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Kinetics and Mechanism of End-Quenching of Quasiliving Polyisobutylene with Sterically Hindered Bases

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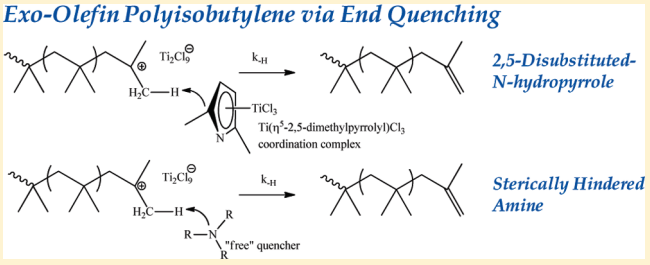
Supporting Information

ABSTRACT: Kinetic investigation of end-quenching (β-proton abstraction to form *exo*-olefin) of quasiliving polyisobutylene ($TiCl_4$, −60 °C, 60/40 hexane/methyl chloride) with sterically hindered amines, 2-*tert*-butylpyridine (2TBP), 1,2,2,6,6-pentamethylpiperidine (PMP), 2,2,6,6-tetramethylpiperidine (TMP), and 2,5-dimethylpyrrole (25DMP), was conducted to determine the mode of interaction of these quenchers with $TiCl_4$ and identify the active species responsible for β-proton abstraction. Strongly basic, sterically hindered amines such as 2TBP, PMP, and TMP formed reversible 1:1 complexes with $TiCl_4$. A minor fraction of the base remained uncomplexed and was the active species responsible for proton abstraction. For these bases, the rate of β-proton abstraction decreased in the order PMP > TMP > 2TBP and was directly proportional to $[TiCl_4]$. The weakly basic 25DMP behaved differently. NMR spectroscopy showed that it reacted quantitatively and irreversibly with $TiCl_4$ to form the Ti(η^5-2,5-dimethylpyrrolyl)Cl_3 coordination complex, which was the active species responsible for β-proton abstraction. In the presence of a stronger base, e.g., 2,6-lutidine, the complex was rapidly regenerated and maintained at a constant concentration. With increasing $[25DMP]_0$, the rate of quenching increased to a maximum at $[25DMP]_0 = ([TiCl_4]_0 - [2,6\text{-lutidine}])/6$ and then decreased. The rate of quenching with 25DMP was proportional to $[TiCl_4]^2$. The behavior of 25DMP was predicted to extend to other 2,5-disubstituted-*N*-hydropyrroles, such as 2,3,4,5-tetramethylpyrrole.



INTRODUCTION

We recently reported that direct addition of certain sterically hindered organic bases to $TiCl_4$-catalyzed quasiliving polyisobutylene (PIB) leads to quantitative *exo*-olefin chain end formation.[1] This regioselective elimination at the carbenium ion chain end occurred via reaction with a small fraction of the base that remained uncomplexed with $TiCl_4$ due to steric hindrance. The degree of complexation with $TiCl_4$ determined the nominal amount of base necessary in the reaction to provide a concentration of "free" base sufficiently high to scavenge carbenium ion chain ends and prevent chain coupling. The examples of 2-*tert*-butylpyridine (2TBP) and 1,2,2,6,6-pentamethylpiperidine (PMP) were provided, the former of which apparently complexed with $TiCl_4$ to a greater extent and therefore led to greater chain coupling under the same set of reaction conditions. Quenching to *exo*-olefin was also demonstrated with the base, 2,5-dimethylpyrrole (25DMP), which worked remarkably well and was suggested to operate by a fundamentally different mechanism. Here we provide a more detailed analysis of the kinetics and mechanism for quenching of $TiCl_4$-catalyzed quasiliving PIB with various sterically hindered amines (Scheme 1) as well as delineate the difference between the mechanism of reaction of simple tertiary and second amines and that of 2,5-disubstituted-*N*-hydropyrroles.

EXPERIMENTAL SECTION

Materials. Hexane (anhydrous, 95%), titanium tetrachloride ($TiCl_4$) (99.9%,), 2,6-lutidine (redistilled, 99.5%), 2,5-dimethylpyrrole (25DMP) (98%), 2-*tert*-butylpyridine (2TBP) (98%), 1,2,2,6,6-pentamethylpiperidine (PMP) (97%), 2,2,6,6-tetramethylpiperidine (TMP) (99%), cyclohexane (anhydrous, 99.5%), methanol (anhydrous, 99.8%), and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich Co. and used as received. Methyl chloride from Alexander Chemical Corp. was dried by passing the gas through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glovebox immediately prior to use. Monofunctional *tert*-chloride-terminated PIB (2.0×10^3 g/mol) was prepared via BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[2] at −60 °C.

Instrumentation. Nuclear magnetic resonance (NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR spectrometer. Standard ^1H and ^{13}C pulse sequences were used. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^1H chemical shifts were referenced to TMS (0 ppm), and all ^{13}C shifts were referenced to the residual $CDCl_3$ solvent resonance (77.0 ppm). PIB

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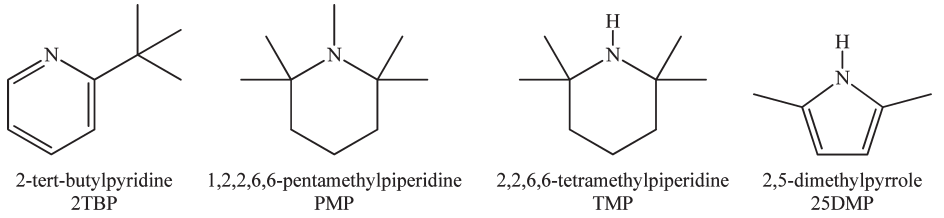
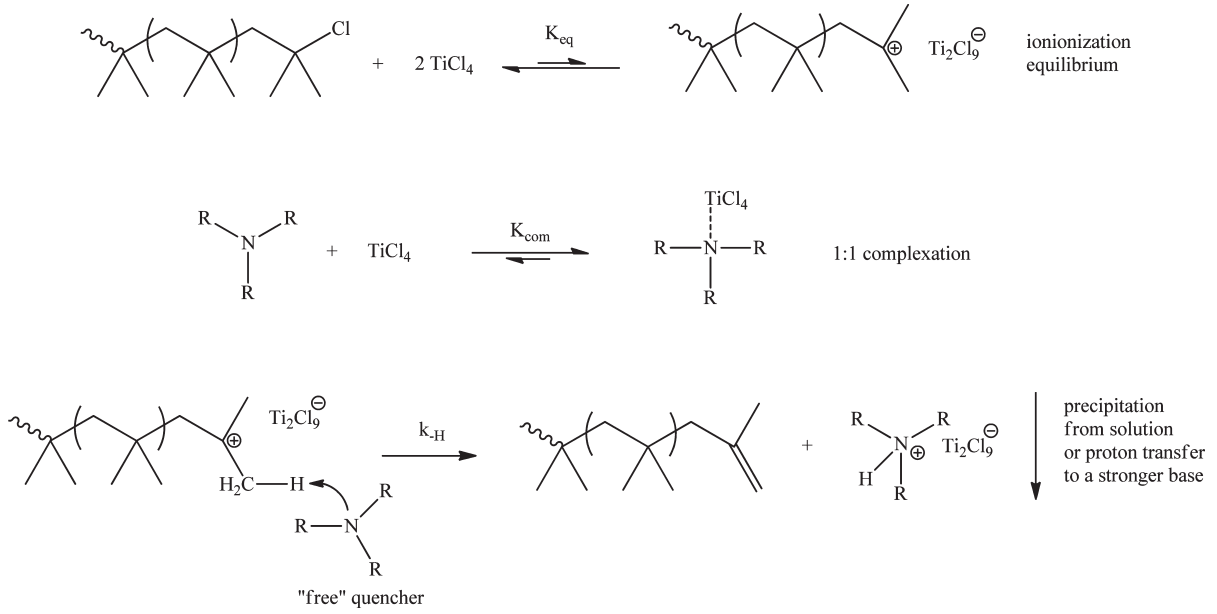
Scheme 1. Sterically Hindered Organic Bases Studied as Quenchers of $TiCl_4$-Catalyzed Quasiliving PIB



Scheme 2. Mechanism for β-Proton Abstraction from the PIB Carbenium Ion Chain End When Using Sterically Hindered Amines That Undergo 1:1 Complexation with $TiCl_4$



samples were prepared by dissolving the polymer in $CDCl_3$ (20−50 mg/mL) and charging the solution to 5 mm o.d. NMR tubes.

Kinetics of Quenching. The kinetics for β-proton abstraction from quasiliving PIB were determined by addition of amines to *tert*-chloride PIB in 60/40 (v/v) hexane/methyl chloride at −60 °C and subsequent activation with $TiCl_4$. Within a N_2-atmosphere glovebox, 1.6 g (8×10^{-4} mol) of monofunctional *tert*-chloride-terminated PIB (2.0×10^3 g/mol) was dissolved in 480 mL of hexane at room temperature. The mixture was chilled to −60 °C in a four-neck round-bottom flask equipped with an overhead stirrer, and 320 mL of methyl chloride was then added. To this solution were added 0.47 mL (4×10^{-3} mol) of 2,6-lutidine and various amounts of the amine quenchers, ranging from 0.5 to 8 equiv per chain end ($(4-64) \times 10^{-4}$ mol). After thermal equilibration, $TiCl_4$ was charged to the reactor in amounts ranging from 25 to 40 equiv per chain end ($(2.0-3.2) \times 10^{-2}$ mol). Aliquots of 100 mL were taken from the reaction and poured into beakers containing 25 mL of chilled methanol. Conversion from *tert*-chloride to *exo*-olefin chain ends was estimated by integration of the ^{1}H NMR spectra of aliquots taken from the reactions. *tert*-Chloride chain ends were characterized by resonances at 1.69 (methyl) and 1.96 ppm (methylene) and *exo*-olefin chains ends by resonances at 1.78 (methyl), 2.00 (methylene), and 4.82 and 4.84 ppm (olefinic).[3] No resonances were observed at 5.15 ppm due to *endo*-olefin chain ends or 4.82 ppm due to chain coupling.[4]

Formation of Ti(η^5-25DMP)Cl_3 Coordination Complex. 25DMP was reacted with $TiCl_4$ in the presence of 2,6-lutidine for spectroscopic identification of a pyrrolyl-$TiCl_3$ complex. Within a N_2-atmosphere glovebox, 0.1 mL (9.3×10^{-4} mol) of cyclohexane (as an internal reference), 0.108 mL (1.0×10^{-3} mol) of 25DMP, and 0.116 mL (1.0×10^{-3} mol) of 2,6-lutidine were added to 10 mL of $CDCl_3$ at −60 °C. Adduct formation was achieved by addition of 0.658 mL (6.0×10^{-3} mol) of $TiCl_4$. The reaction produced HCl, resulting in the immediate formation of a brown precipitate consisting of 2,6-lutidinium$^+$ $Ti_2Cl_9^-$ salt . Aliquots were taken before and after addition of $TiCl_4$ (once the solids had settled), warmed to room temperature, and charged directly to 5 mm o.d. NMR tubes for analysis.

The above preparation was repeated at room temperature in C_6D_6 without cyclohexane, and after addition of $TiCl_4$ and separation of the solid precipitate, the resulting clear solution was also subjected to NMR analysis.

RESULTS AND DISCUSSION

In our previous report[1] we proposed that end-quenching of $TiCl_4$-catalyzed quasiliving PIB with certain amines, e.g., 2TBP or PMP, proceeded according to the mechanism shown in Scheme 2. Complexation of these amine bases with $TiCl_4$ is incomplete due to steric hindrance, resulting in a finite concentration of free base in solution; the free base regiospecifically

abstracts a β-proton from the PIB carbenium ion to produce exclusively *exo*-olefin chain ends. It was further proposed that the hindered base may be regenerated when a stronger, fully complexed base such as 2,6-lutidine is present and capable of acting as a proton sink. We also showed that 25DMP was an effective quencher but suggested that it might operate through a different mechanism.

To further elucidate the mechanism of quenching by sterically hindered amines, reaction kinetics were investigated in 60/40 (v/v) hexane/methyl chloride at −60 °C. In general, the rate of disappearance of *tert*-chloride chain ends, [PIBCl], is directly proportional to the concentration of carbenium ion chains, $[PIB^+]$, and the concentration of the species, [Q], responsible for β-proton extraction from the ionized chain end.

$$-\frac{d[PIBCl]}{dt} = k_{-H}[PIB^+][Q] \quad (1)$$

Assuming that ionization involves two equivalents of $TiCl_4$ to form $Ti_2Cl_9^-$ counterions[5] and is fast and unperturbed by proton abstraction, we may reduce eq 1 to a more accessible form

$$-\frac{d[PIBCl]}{dt} = k_{-H}K_{eq}[PIBCl][TiCl_4]^2[Q] \quad (2)$$

where K_{eq} is the ionization equilibrium constant. Integration of eq 2 in terms of conversion (p) of *tert*-chloride chain ends yields

$$\ln\left(\frac{1}{1-p}\right) = k_{-H}K_{eq}[TiCl_4]^2[Q]t \quad (3)$$

Plots of $\ln(1/1-p)$ versus time (t) should be linear, and the quenching reaction should exhibit first-order kinetics provided that $k_{-H}K_{eq}[TiCl_4][Q]$ remains constant during measurement. Unfortunately, $[TiCl_4]$ is expected to decrease over the course of the reaction via the formation of onium salts, and [Q] may also decrease in the absence of a stronger base. Since it is fully complexed with the Lewis acid, 2,6-lutidine is not capable of proton extraction under typical conditions for $TiCl_4$-catalyzed quasiliving isobutylene polymerization;[6] however, proton transfer from Q to 2,6-lutidine is expected to occur if Q is the weaker base. Relative basicities of organic bases in nonaqueous solution have been reported,[7] and these data show that a 2-alkylpyridine such as 2-*tert*-butylpyridine is a weaker base than 2,6-lutidine but that aliphatic amines such as PMP and TMP are likely to be stronger. The potential variation of [Q] and $[TiCl_4]$ can be readily dealt with by considering only initial rates. However, we chose to use somewhat dilute reaction systems to enable the more useful integral analysis. The chain end concentration was lowered to 0.001 M, and the nominal $TiCl_4$ concentration was set to $[TiCl_4]_0 = 20[PIBCl]_0$.

First-order kinetic plots for end-quenching of $TiCl_4$-catalyzed quasiliving PIB with 2TBP are shown in Figure 1. The plots are linear in accordance with eq 3, and plots similar to Figure 1 were obtained for quenching with TMP, PMP, and 25DMP. Figure 2 shows the observed first-order rate constants for the various amines as a function of nominal quencher concentration. For 2TBP, TMP, and PMP the plotted data are more or less linear, monotonically increasing over the range of 4−8 equiv per chain end. In contrast, the observed first-order rate constant for 25DMP is proportional to nominal quencher concentration only at low quencher concentrations; it then reaches a maximum and finally decreases with increasing concentration. The early

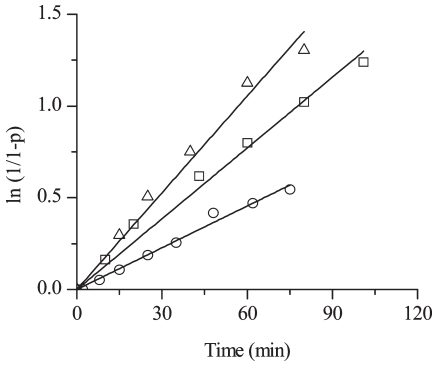


Figure 1. First-order kinetic plots for quenching of $TiCl_4$-catalyzed quasiliving PIB with 2TBP at −60 °C in 60/40 (v/v) hexane/methyl chloride. $[PIBCl]_0 = 0.001$ M, [2,6-lutidine] = 0.005 M, $[TiCl_4]_0 = 0.025$ M, and $[Q]_0 = 0.003\,25$ (○), 0.005 (□), and 0.007 M (△).

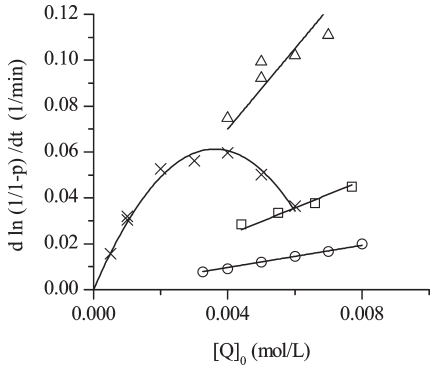


Figure 2. Plot of the apparent rate constant for quenching of $TiCl_4$-catalyzed quasiliving PIB as a function of the nominal quencher concentration, $[Q]_0$. Reactions were carried out at −60 °C in 60/40 (v/v) hexane/methyl chloride with $[PIBCl]_0$ = 0.001 M, [2,6-lutidine] = 0.005 M, $[TiCl_4]_0 = 0.025$ M. 25DMP (×), 2TBP (○), TMP (□), and PMP (△).

appearance of this maximum for 25DMP suggests a significant difference in the mechanism of reaction, a difference attributable to the manner of interaction with $TiCl_4$.

As suggested in Scheme 2, for amine bases such as 2TBP, the mode of interaction with $TiCl_4$ is formation of a reversible 1:1 complex. The complex that forms is unreactive toward β-proton abstraction at the carbenium ion chain end. However, if steric hindrance around nitrogen prevents exhaustive complexation, then residual free base is available to react with the carbenium ion to produce *exo*-olefin chain ends.[8] We may revise eqs 1−3 to account for complexation in terms of a complexation equilibrium constant (K_{com})

$$K_{com} = \frac{[Q{:}TiCl_4]}{[Q][TiCl_4]} = \frac{[Q]_0 - [Q]}{[Q][TiCl_4]} \quad (4)$$

where $[Q]_0$ is the initial, nominal concentration of quencher and $[Q{:}TiCl_4]$ is the concentration of the complex. The concentration of $TiCl_4$ is decreased by 1:1 complexation with base, and assuming near-complete complexation of the quencher ($1 \ll K_{com}[TiCl_4]$), eq 3 becomes

$$\ln\left(\frac{1}{1-p}\right) = k_{-H}\frac{K_{eq}}{K_{com}}[TiCl_4]_{effective}[Q]_0 t \quad (5)$$

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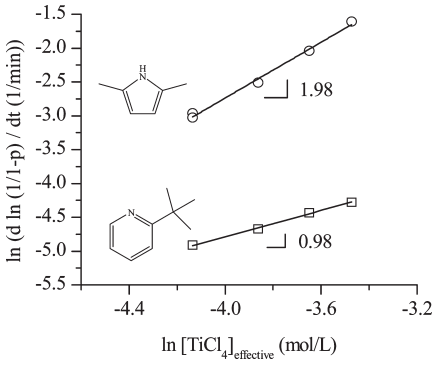


Figure 3. A ln−ln plot of the apparent rate constant for quenching vs $[TiCl_4]_{effective}$ for $TiCl_4$-catalyzed quasiliving PIB at −60 °C in 60/40 (v/v) hexane/methyl chloride, with $[PIBCl]_0$ = 0.001 M, [2,6-lutidine] = 0.005 M, and $[TiCl_4]_0$ = 0.025, 0.030, 0.035, and 0.040 M. 2TBP (□): $[Q]_0$ = 0.004, $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - [Q]_0$. 25DMP (○): $[Q]_0$ = 0.002 M and $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - 2[Q]_0$.

The effective $TiCl_4$ concentration is approximately $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - [Q]_0$, where $[TiCl_4]_0$ is the nominal $TiCl_4$ concentration charged to the reactor. Equation 5 predicts that the rate of quenching rises linearly at low $[Q]_0$, but a maximum will occur and the rate will eventually fall with increasing $[Q]_0$ (a parabolic dependence on $[Q]_0$). As more quencher is used, the rate initially increases due to higher amounts of free base; however, the rate is simultaneously retarded due to a decrease in available $TiCl_4$ due to complexation with the quencher. A maximum rate is predicted from the kinetic model at $[Q]_0 = ([TiCl_4]_0 - [2,6\text{-lutidine}])/2$. In Figure 2, the maximum should appear at $[Q]_0$ = 0.01 M, a value outside the experimental space; hence, the maximum is not observed. The rates of quenching with the piperidines in Figure 2 were faster than that with 2TBP, and this observation can be explained by higher free base concentration for the piperidines caused by increased steric hindrance around nitrogen that prevents complexation with $TiCl_4$. The fastest rates of proton abstraction, other than with 25DMP, were observed with the extremely hindered PMP. Figure 3 shows a plot of the first-order rate constant for quenching with 2TBP as a function of $[TiCl_4]_{effective}$. The slope of the plot indicates a first-order dependence on the effective concentration of $TiCl_4$ as predicted by eq 5.

For 25DMP in Figure 2 the rate of quenching for a given nominal concentration of quencher is fast compared with the other amines, and it is unlikely that such a relatively fast rate could be due to only a minute concentration of the free quencher available for proton abstraction. In fact, using a calculated value[9] for K_{eq} under these conditions of 5.5×10^{-8} M^{-2}, for the first few data points in Figure 2, eq 3 predicts a value of k_{-H} that is approximately at the diffusion limit even when [Q] is set to the nominal concentration of 25DMP charged. In addition, the maximum rate of proton abstraction for 25DMP in Figure 2 occurs at a lower $[Q]_0$ than predicted by eq 5, and as discussed later, ^{1}H NMR spectroscopy showed that reaction of 25DMP and $TiCl_4$ appears to be irreversible, in contrast to a reversible complexation with $TiCl_4$ that is typical of other amines. These observations indicate that interaction between $TiCl_4$ and 25DMP is not happening to the extent or in the manner outlined in Scheme 2. Instead, we propose that the reaction proceeds according to the mechanism shown in Scheme 3. Immediately upon introduction of 25DMP to the reaction, it reacts irreversibly with $TiCl_4$ to form a coordination complex. According to Veiros et al.,[10] the expected complex is the η^5-2,5-dimethylpyrrolyltrichlorotitanium(IV), Ti(η^5-25DMP)Cl_3, rather than the more energetic σN-coordination complex in which titanium is bonded directly to nitrogen. Formation of the complex releases 1 equiv of HCl, which is scavenged by 2,6-lutidine-$TiCl_4$ complex. When 2,6-lutidine is present in excess, complex formation is quantitative, driven by precipitation of the resulting onium salt. This process produces a brown precipitate, which is visible in the reactor. The bulky Ti(η^5-25DMP)Cl_3 complex abstracts a β-proton from the carbenium ion in a regiospecific manner to produce *exo*-olefin. 2,6-Lutidine is more basic than 25DMP (pK_a of 2,6-lutidine = 6.75,[11] pK_a of 25DMP = −0.71,[12] both measured in water) and is certainly expected to be more basic than the [Ti(η^5-25DMP)Cl_3] complex. Therefore, the protonated complex rapidly transfers the proton to 2,6-lutidine to regenerate the η^5-complex. Thus, under our conditions, the concentration of soluble Ti(η^5-25DMP)Cl_3 complex remains constant and is essentially equivalent to the nominal concentration of 25DMP charged to the reactor.

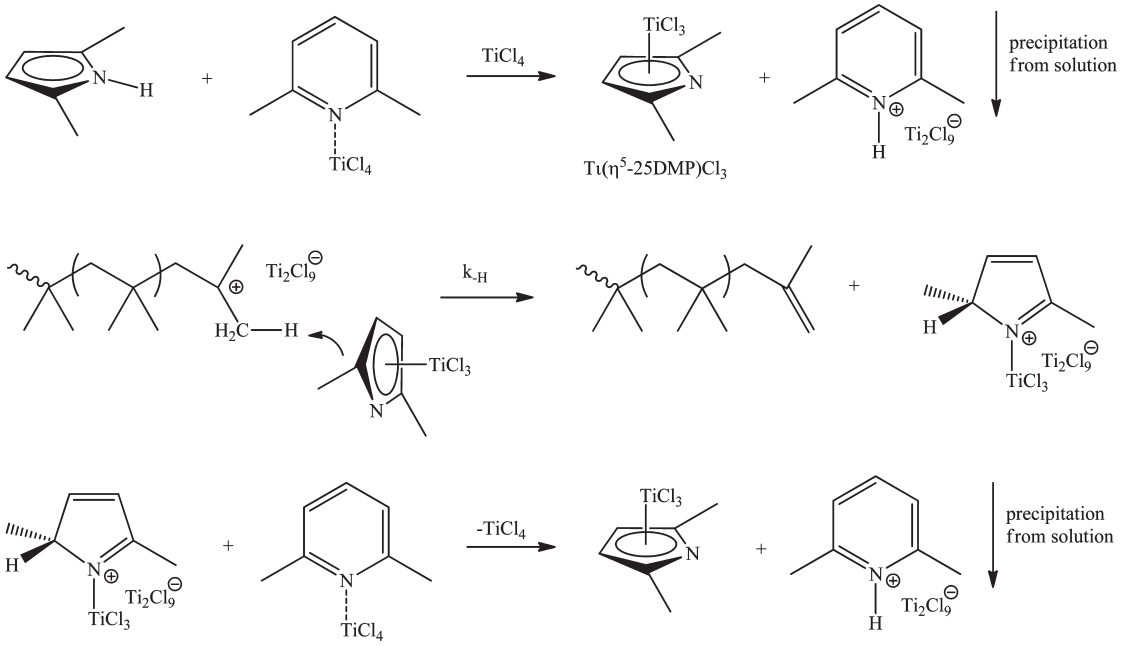
According to this mechanism, the correct form of eq 3 for 25DMP then becomes

$$\ln\left(\frac{1}{1-p}\right) = k_{-H}K_{eq}[TiCl_4]^2_{effective}[Q]_0 t \qquad (6)$$

where $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - 2[Q]_0$. The coefficient of 2 on $[Q]_0$ accounts for the fact that a net consumption of two molecules of $TiCl_4$ occurs for every Ti(η^5-25DMP)Cl_3 complex formed, when [2,6-lutidine] > $[Q]_0$. If the concentration of 25DMP exceeds that of 2,6-lutidine, the consumption of $TiCl_4$ is higher, and the rate will decrease even faster, as some fraction of 25DMP or Ti(η^5-25DMP)Cl_3 complex will precipitate from the reaction due to formation of onium salts. Again, a maximum rate is predicted by the model, but at a much lower $[Q]_0$, namely at $[Q]_0 = ([TiCl_4]_0 - [2,6\text{-lutidine}])/6$. In Figure 2, the maximum occurs at approximately $[Q]_0$ = 0.003 M as predicted from eq 6. The dependence of the rate on $[TiCl_4]_{effective}$ is illustrated in Figure 3 for the case of 25DMP, and the slope of approximately two indicates a second-order dependence on $[TiCl_4]_{effective}$, again, consistent with eq 6.

Direct spectroscopic evidence for the Ti(η^5-25DMP)Cl_3 complex was obtained by adding $TiCl_4$ to an approximately equimolar mixture of 25DMP and 2,6-lutidine in $CDCl_3$ at −60 °C. Upon addition of $TiCl_4$ to the mixture, precipitation of onium salts immediately occurred. Once the precipitate settled, an aliquot was taken, and the room temperature ^{1}H NMR spectrum of the aliquot was acquired (Figure 4B). The spectrum in Figure 4A is of the solution before addition of $TiCl_4$ and is included as a reference. Note that the solution also contained a small quantity of cyclohexane as an internal reference for ^{1}H NMR integration. In Figure 4B, the resonances due to the pyrrolyl moiety have an intensity approximately equal to that before addition of $TiCl_4$, indicating that the Ti(η^5-25DMP)Cl_3 complex remains in solution. The resonances have been shifted downfield from their original values at 2.22 and 5.75 ppm for 25DMP to 2.80 and 7.02 ppm for the Ti(η^5-25DMP)Cl_3 complex. This downfield shift would be expected from the deshielding effect of the $TiCl_3$ ligand. The resonances due to 2,6-lutidine are also shifted downfield from their original values at 2.52, 9.94, and 7.45 ppm, to 2.97, 7.67, and 8.35 ppm due to complexation

Scheme 3. Mechanism for β-Proton Abstraction from the PIB Carbenium Ion Chain End When Using 2,5-Disubstituted-*N*-hydropyrroles That Form Pyrrolyl-$TiCl_3$ Coordination Complexes



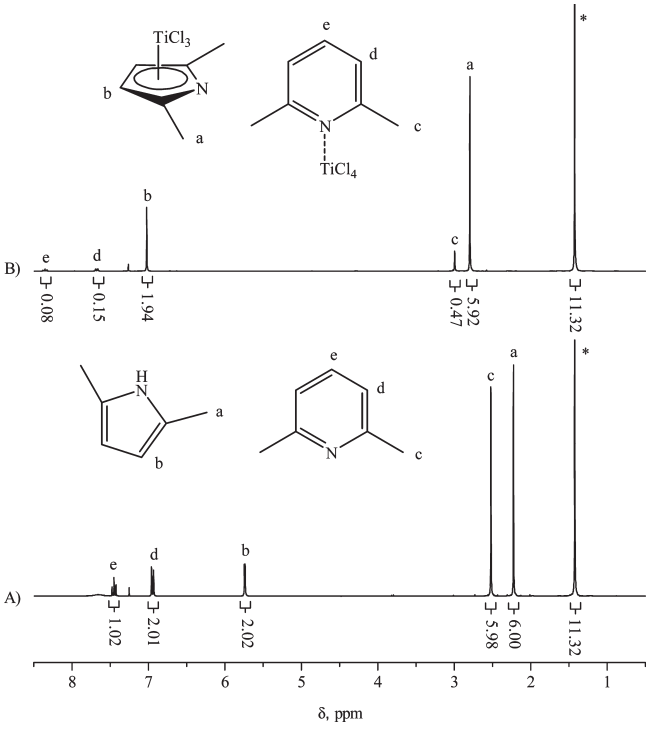


Figure 4. ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) of 25DMP and 2,6-lutidine (A) before and (B) after addition of excess $TiCl_4$ at −60 °C. Cyclohexane (∗) included as an internal reference.

with $TiCl_4$. However, the signal intensity for 2,6-lutidine has diminished significantly due to formation of onium salts that have precipitated from solution.

Ferreira da Silva et al.[13] have recently shown that ^{13}C NMR chemical shifts of the pyrrolyl ring carbons of Ti-pyrrolyl coordination complexes are a reliable indicator for distinguishing between the η^5 and σN coordination modes, and they have reported ^{1}H and ^{13}C NMR chemical shifts of the Ti(η^5-25DMP)Cl_3 complex in C_6D_6. The ^{13}C NMR spectrum of the sample of Figure 4B (Supporting Information, Figure A) exhibits resonances for the complex at 19.7 (s, CH_3), 126.6 (s, $C_{3,4}$), and 157.1 ppm (s, $C_{2,5}$). These values are in excellent agreement with the values reported by Ferreira da Silva et al. of 19.14, 126.56, and 157.15 ppm, and the large downfield shifts of 31.6 ($C_{2,5}$) and 20.3 ppm ($C_{3,4}$) relative to 25DMP indicate the η^5 coordination mode. However, the ^{1}H NMR chemical shifts of the complex in $CDCl_3$ (Figure 4B) did not match those of Ferreira da Silva et al., which were obtained in C_6D_6. We were confident that this difference was due to the NMR solvent; however, to address this point and eliminate any doubt as to the coordination mode of the complex formed in our system, we added $TiCl_4$ to an equimolar mixture of 25DMP and 2,6-lutidine in C_6D_6 at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded (see Supporting Information, Figures B and C), and the ^{1}H NMR chemical shifts that we observed, 5.92 (s, 2H, $H_{3,4}$) and 2.25 ppm (s, 6H, $CH_3-C_{2,5}$) were virtually identical to those reported by Ferreira da Silva et al. (5.87 and 2.23 ppm).

Additional support for the formation of the pyrrole−$TiCl_3$ η^5-complex and its activity as a quenching agent comes from the fact that 1,2,5-trimethylpyrrole proved ineffective as a quencher of $TiCl_4$-catalyzed isobutylene polymerizations;[14] this quencher returned only *tert*-chloride chain ends. With the *N*-methyl substituent present the η^5-complex cannot form; electrophilic aromatic substitution also does not occur apparently due to the methyl substituents at the C-2 and C-5 positions.[15] 2,3,4,5-Tetramethylpyrrole, which has the requisite replaceable hydrogen on nitrogen, and due to greater electron density in the ring is expected to form a titanium η^5-complex even more readily than 25DMP, was also shown to be a highly effective quencher, yielding exclusively *exo*-olefin chain ends.[14]

Quenching reactions involving 2,5-disubstituted-*N*-hydropyrroles, such as 25DMP or 2,3,4,5-tetramethylpyrrole, are able to proceed rapidly at low $[Q]_0/[TiCl_4]_0$ ratios because most or all of the pyrrole charged to the reaction, after reaction with $TiCl_4$, can actively abstract protons from the carbenium ion chain end. For strongly basic, sterically hindered amines, such as 2TBP, a dominant fraction of the base is complexed with $TiCl_4$ and therefore unavailable for reaction at the carbenium ion chain end. As shown previously,[1] the nominal concentration of hindered amine, especially for those that complex with $TiCl_4$ to the greatest extent, must be adjusted upward to reduce chain coupling. The rate of coupling (r_c) is proportional to the concentration of ionized chain ends as well as the concentration of *exo*-olefin chain ends [PIB=].

$$r_c = k_c K_{eq}[PIBCl][TiCl_4]^2[PIB{=}] \quad (7)$$

Taking the ratio of the rate of quenching (proton abstraction, r_{-H}) relative to the rate of coupling for sterically hindered amines involved in 1:1 complexation with $TiCl_4$

$$\frac{r_{-H}}{r_c} = \frac{k_{-H}}{k_c K_{com}} \frac{[Q]_0}{[TiCl_4][PIB{=}]} \quad (8)$$

it is evident that coupling can be minimized using lower chain end concentrations, lower $TiCl_4$ concentrations, and higher nominal quencher concentrations. It is noteworthy that the prediction that higher $[TiCl_4]$ leads to higher rates of coupling is supported by the results of Bae and Faust,[8] who observed precisely this behavior when they measured the rate of elimination by 2TBP as a function of $[TiCl_4]$.[16] To optimize the ratio r_{-H}/r_c at a given chain-end concentration, the ratio $[Q]_0/[TiCl_4]$ should be maximized, and this is most easily accomplished by an increase in $[Q]_0$, which will also lead to a decrease in $[TiCl_4]$ due to complexation. For amines such as 25DMP, the ratio of the rate of quenching to that of coupling is expressed differently:

$$\frac{r_{-H}}{r_c} = \frac{k_{-H}}{k_c} \frac{[Q]_0}{[PIB{=}]} \quad (9)$$

Equation 9 predicts that elimination of coupling is easier with 25DMP because the concentration of active quencher is not reduced by complexation with $TiCl_4$. However, eq 9 assumes that the entire concentration of 25DMP is present as the Ti(η^5-25DMP)Cl_3 complex, and maintaining this condition throughout the quenching reaction requires careful specification of the concentrations of Lewis acid and strong base, e.g., 2,6-lutidine, that serves as the eventual proton acceptor. Specifically, [2,6-lutidine] should be greater than the sum of $[PIBCl] + [Q]_0$, and $[TiCl_4]$ should be greater than the sum of [2,6-lutidine] + $[PIBCl] + 2[Q]_0$.

CONCLUSION

Using controlled kinetic experiments, we were able to demonstrate a fundamentally different mode of interaction of $TiCl_4$ with 2,5-disubstituted-*N*-hydropyrroles as compared to other sterically hindered amines during end-quenching of quasiliving isobutylene polymerizations. With strongly basic, sterically hindered tertiary and secondary amines, the mode of interaction is simple 1:1 complexation; however, with pyrroles such as 2,5-dimethylpyrrole or 2,3,4,5-tetramethylpyrrole, reaction occurs with $TiCl_4$ to form a Ti(η^5-pyrrolyl)Cl_3 coordination complex. The η^5-complex is capable of extracting β-protons from the PIB carbenium ion chain end, effectively producing *exo*-olefin-terminated PIB with rates faster than can be attained with other sterically hindered amines at low quencher/$TiCl_4$ ratios.

ASSOCIATED CONTENT

Supporting Information. ^{13}C NMR spectrum ($CDCl_3$, 22 °C) of Ti(η^5-25DMP)Cl_3 coordination complex obtained by adding $TiCl_4$ to an approximately equimolar mixture of 25DMP and 2,6-lutidine in $CDCl_3$ at −60 °C. ^1H and ^{13}C NMR spectra (C_6D_6, 22 °C) of Ti(η^5-25DMP)Cl_3 coordination complex obtained by adding $TiCl_4$ to an equimolar mixture of 25DMP and 2,6-lutidine in C_6D_6 at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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