co-workers emphasized that proton elimination should be avoided for the synthesis of well-defined macromolecules.

We now report our study where we have purposefully sought to optimize β-proton abstraction by hindered bases to produce *exo*-olefin-terminated PIB. The method entails end-quenching of $TiCl_4$-catalyzed quasiliving isobutylene polymerizations with a hindered base, as shown in Scheme 1. We have examined

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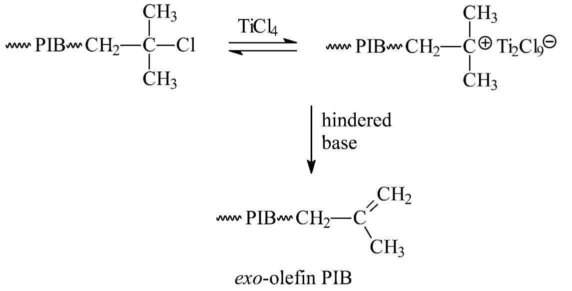
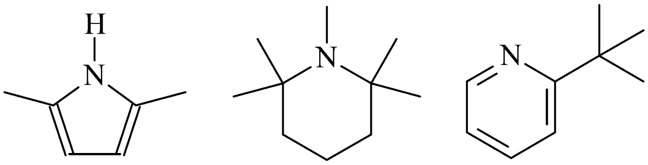
Scheme 1. End-Quenching of Quasiliving Isobutylene with a Hindered Base To Yield *exo*-Olefin-Terminated Polyisobutylene



Scheme 2. Compounds Representing Three Classes of Hindered Bases Examined as End Quenchers in Quasiliving Isobutylene Polymerization (from Left): 2,5-Disubstituted Pyrroles, Hindered Aliphatic Tertiary Amines, and Partially Hindered Pyridines



three distinct classes of hindered bases, as shown in Scheme 2: 2,5-disubstituted pyrroles, hindered aliphatic tertiary amines, and partially hindered pyridines. We have achieved quantitative β-proton elimination to yield exclusively *exo*-olefin end groups, when the base is sufficiently sterically hindered to prevent complete complexation with $TiCl_4$, but not so sterically hindered as to prevent abstraction of a β-proton from the carbenium ion. The principal side reaction, which can be avoided under optimized conditions, is reaction of carbenium ions with *exo*-olefin to yield coupled product.

Experimental Section

Materials. 2-Chloro-2,4,4,-trimethylpentane (TMPCl) was prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich Corp., 99%) in an external water/ice bath.[28] The product was stored under saturated HCl conditions and, just prior to use, was stirred over sodium bicarbonate ($NaHCO_3$) and isolated by filtration. Anhydrous hexane (Hex, 95%), 2,6-lutidine (26Lut, 99+%, redistilled), titanium(IV) chloride ($TiCl_4$, 99.9%, redistilled), methanol (MeOH, anhydrous, 99.8%), and $CDCl_3$ were used as received from Sigma-Aldrich Corp. 2-*tert*-Butylpyridine (2tBP) and 1,2,2,6,6-pentamethylpiperidine (PMP) were used as received from the Rare Chemical Library of Sigma-Aldrich Corp. 2,5-Dimethylpyrrole (25DMPy, 98%, Sigma-Aldrich Corp.) was purified by vacuum distillation from CaH_2. The source and purity of 1,3-bis-(2-chloro-2-propyl)-5-*tert*-butylbenzene (bDCC)[29] and methyl chloride (MeCl) and isobutylene (IB)[30] have been described.

ATR-FTIR Spectroscopic Monitoring. A ReactIR 4000 reaction analysis system (ASI Applied Systems, Millersville, MD), previously described,[30] was integrated with an inert atmosphere glovebox (MBraun Labmaster 30) to obtain real-time FTIR spectra and temperature profiles 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.

Procedures. Isobutylene polymerizations were initiated using a $TMPCl/TiCl_4$ or $bDCC/TiCl_4$ system under dry N_2 gas within the inert-atmosphere glovebox. Unless otherwise noted, polymerizations were conducted in Hex/CH_3Cl 60/40 (v/v) cosolvents at −60 °C with [IB] = 0.5 M, [TMPCl] = 0.014 M, [26Lut] = 0.010 M, and $[TiCl_4]$ = 0.083 M.

A representative procedure was as follows: A 250 mL four-neck round-bottom flask, equipped with an overhead mechanical stirrer and platinum resistance thermometer, was fitted to the end of the DiComp probe of the ReactIR 4000, and this assembly was immersed into a constant-temperature heptane bath. An air background spectrum was acquired and subtracted from all subsequent spectra. The flask was then charged with prechilled solvents, initiator, and 26Lut. The mixture was stirred to achieve thermal equilibrium, and then FTIR data were continuously acquired for ∼10 min to establish a solvent reference absorbance area, A_r, prior to monomer addition. Next, IB was charged to the reactor, thermal equilibration was established, and data were again acquired for about 10 min prior to initiation, to establish the initial absorbance area, A_0, associated with the initial monomer concentration. The coinitiator, $TiCl_4$, was then charged to the reactor, neat and at room temperature. FTIR data were acquired continuously, and monomer conversion was calculated in real time as

$$\frac{[IB]_0 - [IB]_t}{[IB]_0} = 1 - \frac{A_t - A_r}{A_0 - A_r} \qquad (1)$$

where A_t is the instantaneous absorbance area at 887 cm^{-1}. The reaction was allowed to proceed to high conversion (∼95%), at which time an aliquot (5−10 mL) was removed using a glass pipet and terminated by charging into a scintillation vial containing 4 mL of prechilled (reaction temperature) anhydrous MeOH. The quenching agent was next charged to the flask when the IB conversion was ≥98%. Subsequent postquench aliquots were taken at various reaction times and terminated into prechilled anhydrous MeOH.

The terminated reaction mixtures were allowed to warm to room temperature. Hexane (1−2 mL) was added to each sample, and then each polymer was precipitated into MeOH. The recovered PIB was agitated (vortexed) with fresh MeOH to remove any remaining contaminants, and then the MeOH was decanted. Samples were put in a vacuum oven for at least 24 h at room temperature to remove any remaining solvents prior to GPC and NMR analysis.

Polymer Characterization. Gel permeation chromatography (GPC) was used to determine number-average (M_n) and weight-average (M_w) molecular weights and polydispersity index (PDI, M_w/M_n). The GPC system, equipped with a mini-DAWN on-line MALLS detector and Optilab differential refractometer (both Wyatt Technology Inc.), has been previously described.[31] Values for d*n*/d*c* were determined from the response of the differential refractometer and by assuming 100% mass recovery from the columns. GPC was also used to qualitatively detect coupled PIB, formed by the addition of a carbenium ion to the *exo*-olefinic end group of another chain. Coupled PIB was observed as a shoulder at an elution volume corresponding to approximately twice the molecular weight of the main peak.

The fractional molar amounts of *exo*-olefin, *endo*-olefin, *tert*-chloride, and coupled PIB chains (Scheme 3) were quantified via ^1H NMR integration using a Bruker AC-300 (300 MHz) spectrometer at sample concentrations of 3−5% (w/w) in $CDCl_3$. The fraction of *endo*-olefin was found to be negligible or undetectable in all samples except those produced at the highest quenching temperature studied (−40 °C). For TMPCl-initiated systems, it was assumed that these four species represent 100% of the chain ends. The fractional molar amount of each type of chain end was obtained using equations such as that given below for determining the fraction of *exo*-olefin (F_{exo})

$$F_{exo} = (A_{exo})/(A_{exo} + A_{endo} + A_{tert-Cl}/6 + 2A_{coupled}) \qquad (2)$$

where A_{endo} is the area of the single olefinic resonance at 5.15 ppm, A_{exo} is the area of the upfield *exo*-olefinic resonance at 4.63 ppm, and $A_{tert\text{-}Cl}$ was calculated as

$$A_{tert\text{-}Cl} = (A_{1.65-1.72}) - 6A_{endo} \qquad (3)$$

where $A_{1.65-1.72}$ is the integrated area of the convoluted peaks associated with the *gem*-dimethyl protons of the *endo*-olefin and the *tert*-chloride chain ends. The $A_{coupled}$ term in eq 2 carries a coefficient of 2 to account for the fact that the coupled product

Scheme 3. Structures of *tert*-Chloride, *exo*-Olefin, *endo*-Olefin, and Coupled PIB

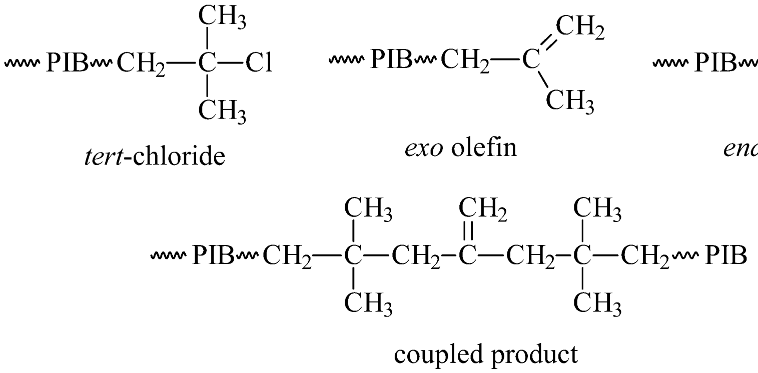
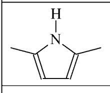
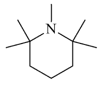
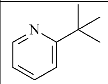


Table 1. *exo*-Olefin (mol %) via End-Quenching of Quasiliving PIB[a] with Various Hindered Bases at −60 °C

Quencher	Quencher Conc. (mol/L)	M_n[b] (g/mol)	PDI	Chain End Products[c]	Quenching Time (min)				
					8	15	30	45	60
					(mol %)				
	**0.020**	2,030	1.07	***Exo* olefin** **Coupled**	- -	99 0	100 0	100 0	100 0
	**0.020**	2,130	1.08	***Exo* olefin** **Coupled**	95 5	95 5	- -	95 5	- -
	0.028	2,350	1.09	***Exo* olefin** **Coupled**	- -	98 2	- -	98 2	- -
	0.040	2,230	1.20	***Exo* olefin** **Coupled**	99 0	100 0	- -	100 0	- -
	**0.020**	1,540	1.06	***Exo* olefin** **Coupled**	- -	62 27	65 32	69 30	66 34
	0.040	1,970	1.09	***Exo* olefin** **Coupled**	80 5	88 6	- -	94 6	- -

[a] [IB] = 0.5 M; [TMPCl] = 0.014 M; [26Lut] = 0.010 M; [$TiCl_4$] = 0.083 M; 60/40 Hex/MeCl (v/v); −60 °C; end quencher added at full IB conversion (polymerization time ≅ 16 min). [b] For each experiment, M_n and PDI are average values for all aliquots with no coupling. [c] Balance of end groups are *tert*-chloride.

accounts for two original PIB chains. A_{coupled} was calculated as follows:

$$A_{\text{coupled}} = (A_{5.0-4.75} - A_{\text{exo}})/2 \tag{4}$$

where $A_{5.0-4.75}$ is the integrated area of the convoluted peaks associated with the downfield *exo*-olefinic proton at 4.85 ppm and the two identical protons of the coupled product at 4.82 ppm.

For bDCC-initiated systems, if the conversion of *tert*-chloride chain ends was complete, then the fractional yield of the desired product, i.e., α,ω-di-*exo*-olefin PIB ($F_{\text{di-exo}}$) was calculated as follows

$$F_{\text{di-exo}} = (2A_{\text{exo}} - A_{5.0-4.75})/A_{5.0-4.75} \tag{5}$$

with the balance of the chains assigned to coupled product. Additionally, the aromatic initiator residue provided an internal reference to which peak integrations could be compared.

Results and Discussion

Table 1 presents the results for end quenching at −60 °C (chain end concentration = 0.014 M) using the three hindered bases shown in Scheme 2. All three bases were effective, to varying degrees, in causing elimination to produce *exo*-olefin-terminated PIB. Comparison at 0.020 M (1.4× chain ends) showed that the most effective quencher is 2,5-dimethylpyrrole (25DMPy), which was the only quencher to yield 100% *exo*-olefin, without any coupled product, at this quencher concentration. Figure 1 shows the ^1H NMR spectrum of the product PIB after 15 min reaction with 25DMPy. The *exo*-olefin resonances appear at 4.64 and 4.85 ppm. There are no peaks at 1.68 or 5.15 ppm, indicating the absence of *tert*-chloride and *endo*-olefin end groups, respectively. Coupling was also absent as indicated by the absence of a peak at 4.82 ppm, which otherwise would be visible as a shoulder to the downfield *exo*-olefin peak at 4.85 ppm.

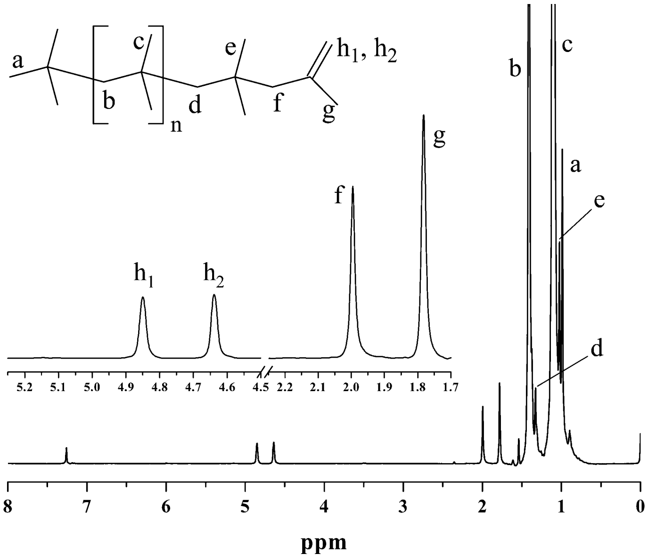
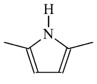


Figure 1. ^1H NMR spectrum of quasiliving PIB end-quenched with 0.020 M 2,5-dimethylpyrrole for 15 min at −60 °C: 100% *exo*-olefin end groups. [IB] = 0.5 M; [TMPCl] = 0.014 M; [2,6-lutidine] = 0.010 M; [$TiCl_4$] = 0.083 M; 60/40 Hex/MeCl (v/v). End quencher was added at full IB conversion.

We hypothesize that elimination occurs through reaction of the carbenium ion with free base, i.e., a small fraction of the quencher that remains uncomplexed by $TiCl_4$ as a consequence

Table 2. *exo*-Olefin (mol %) via End-Quenching of Quasiliving PIB[a] with 2,5-Dimethylpyrrole[b] at Various Temperatures

Quencher	Temp.[c] (°C)	M_n[d] (g/mol)	PDI	Chain End Products[e]	Quenching Time (min)					
					10	15	30	60	75	170
					(mol %)					
	**-70**	2,580	1.08	***Exo* olefin**	-	61	61	60	62	-
				Coupled	-	18	22	28	28	-
	-60	1,960	1.08	***Exo* olefin**	-	99	100	100	-	-
				Coupled	-	0	0	0	-	-
	-50	1,540	1.05	***Exo* olefin**	100	100	-	100	-	-
				Coupled	0	0	-	0	-	-
	-40	1,490	1.17	***Exo* olefin**	-	-	99	99	-	99
				***Endo* olefin**	-	-	1	1		1
				Coupled	-	-	0	0		0
	-40	2,150	1.03	***Exo* olefin**	-	97	96	96	96	-
				***Endo* olefin**	-	2	3	4	3	-
				***Exo*-olefin**	-	0	0	0	0	-

[a] [IB] = 0.5 M; [TMPCl] = 0.014 M; [26Lut] = 0.010 M; $[TiCl_4]$ = 0.083 M; 60/40 Hex/MeCl (v/v). [b] [25DMPy] = 0.020 M added at full IB conversion. [c] The −70 °C entry is the average of eight separate experiments conducted under the same conditions; the −60 °C entry is the average of three separate experiments conducted under the same conditions; the −50 and −40 °C entries are each from a single experiment. [d] M_n and PDI are reported for the prequench aliquot (data for −70 and −60 °C are averages). [e] Balance of end groups is *tert*-chloride.

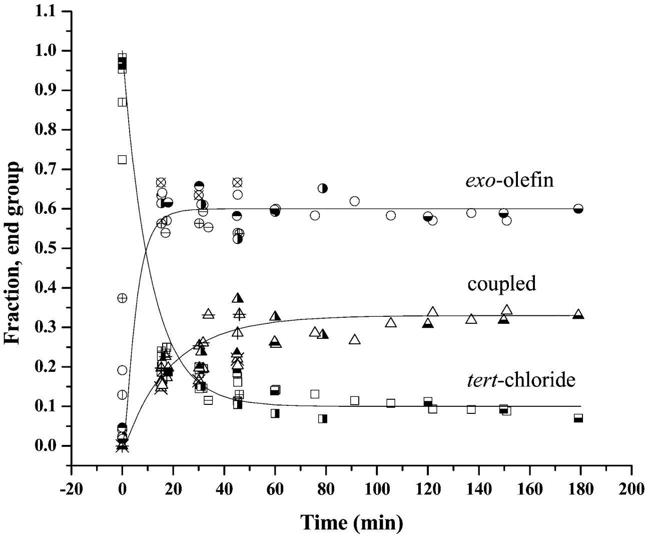


Figure 2. PIB end group fractions vs quenching time with 2,5-dimethylpyrrole at −70 °C. Aliquots from eight individual reactions are plotted; lines are included for clarity. [IB] = 0.5 M; [TMPCl] = 0.014 M; [2,6-lutidine] = 0.010 M; $[TiCl_4]$ = 0.083 M; 60/40 Hex/MeCl (v/v); [25DMPy] = 0.20 M. End quencher was added at full IB conversion.

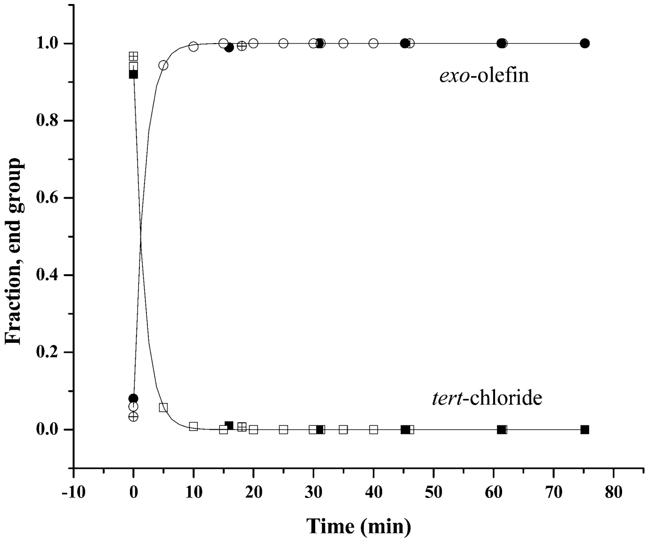


Figure 3. PIB end-group fractions vs quenching time with 2,5-dimethylpyrrole at −60 °C. Aliquots from three individual reactions are plotted; lines are included for clarity. [IB] = 0.5 M; [TMPCl] = 0.014 M; [2,6-lutidine] = 0.010 M; $[TiCl_4]$ = 0.083 M; 60/40 Hex/MeCl (v/v); [25DMPy] = 0.20 M. End quencher was added at full IB conversion.

of steric hindrance. Coupling can be avoided only when carbenium ions are rapidly scavenged by free base, which prevents them from reacting with the *exo*-olefin product. Rapid scavenging requires a sufficiently high free-base concentration, which in turn depends on the total concentration of base charged to the reactor and the value of the equilibrium constant for complexation of the base with $TiCl_4$. The results in Table 1 for 1,2,2,6,6-pentamethylpiperidine (PMP) demonstrate this concept. PMP apparently complexes with $TiCl_4$ to a greater extent than does 25DMpy. At 0.020 M PMP, elimination was slow; i.e., the concentration of free base was apparently too low, and 5% of the chains became involved in coupled product. Increasing the total concentration of PMP increased the rate of elimination and caused a reduction in the amount of coupled product. At 0.028 M PMP, coupling was reduced to 2%, and at 0.040 M PMP, it was eliminated entirely. Thus, at a given chain end concentration, the quencher concentration should be optimally set to the minimum value that provides 100% *exo*-olefin with zero or negligible coupling. A higher quencher concentration cannot further improve the product ratio and simply retards the overall quenching kinetics, through complexation and/or reaction with $TiCl_4$. Therefore, the optimum [PMP] at this chain end concentration is ~0.040 M. For 25DMPy it is obviously lower, ~0.020 M, although we have not fully explored the bare minimum effective concentration in this case.

On the basis of the work by Bae and Faust,[27] we included in our study the partially hindered pyridine, 2-*tert*-butylpyridine (2tBP). Faust et al. obtained about 67% depletion of *tert*-chloride chain ends within about 3 h, when 2tBP was present from the beginning of the polymerization. The relative proportions of *exo*-olefin and coupled product within this depleted fraction were not reported, although the authors did state that the elimination product was exclusively *exo*-olefin. Unlike Faust et al., we charged 2tBP to the reactor after complete conversion of isobutylene, with the deliberate intention of creating *exo*-olefin. As shown in Table 1, 2tBP is not a particularly effective end quencher. At 0.020 M, 2tBP was able to convert only about 66−69% of the chains to *exo*-olefin, with the balance involved in coupled product. Doubling the concentration of 2tBP to 0.040 M improved the product ratio significantly; however, the yield of the desired product was still only 94%.

The slow elimination kinetics displayed by 2tBP suggests that complexation of 2tBP with $TiCl_4$ is too exhaustive and that the

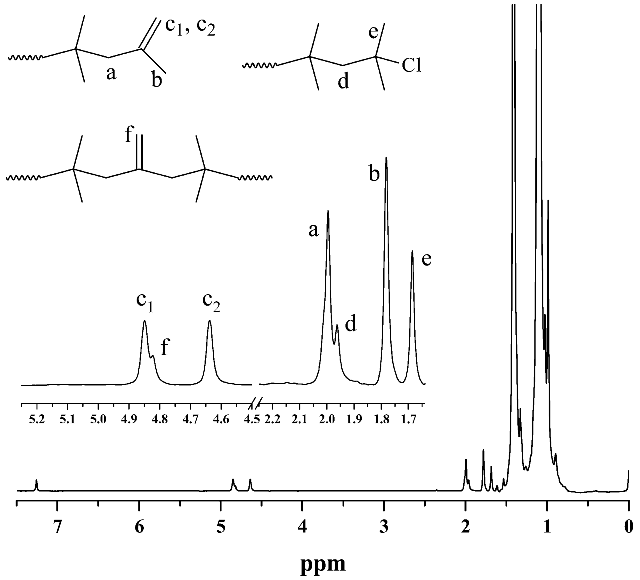


Figure 4. ^{1}H NMR spectrum of quasiliving PIB end-quenched with 0.020 M 2,5-dimethylpyrrole for 45 min at −70 °C. [IB] = 0.5 M; [TMPCl] = 0.014 M; [2,6-lutidine] = 0.010 M; [TiCl$_4$] = 0.083 M; 60/40 Hex/MeCl (v/v). End quencher was added at full IB conversion.

concentration of free base is too low. We predict that, although further increases in 2tBP concentration may be capable of achieving 100% *exo*-olefin under these conditions, the required quenching times may become impractically long since the total concentration of base (2tBP plus 26Lut) will become a significant fraction of the TiCl$_4$ concentration. Under these conditions, the rate of ionization slows and the concentraton of carbenium ions becomes too low.

Effect of Temperature. The effect of temperature on end-quenching is illustrated in Table 2 for 25DMPy at 0.020 M (1.4× chain ends); the remaining experimental conditions were the same as those used in Table 1. The results show that lower temperatures promote coupling and higher temperatures favor the formation of *exo*-olefin. In fact, it is remarkable that extensive (~30%) coupling occurred at −70 °C, while none occurred at −60 °C. Moreover, these results were very reproducible. The −70 °C result reported in Table 2 is actually the average of eight individual reactions, and the −60 °C result is the average of three individual reactions. Figures 2 and 3 display all of the data at −70 and −60 °C, respectively (tabular data for Figures 2 and 3 are listed in the Supporting Information). Although there is some minor scatter in the data, the trend is clear; at −70 °C, 55−65% of the chains acquire the desired *exo*-olefin structure, 25−35% of the chains become coupled, and ~10% of the chains remain unreacted with *tert*-chloride end groups. In contrast, at −60 °C the chains are rapidly and quantitatively converted to the desired *exo*-olefin. We believe that the effect of temperature is due to a relatively high negative enthalpy for complexation, and possibly irreversible reaction, between the quencher (in this case 2,5-dimethylpyrrole) and TiCl$_4$. Below −60 °C, the concentration of uncomplexed quencher is too low for efficient quenching to take place. Table 2 data show that increasing the temperature further, to −50 or −40 °C, also results in quantitative conversion to olefin without coupling, although, at −40 °C only, small fractions of *endo*-olefin were also observed.

Figure 4 shows the ^{1}H NMR spectrum of a representative reaction product at −70 °C, obtained after end-quenching for 45 min (experiment 413107, Supporting Information). The composition of this polymer was 54% *exo*-olefin, 13% *tert*-chloride, and 33% coupled chains. In addition to the *exo*-olefin proton resonances, only one additional olefinic resonance was observed at 4.82 ppm, which was assigned to the two identical protons (f) of coupled product possessing exclusively the vinylidene structure (Scheme 3). We made this assignment based on the fact that only one extra resonance (4.82 ppm) was observed in the olefinic region and that, under quenching conditions, the coupled-chain carbenium ion will undergo β-proton loss, subject to the same steric constraints as the regular PIB chain end. The *tert*-chloride fraction is evidenced by the

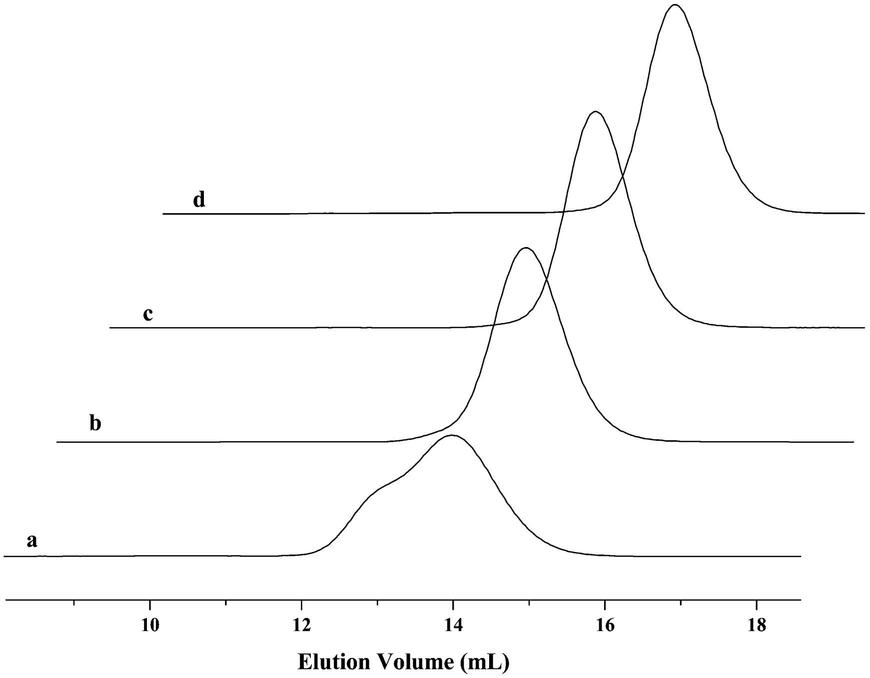


Figure 5. GPC chromatograms of PIBs end-quenched at various temperatures with 0.020 M 2,5-dimethylpyrrole: (**a**) −70 °C, 45 min, bimodal; (**b**) −60 °C, 15 min, M_n = 1970 g/mol, PDI = 1.08; (**c**) −50 °C, 10 min, M_n = 1580 g/mol, PDI = 1.09; (**d**) −40 °C, 170 min, 1760 g/mol, 1.35. The chromatograms have been staggered along the *x*-axis for clarity. [IB] = 0.5 M; [TMPCl] = 0.014 M; [2,6-lutidine] = 0.010 M; [TiCl$_4$] = 0.083 M; 60/40 Hex/MeCl (v/v). End quencher was added at full IB conversion.

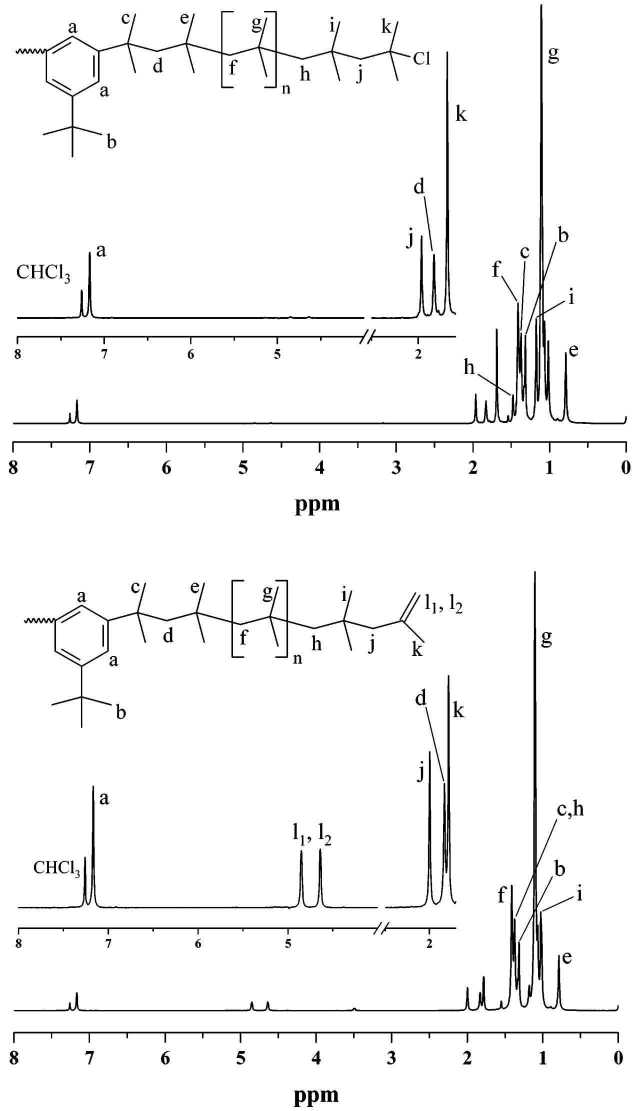
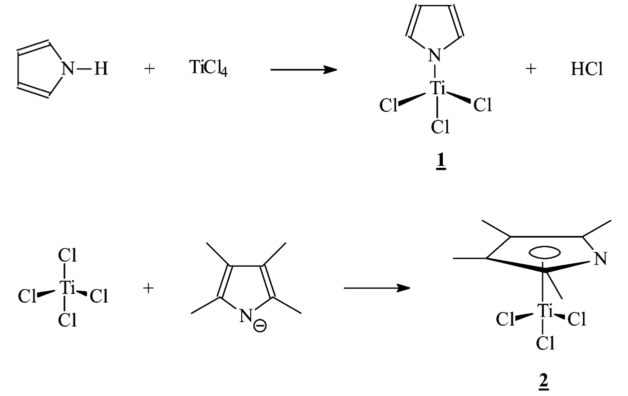


Figure 6. ^{1}H NMR spectra of difunctional PIB end-quenched with 0.088 M 2,5-dimethylpyrrole at −50 °C: (a, top) aliquot removed prior to end-quenching; (b, bottom) aliquot after 11 min reaction with 2,5-dimethylpyrrole. [IB] = 0.5 M; [bDCC] = 0.016 M; [2,6-lutidine] = 0.010 M; [TiCl$_4$] = 0.19 M; 60/40 Hex/MeCl (v/v). End quencher was added at full IB conversion.

characteristic peaks at 1.68 (*gem*-dimethyl) and 1.96 ppm (methylene). The ^{1}H NMR spectra of the polymers obtained at the higher temperatures were identical to Figure 1, except for the presence of a minor amount of *endo* olefin at −40 °C. GPC chromatograms of the PIBs produced at the various temperatures are shown in Figure 5. The polymer produced at −70 °C was bimodal as a result of coupling; polymers produced at all higher temperatures were monomodal.

Difunctional *exo*-Olefin-Terminated PIB. 2,5-Dimethylpyrrole was also used as an end quencher for difunctional quasiliving PIB initiated from 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene (blocked dicumyl chloride, bDCC). Figure 6a shows the ^{1}H NMR spectrum of the polymer prior to introduction of 25DMPy. This particular polymer had a degree of polymerization ($\bar{X}_n$) = 32. Resonances due to the *tert*-chloride end groups are visible at 1.68 and 1.96 ppm. Resonances due to the initiator residue are visible at 7.17 (phenyl protons) and 1.82 ppm (methylene nearest bDCC residue). Figure 6b shows the ^{1}H NMR spectrum of the same polymer after 11 min reaction with 25DMPy. The resonances associated with the *tert*-chloride end groups are no longer visible, and characteristic resonances due to *exo*-olefin end groups have appeared at 1.79 (methyl), 2.00 (methylene), 4.64 (olefin), and 4.85 ppm (olefin). Peak integration showed that the two *exo*-olefinic resonances were essentially identical in area; thus, according to eq 5, the percentage of quasiliving chains converted to di-*exo*-olefin PIB was 100%, and the fraction of coupled product was zero. Furthermore, the combined peak areas of the 4.64 and 4.85 ppm resonances (four protons total) was exactly 1.33 times the area of the aromatic proton resonance at 7.2 ppm (three protons), indicating perfect bifunctionality.

Scheme 4. Reaction of Pyrrole with TiCl$_4$ To Form the η^1 Titanium Compound 1 (Top); Reaction of 2,3,4,5-Tetramethylpyrrole To Form the η^5 Titanium Complex 2 (Bottom)



Mechanistic Considerations. We are reasonably confident of the mechanism of end-quenching for the strong hindered bases, PMP (pK_a = 11.25[32]) and 2tBP (pK_a = 5.69[33]). They behave essentially in the manner described by Faust:[27] steric hindrance around nitrogen is sufficiently severe to prevent exhaustive complexation by TiCl$_4$ but not so severe as to prevent β-proton abstraction from the PIB carbenium ion. This interpretation is supported by the behavior of bases at either extreme of the steric hindrance scale. Unhindered strong bases such as 2,4-lutidine,[29] and the 2,6-lutidine used herein, are routinely employed in cationic polymerization systems to scavenge protic impurities and simultaneously suppress ion-pair dissociation via the common-ion effect.[31] These bases either become protonated or exhaustively complexed by TiCl$_4$ (no free base) and β-elimination is not observed. At the other end of the scale is 2,6-di-*tert*-butylpyridine (DTBP), which is also routinely used in carbocationic polymerizations to confer controlled/living behavior.[34] DTBP is generally thought to be incapable of forming complexes with Lewis acids and to be inert toward carbenium ions due to severe steric hindrance.[35]

The high effectiveness of 2,5-dimethylpyrrole toward elimination is surprising. Other pyrroles react characteristically via electrophilic aromatic substitution. For example, pyrrole itself reacts with quasiliving PIB to yield a mixture of mono- and dialkylated products,[36] and *N*-methylpyrrole reacts in a controlled fashion to yield exclusively the mono-alkylated product.[37] The action of 2,5-dimethylpyrrole is particularly surprising in view of its low basicity (pK_a = −0.71[38]). Although addition of two methyl substituents significantly enhances basicity relative to pyrrole itself (pK_a = −3.8[38]), 2,5-dimethylpyrrole remains a relatively weak base compared to the strong tertiary amine bases, PMP and 2tBP. In further contrast to tertiary amines, 2,5-DMP has a replaceable hydrogen atom bonded to nitrogen, which provides a site for reaction with TiCl$_4$. For example, it is well-known[39] that TiCl$_4$ reacts with the N−H bond of secondary amines to produce TiCl$_3$NR$_2$. Presumably, TiCl$_4$ may react in a similar way with pyrrole to produce the η^1 titanium compound

1 (Scheme 4).[40] Alternatively, when the pyrrole ring is made electron rich by methyl group substitution,[41] the η^5 titanium complex **2** can be formed. Reaction of 25DMPy with $TiCl_4$, to an extent that quenching activity is eventually lost, is suggested by the fact that quenching failed to proceed to completion (persistence of unreacted *tert*-chloride PIB) under the conditions of Figure 2. Preliminary experiments have suggested that reaction of 25DMPy with $TiCl_4$ does indeed occur, possibly to form structures such as **1** and **2**. The question of whether elimination is caused by uncomplexed 25DMPy itself or possibly by one of the products of its reaction with $TiCl_4$ is the focus of our current investigations. These results will be reported in a timely fashion.

Conclusions

We have produced 100% *exo*-olefin-terminated PIB by end-quenching a quasiliving IB polymerization with a partially sterically hindered base such as 2,5-dimethylpyrrole or 1,2,2,6,6-pentamethylpiperidine. The base must be sufficiently sterically hindered to prevent complete complexation with Lewis acid, but not so sterically hindered as to prevent its approach to the carbenium ion. At a chain end concentration of 0.014 M, 0.020 M 25DMPy yields 100% *exo*-olefin PIB chain ends within 10 min of quencher addition at −50 °C and within about 15−30 min at −60 °C. Coupling of ionized chain ends with *exo*-olefin-terminated chains is a complicating side reaction whose severity increases as [CE] increases and/or as temperature decreases. Higher temperatures produce higher concentrations of free base, which suppresses coupling and enables faster proton abstraction.

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Supporting Information Available: Tabular data for Figures 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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