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TiCl$_4$ Reaction Order in Living Isobutylene Polymerization at Low [TiCl$_4$]:[Chain End] Ratios

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ABSTRACT: Isobutylene (IB) polymerization kinetics at −80 °C were monitored in real time using mid-infrared ATR-FTIR spectroscopy, with diamond-composite insertion probe and light conduit technology. Monomer concentration as a function of time was obtained by monitoring the absorbance at 887 cm^{-1} associated with the $=CH_2$ wag of IB. Polymerizations were initiated using 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC) or 2-chloro-2,4,4-trimethylpentane (TMPCl) in conjunction with TiCl$_4$ co-initiator, in hexane/methyl chloride or methylcyclohexane/methyl chloride (60:40 v/v) cosolvents. Either 2,4-dimethylpyridine (DMP) or 2,6-di-*tert*-butylpyridine (DTBP) was used as an electron donor (ED). Reaction conditions were $[ED] = 2.00 \times 10^{-3}$ M, $[IB]_0 = 1.0$ M, and [TMPCl] (or 2[*t*-Bu-*m*-DCC]) $= 2.08 \times 10^{-2}$ M. Co-initiator concentrations were designed to be less than or equal to the growing chain end concentration and ranged from $[TiCl_4] = 7.20 \times 10^{-3}$ to 2.28×10^{-2} M. Steady-state polymerization kinetics were found to be independent of the nature of initiator, slightly faster when conducted with the noncomplexing DTBP rather than DMP and slightly faster when methylcyclohexane rather than hexane was utilized as the hydrocarbon diluent. In all cases, polymerizations exhibited a second-order dependence on the effective TiCl$_4$ concentration ($[TiCl_4]_{eff}$). The latter was defined in terms of the nominal amount of TiCl$_4$ added to the reactor minus the fraction calculated to be unavailable for co-initiation of the polymerization due to formation of a neutral complex with the ED and/or pyridinium salts as a result of proton scavenging. Second-order dependence on the effective TiCl$_4$ concentration was attributed to the predominance in the propagation reaction of active carbocations associated with dimeric counteranions of the form $Ti_2Cl_9^-$.

Introduction

Living carbocationic polymerization of isobutylene (IB) has been the subject of intense investigations by a number of research groups.[1−13] The vast majority of this work has been applied to systems using either TiCl$_4$ or BCl$_3$ co-initiators. For these particular Lewis acids, livingness is conferred by inherently low rates of chain transfer to monomer and β-proton elimination and the use of electron donor (ED) additives to suppress protic initiation (TiCl$_4$ systems) and/or participation of free ions in propagation (BCl$_3$ systems). For TiCl$_4$ systems in mixed hydrocarbon/chlorinated hydrocarbon solvents, livingness can be maintained to about 50−75 000 g/mol for a monofunctional initiator (100−150 000 g/mol for a difunctional initiator) at −80 °C. For BCl$_3$ systems, which must be run in chlorinated hydrocarbon solvents to achieve practical rates of polymerization, attainable molecular weights are typically not limited by the livingness of the system, but rather by the marginal solubility of higher molecular weight polyisobutylene (PIB) in the polymerization medium.

Living IB polymerizations are classified as quasi-living polymerizations,[14,15] meaning they are characterized by a rapid equilibrium between active and dormant chain ends. This ionization equilibrium strongly favors the dormant species, and thus only a small fraction of chains are ionized at any given time. Figure 1 depicts the overall stoichiometry of the equilibrium, where the average number of equivalents of TiCl$_4$ involved in ionization is denoted by *n*. Since the rate of propagation is proportional to the concentration of active species, it has been proposed[3,4] that the value of *n* will dictate the observed kinetic order of the propagation reaction with respect to the Lewis acid co-initiator. There is virtually unanimous agreement in the literature that both decreasing temperature and increasing [TiCl$_4$] shift this equilibrium toward the active state (thus increasing the rate of polymerization);[4,5,16−19] there is some disagreement, however, regarding the kinetic order of the propagation rate with respect to the Lewis acid. Under the most common reaction conditions, i.e., [TiCl$_4$] > the concentration of polymer chain ends (CE), a second-order dependence on the [TiCl$_4$] has been consistently reported in a number of papers by at least two different groups.[3−6] The sole contrary report under these reaction conditions is that of Kennedy and co-workers,[19] who claimed a first-order [TiCl$_4$] dependence. A polymerization mechanism (Figure 2) involving dimeric counterions of the type $Ti_2Cl_9^-$ has been advanced to account for the observed second-order dependency on [TiCl$_4$].[3,4] Figure 2 indicates that the formation of dimeric gegenions proceeds exclusively by reaction of monomeric gegenions with additional TiCl$_4$ (as opposed to direct ionization by Ti_2Cl_8)[4] and that propagation can theoretically occur through chains carrying either monomeric or dimeric gegenions, or both. However, the experimental observation of a second-order dependency on [TiCl$_4$] suggests that propagation via monomeric gegenions is insignificant.

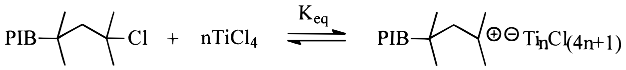

Figure 1. PIB ionization equilibrium stoichiometry.

The more serious controversy over TiCl$_4$ reaction order has centered around polymerizations in which [TiCl$_4$] ≤ [CE]. As a practical matter, these conditions make data interpretation difficult since they dictate the

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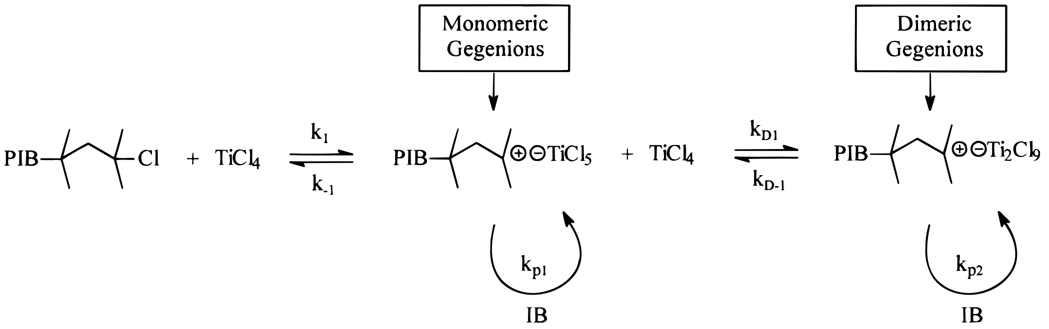

Figure 2. Proposed mechanism for propagation in $TiCl_4$-co-initiated polymerization of isobutylene.

use of relatively low $[TiCl_4]$. Thus, losses of $TiCl_4$, through avenues related to the proton scavenging function of EDs, become significant as a fraction of the total $[TiCl_4]$, and therefore, the actual $[TiCl_4]$ is known with less certainty. Under these conditions Kaszas and Puskas[20] reported a first-order dependence on $[TiCl_4]$ for IB polymerizations at −90 °C; this work has been recently revisited by Puskas and Lanzendörfer,[21] and essentially the same conclusions were reached for polymerizations at −80 °C. It was proposed that a "shortage" of $TiCl_4$ forces propagation to proceed through a mechanism that involves gegenions of the form $TiCl_5^-$ rather than $Ti_2Cl_9^-$. As these findings are of significant importance to the complete elucidation of the mechanism of the living polymerization of isobutylene, we decided to also examine this unique range of $[TiCl_4]$:[CE] ratios. However, our initial investigations[7] under similar conditions were unable to reproduce the results of Puskas et al. Therefore, in this paper we report a more comprehensive investigation of polymerizations conducted under these reaction conditions.

Experimental Section

Materials. $TiCl_4$ was obtained from Aldrich Chemical Co. (99.9%, packaged under nitrogen in SureSeal bottles) and used without further purification. The source and preparation of all other reagents have been previously reported.[4]

Instrumentation. Molecular weights and molecular weight distributions were determined using a gel permeation chromatography (GPC) system equipped with a Wyatt Technology miniDAWN on-line MALLS detector, as previously described.[22] A ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT) was used to collect infrared spectra of the polymerization components and monitor reactor temperature in real time as previously described.[23]

Procedures. Polymerizations were carried out under dry nitrogen gas in a MBraun Labmaster 130 glovebox (M. Braun, Newburyport, MA), equipped with an integral heptane bath cooled by both a FTS RC210 recirculating chiller (FTS Systems, Stone Ridge, NY) and liquid nitrogen, the latter regulated by a CN76000 series temperature controller (Omega Engineering, Stamford, CT). A representative polymerization procedure was as follows: the DiComp probe was inserted into a stainless steel scabbard and was allowed to equilibrate in the −80 °C heptane bath prior to acquisition of a background spectrum (1024 scans, 4 or 8 cm^{-1} resolution). From this point forward, the probe remained stationary. The heptane bath was partially drained, the scabbard was removed, and a 250 mL four-neck round-bottom flask was fitted around the probe. The bath was then raised and allowed to return to −80 °C. To the chilled flask, equipped additionally with a mechanical stirrer and RTD, were added sequentially 110.5 mL of hexane, 73.7 mL of MeCl, 4.16×10^{-3} mol (0.6184 g) of TMPCl, and 4.0×10^{-4} mol (46.2 μL) of 2,4-DMP. The reaction mixture was stirred until the solution reached thermal equilibrium as indicated by the RTD and was stirred for an additional 10 min. Subsequently, 0.20 mol (15.8 mL) of chilled IB (−80 °C) was added to the reaction mixture and allowed to reach thermal equilibrium. After the reaction was stirred for an additional 10 min, 4.56×10^{-3} mol (0.500 mL) of $TiCl_4$ (neat and at room temperature) was rapidly injected into the reactor.

The standard acquisition mode of the ReactIR 1000 was used to collect IR spectra for both the premixing and reaction periods. Each spectrum was the Fourier transformation of either 64 or 128 acquisitions collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}, within a time period of less than 60 s, with an instrument resolution of 4 or 8 cm^{-1}, respectively. Reaction conversion was determined by monitoring the $=CH_2$ wag at 887 cm^{-1} as previously described[23] with one modification: the peak area at extremely long reaction times (approximately 100% conversion) was used as the absorbance value for [IB] = 0.0 M. The use of this value for [IB] = 0.0 M accounts for the decrease in the strength of the solvent signal when it is diluted by the addition of monomer.

Results and Discussion

The kinetics of $TiCl_4$-co-initiated polymerizations of IB were studied to determine the reaction order with respect to the co-initiator at low $[TiCl_4]$:[CE] ratios. As described in detail previously,[4] such analyses can yield information concerning the mechanism of propagation. Specifically, it can provide strong evidence regarding the nature of the counterion, i.e., $TiCl_5^-$ or $Ti_2Cl_9^-$, which is associated with the propagating carbocation as shown in Figure 2. Propagation predominantly by chain ends carrying monomeric counterions would be expected to yield unit kinetic order with respect to $[TiCl_4]$; conversely, predominance of dimeric counterions would result in kinetic orders of approximately two.

Previous investigations of IB polymerization kinetics have relied upon gravimetric measurements of polymer yield.[2−6,9,10,16,19−21,22,24,25] Unfortunately, it is quite difficult to obtain accurate data with this method for polymerizations that have low target degrees of polymerization (X_n), occur on short time scales, or utilize monomers that are difficult to remove from the final polymer (e.g., styrene). Because of these limitations, both Puskas et al.[21,26] and Storey et al.[23,24,27−30] have devoted significant effort to the development of real-time in-situ attenuated total reflectance (ATR)-FTIR spectroscopic monitoring for IB and styrene polymerizations. This direct method for monitoring [IB] provides the speed and sensitivity required to monitor polymerizations that exceed the limits of traditional gravimetry. Since the subject polymerization recipes have low target X_n's, the monomer concentration was measured in real time using this newly developed spectroscopic technique. The initial monomer concentration (1.0 M), cosolvent composition (hydrocarbon/MeCl 60/40, v/v), ED concentration (2.0×10^{-3} M), chain end concentration ([CE] = [TMPCl] = 2[*t*-Bu-*m*-DCC] = 2.08×10^{-2} M), and reaction volume (200 mL) were held constant in all cases, and $TiCl_4$ was the final component added.

The data were treated using the kinetic expression for a quasi-living polymerization with fast initiation, characterized by a rapid equilibrium between a small fraction of ionized chains and a large population of dormant species,

$$r_p = -\frac{d[M]}{dt} = k_p[R^+][M] = k_pK_{eq}[CE][TiCl_4]^n[M] \tag{1}$$

where r_p is the rate of propagation, k_p is the second-order rate constant for propagation, $[R^+]$ is the instantaneous concentration of active species, and [M] is the monomer concentration. Through the ionization equilibrium in Figure 1, $[R^+] = K_{eq}[CE][TiCl_4]^n$ (for small K_{eq}), where [CE] is the total concentration of chain ends ([CE] = [TMPCl] = 2[*t*-Bu-*m*-DCC]) and n is number of equivalents of $TiCl_4$ involved in the ionization equilibrium. Integration of eq 1 yields the following relationship in which k_{app} is the apparent rate constant for propagation:

$$\ln\frac{[M]_0}{[M]} = k_pK_{eq}[CE][TiCl_4]^n t = k_{app}t \tag{2}$$

Polymerization data were plotted in the form of eq 2 to determine k_{app} for each reaction. Linearity of these first-order kinetic plots is indicative of the absence of absolute termination (the number of growing chains remains constant).

Four series of polymerizations were performed to permit comparison of three different reaction variables: type of initiator (i.e., aromatic vs aliphatic), type of ED (i.e., complexing vs noncomplexing), and identity of hydrocarbon diluent. The first series of experiments was designated the control series and employed an aromatic initiator (*t*-Bu-*m*-DCC), a complexing ED (DMP), and hexane as the hydrocarbon diluent. The second series utilized an aliphatic initiator (TMPCl) in lieu of the aromatic initiator; the third substituted a noncomplexing ED (DTBP) for DMP, and the final series employed methylcyclohexane (MCHex) as the hydrocarbon diluent instead of hexane.

First-Order Kinetic Analysis. For each series, five polymerizations were performed over a range of $TiCl_4$ concentrations while holding the concentration of all other reaction components constant. For each polymerization, real-time FTIR data were collected, from which k_{app} was calculated. When essentially complete monomer conversion had been reached according to the ReactIR, each reaction was quenched with methanol, and the polymer product was subjected to GPC analysis. Reaction conditions, k_{app}'s, number-average molecular weights and polydispersities (MALLS detection), and calculated initiation efficiencies, I_{eff}, are listed in Table 1. In all cases, molecular weights were very close to theoretical, and I_{eff} was nearly 100%.

Table 1. Apparent Rate Constants and Final Polymer Molecular Weights and Polydispersities for Isobutylene Polymerizations[a]

polymerization series	$[TiCl_4]$ $\times 10^3$ M	k_{app} $\times 10^4$ s^{-1}	M_n (PDI)	I_{eff} (%)
control	22.8	16	5950 (1.02)	96
	17.6	9.3	5590 (1.03)	102
	12.4	3.7	6070 (1.04)	94
	9.35	1.1	6020 (1.08)	94
	7.20	0.38	5720 (1.08)	99
aliphatic initiator[b]	22.8	15	2980 (1.16)	96
	17.6	9.2	2960 (1.16)	96
	12.4	3.7	2890 (1.17)	98
	9.35	1.2	3060 (1.15)	93
	7.20	0.32	2820 (1.20)	101
noncomplexing ED[c]	22.8	19		
	17.6	12		
	12.4	4.3		
	9.35	1.8		
	7.20	0.78		
MCHex cosolvent[d]	22.8	23	5860 (1.13)	97
	17.6	12	6000 (1.10)	95
	12.4	4.1	5850 (1.12)	97
	9.35	1.9	5700 (1.08)	100
	7.20	0.49	5710 (1.12)	100

[a] All polymerizations were performed at −80 °C, [CE] = 2.08×10^{-2} M, [ED] = 2.0×10^{-3} M, $[IB]_0$ = 1.0 M, and 60/40 hydrocarbon/MeCl cosolvents (v/v) and utilized *t*-Bu-*m*-DCC as initiator, DMP as the electron donor, and hexane as the hydrocarbon diluent except where noted. [b] TMPCl was used in lieu of *t*-Bu-*m*-DCC. [c] DTPB was used in lieu of DMP. [d] MeCHex was used in lieu of hexane.

Inspection of the apparent rate constants reveals that the nature of the initiator (aromatic vs aliphatic) has no effect on the apparent rate of polymerization once a steady-state concentration of growing species has been reached; the k_{app}'s for the control and aliphatic initiator series of polymerizations are essentially equivalent. The use of the noncomplexing DTBP in lieu of DMP results in faster polymerizations; there is a greater amount of free $TiCl_4$ in the polymerization medium to participate in propagation reactions (no $TiCl_4$ is bound to free ED). The magnitude of this effect increases as $[TiCl_4]_0$/[ED] decreases. It also may be noted that polymerizations are slightly faster when methylcyclohexane is used as the hydrocarbon diluent instead of hexane (all five runs displayed this trend, with acceleration ranging from 11 to 71%). Storey and Brister[24] have also found, via gravimetric techniques, that polymerizations utilizing MCHex as the hydrocarbon diluent are slightly faster (≈17%). These results are in direct contrast to the findings of Puskas and Lanzendörfer,[21] who found that polymerizations using hexane were nearly an order of magnitude faster (600−700%).

First-order plots for the control, aliphatic initiator, noncomplexing ED, and MCHex cosolvent series are shown in Figures 3−6, respectively. All of the first-order plots are linear to very high conversion, which indicates that the rate of absolute termination is below the limit of detection under these conditions.

Two interesting observations may be made from careful study of the first-order plots. First, the aliphatic initiator TMPCl is slightly sluggish; propagation occurs simultaneously with initiation. This is manifest in the slight upward curvature of the first-order plots at low conversion. Additionally, it may be noted that while the first-order plots shown in Figure 4 (aliphatic initiator) pass through the origin, the remaining figures (aromatic initiator) all exhibit positive *y*-intercepts. These positive *y*-intercepts are the result of a faster rate of monomer consumption in the initial stage of polymerization. It is believed that this initially high rate is due to a higher ionization equilibrium for the *tert*-benzylic chloride initiator. Figure 7 directly compares, under the same experimental conditions, the behavior of *t*-Bu-*m*-DCC- and TMPCl-initiated polymerizations during the early stages of reaction; a positive *y*-intercept is clearly

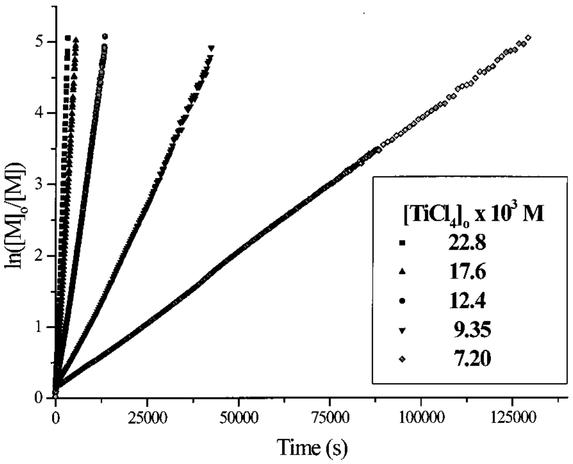

Figure 3. ln $[M]_0/[M]$ vs time plots for IB polymerizations (control series). $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C.

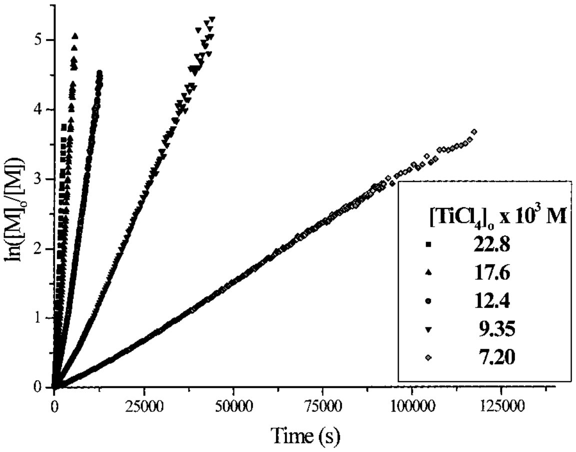

Figure 4. ln $[M]_0/[M]$ vs time plots for IB polymerizations (aliphatic initiator series). $[IB]_0 = 1.0$ M; [TMPCl] $= 2.08 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C.

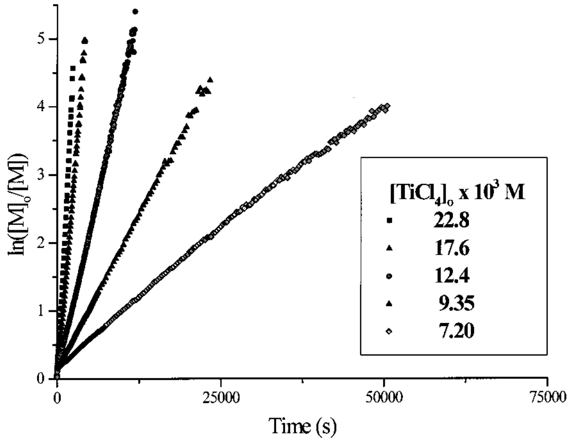

Figure 5. ln $[M]_0/[M]$ vs time plots for IB polymerizations (noncomplexing ED series). $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DTBP] $= 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C.

observed for the aromatic initiator but not for the aliphatic initiator. The inset to Figure 7 shows the same two first-order plots over a broader range of times; here the slight, gradual upward curvature due to slow initiation can be observed for the aliphatic but not the aromatic initiator. A more complete and detailed analysis of both of these phenomena is the subject of a separate line of investigation.[27]

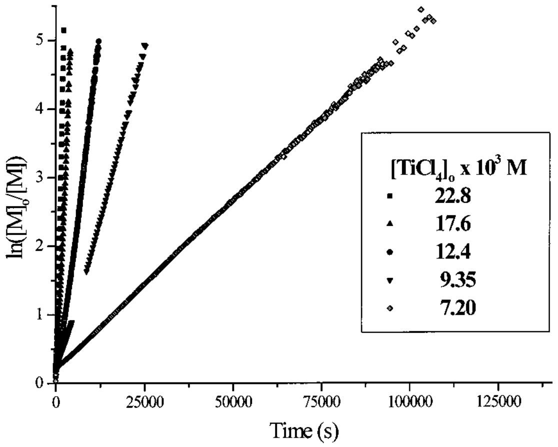

Figure 6. ln $[M]_0/[M]$ vs time plots for IB polymerizations (MCHex cosolvent series). $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 methylcyclohexane/MeCl cosolvents (v/v); −80 °C.

***N*th-Order Kinetic Analysis.** The kinetic order of the polymerization reaction with respect to $TiCl_4$ may be determined by plotting $\ln(k_{app})$ vs $\ln[TiCl_4]_0$, as depicted for the control series of polymerizations in Figure 8. The kinetic order, as determined by linear regression (slope), was 3.25. This value is larger than any reported in the literature,[3−6,19−21] and it suggests an error associated with the underlying values for $[TiCl_4]$.

The error is easily understood when the presence of the Lewis base (ED) is considered. $TiCl_4$ participates in at least two other reactions in addition to propagation: (1) reaction with protic impurities (HA) to form Bronstead acids, which in turn form onium salts with the Lewis base (ED), and (2) complexation with the Lewis base. Because of these two side reactions, the use of the nominal $TiCl_4$ concentration, $[TiCl_4]_0$, in the kinetic expression for polymerization is invalid. A quantity, which represents the amount of free $TiCl_4$ in the polymerization mixture available to co-initiate polymerization, was defined by Storey and Choate.[4] This quantity, termed the effective $TiCl_4$ concentration, assumed quantitative formation of a 1:1 $TiCl_4$:ED complex and the formation of onium salts of the form $EDH^+TiCl_4OH^-$. It was defined as $[TiCl_4]_{eff} = [TiCl_4]_0 -$ [complex] − [onium salts]. Since polymerization reactions are designed such that [ED] > [HA], then [ED] = [complex] + [onium salts], and this expression was more simply expressed as $[TiCl_4]_{eff} = [TiCl_4]_0 - [ED]$. However, Storey and Choate did note that if the negative ions of the onium salt consisted of $TiCl_5^-$, $Ti_2Cl_8OH^-$, $Ti_2Cl_9^-$, or some combination thereof, the aforementioned quantity would be an overestimation of the amount of free $TiCl_4$ available to co-initiate polymerization.

Figure 8 also depicts the *N*th-order analysis for the control series based on $[TiCl_4]_{eff}$. The reaction order based upon this analysis was 2.72, which is still considerably larger than the expected second order. It is believed that this large value is the result of the overestimation of $[TiCl_4]_{eff}$. The fact that the plots in Figure 8 are curved with higher slope at lower $[TiCl_4]$ corroborates our hypothesis that mechanisms for $TiCl_4$ depletion exist, which become relatively more significant as $[TiCl_4]_0$ is diminished. Figure 9 represents some of

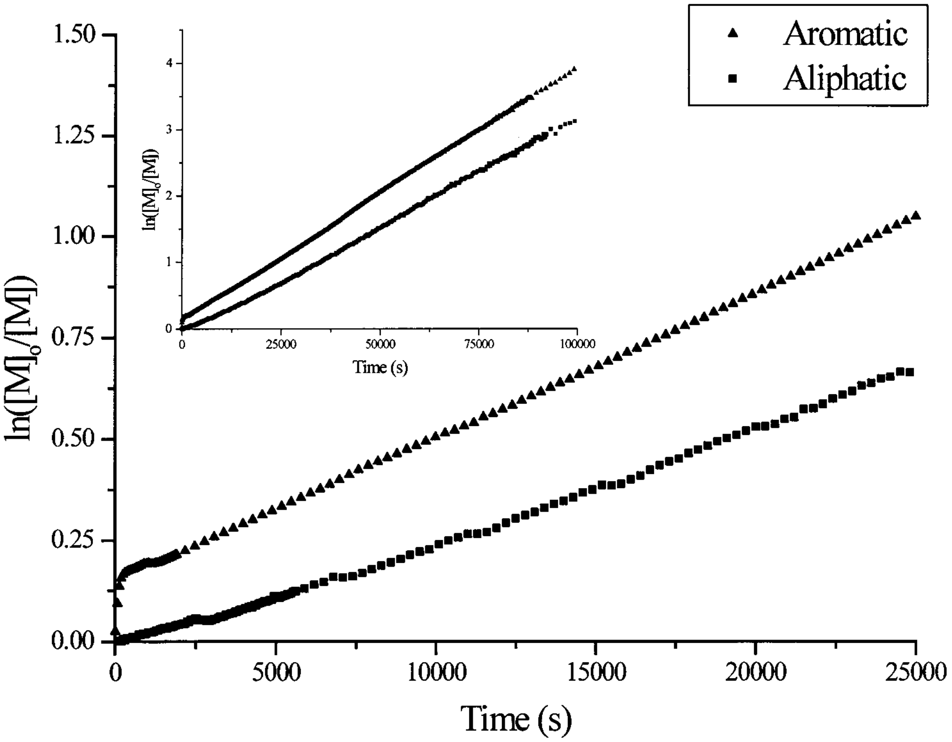

Figure 7. First-order plot for *t*-Bu-*m*-DCC- and TMPCl-initiated isobutylene polymerizations. $[IB]_0 = 1.0$ M; [TMPCl] = 2[*t*-Bu-*m*-DCC] $= 2.08 \times 10^{-2}$ M; $[TiCl_4] = 7.20 \times 10^{-3}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C. Inset shows an extension of the same data set to longer times.

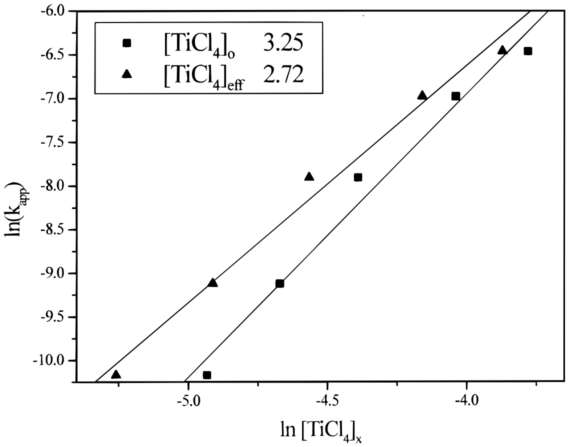

Figure 8. Reaction order of $[TiCl_4]_0$ and $[TiCl_4]_{eff}$ for IB polymerizations (control series). $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C.

the possible pathways for depletion of $TiCl_4$. As it has been shown that neutral dimers of $TiCl_4$ only form under extreme cryogenic conditions (12 K)[31] and/or at high concentration (25 mol % $TiCl_4$ in CCl_4 at 300 K),[32] it seems unlikely that dimeric complexes would form with the ED. However, it seems quite plausible that the negative ions of the onium salts would have counterions of the type $Ti_2Cl_8OH^-$. Storey and Choate demonstrated that the second-order dependence observed under routine living IB polymerization conditions (i.e., $[TiCl_4] \gg [I]_0$) may only be explained by the reaction of additional $TiCl_4$ with monomeric counterions ($TiCl_5^-$).[4] It seems reasonable that a similar reaction would occur in the formation of onium salts. If $[TiCl_4]_0 \gg$ [ED], the error introduced by failing to account for these side reactions is quite small. It is for this reason that reaction orders of 2 are routinely determined without consideration of

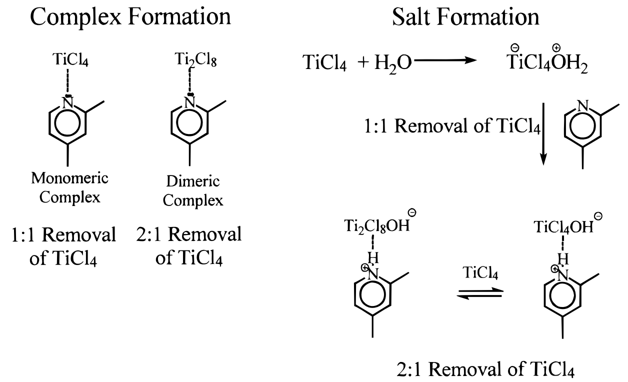

Figure 9. Possible side reactions of $TiCl_4$ with EDs.

dimeric negative ions in formed onium salts. Similarly, if [ED] $\gg$ [HA], the error introduced by assuming the formation of monomeric salts is also negligible (if the complexes are indeed 1:1). However, the concentration of ED used in this system, 2.0×10^{-3} M, is believed to be very close to the concentration of protic impurities in the polymerization medium;[25] thus, the predominant side reaction is the formation of onium salts. If the negative counterions are indeed of the form $Ti_2Cl_8OH^-$, or $Ti_2Cl_9^-$, then $[TiCl_4]_{eff}$ is dramatically underestimated. As such, the effective $TiCl_4$ concentration must be redefined as $[TiCl_4]_{eff} = [TiCl_4]_0 -$ [complex] $-$ 2[onium salts]. If we make the simplifying assumption that [ED] = [HA], the expression for the effective $TiCl_4$ simplifies to the following: $[TiCl_4]_{eff} = [TiCl_4]_0 - 2[ED]$.

In reality, [ED] is slightly greater than [HA]; however, we are perfectly willing to make the aforementioned assumption because we recognize that onium salts actually consume more than 2 equiv of $TiCl_4$. This is because the reaction of $TiCl_4$ with protic impurities is much more complex than the simple analysis shown in

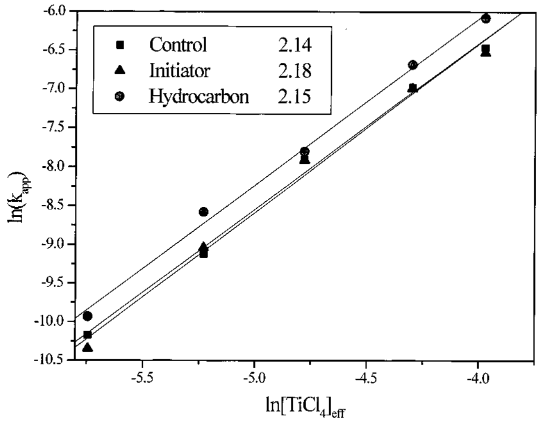

Figure 10. Reaction order of $[TiCl_4]_{eff}$ for IB polymerizations. $[IB]_0 = 1.0$ M; $[CE] = 2.08 \times 10^{-2}$ M; $[ED] = 2.0 \times 10^{-3}$ M; 60/40 hydrocarbon/MeCl cosolvents (v/v); −80 °C. Control series: *t*-Bu-*m*-DCC initiator, DMP, hexane cosolvent. Aliphatic initiator series: TMPCl initiator, DMP, hexane cosolvent. Hydrocarbon cosolvent series: *t*-Bu-*m*-DCC initiator, DMP, methylcyclohexane cosolvent.

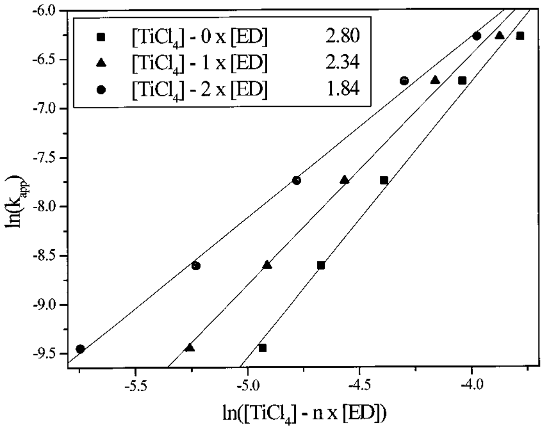

Figure 11. Reaction order of ($[TiCl_4]_0 - n[ED]$) for IB polymerizations (noncomplexing ED series), where $n = 0$, 1, 2. $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}] = 1.04 \times 10^{-2}$ M; $[DTBP] = 2.0 \times 10^{-3}$ M; 60/40 hexane/MeCl cosolvents (v/v); −80 °C.

Figure 9. Additional reactions such as ligand exchange also likely occur. For example, the salt $EDH^+Ti_2Cl_8OH^-$ could ligand exchange to yield $EDH^+Ti_2Cl_9^-$ and $TiCl_3OH$. This exchange reaction would produce a Lewis acid, $TiCl_3OH$, which is considerably less reactive than $TiCl_4$, thus further decreasing the amount of free $TiCl_4$ available to co-initiate polymerization. As these side reactions do occur, the factor 2 is an underestimation of the amount of $TiCl_4$ that is consumed in the formation of onium salts. This underestimation is offset to a certain degree by the ED which does not participate in the formation of onium salts; the remaining ED forms a complex with $TiCl_4$, which depletes only 1 equiv per ED.

As seen in Figure 10, the application of the newly defined $[TiCl_4]_{eff}$ results in a kinetic dependence of 2.14 for the control system, which is very close to second-order dependence. Figure 10 also depicts the same analysis for the initiator series (2.18) and the hydrocarbon solvent series (2.15), both of which are in good agreement with a propagation mechanism based upon $Ti_2Cl_9^-$ gegenions. The fact that each of the kinetic orders is larger than two is strong evidence that there are indeed additional mechanisms of $TiCl_4$ depletion in operation.

The final reaction series utilized the noncomplexing proton trap DTBP in lieu of the complexing DMP. Figure 11 shows the *N*th-order kinetic plots based upon each of the three types of analyses: $[TiCl_4]_0 - 0[ED]$, $[TiCl_4]_0 - 1[ED]$, and $[TiCl_4]_0 - 2[ED]$. DTBP is believed to be a noncomplexing proton trap due to the presence of the extremely bulky *tert*-butyl substituents.[3] As such, the sole side reaction that diminishes the amount of free $TiCl_4$ in the polymerization system is the formation of onium salts; i.e., the defining relationship, $[ED] = [complex] + [onium\ salts]$, is no longer valid; there is no complex formed. The unreacted ED remains free in solution, consuming no additional $TiCl_4$, rather than depleting 1 equiv of $TiCl_4$ through the formation of a complex. As can be seen in Figure 11, a reaction order slightly less than two (1.84) is obtained from *N*th-order kinetic analysis based upon the redefined $[TiCl_4]_{eff}$. While this value is in good agreement with the expected second-order dependence, it is not surprising that it is less than two. Since DTBP is noncomplexing, simplifying the defining relationship $[TiCl_4]_{eff} = [TiCl_4]_0 - [complex] - 2[onium\ salts]$ to $[TiCl_4]_{eff} = [TiCl_4]_0 - 2[ED]$ is clearly a slight underestimation of $[TiCl_4]_{eff}$. This is so because there exists a finite concentration excess of ED over HA, which causes the earlier assumption (i.e., $[ED] = [HA]$) to introduce greater error. Because of this underestimation, the calculated reaction order is similarly depressed.

Comparison to Literature Data. Having consistently obtained kinetic orders of approximately two for $TiCl_4$, under a wide range of experimental conditions, we sought to identify possible reasons for the unit orders reported by Puskas et al.,[20,21] for the regime $[TiCl_4] \leq [CE]$. The only significant difference between the conditions reported herein and those of the latter authors is overall system dilution (1 M vs 2 M IB); the relative concentrations of all reagents are similar. Higher [IB] causes a small decrease in system polarity (66 vs 63 vol % total hydrocarbon), but this is too small to cause such a profound difference. The data of Puskas et al. were acquired through gravimetric analysis, and the data set is small. The earlier analysis[20] was based upon three polymerizations; in the recent work,[21] the authors based the calculation of $TiCl_4$ reaction order in MCHex on two polymerizations only. Further progress toward reconciliation of these conflicting results will require more data and a better understanding of the complex mechanisms of $TiCl_4$ depletion associated with the presence of EDs.

Conclusions

The kinetics of the controlled/living polymerization of isobutylene were studied for $[TiCl_4] \leq [CE]$ utilizing real-time in-situ ATR-FTIR spectroscopy. All polymerizations were performed under conditions where $[ED] \approx [H_2O]$ and $[TiCl_4]$ is on the order of [ED]. By operating in this regime, it is possible to observe dramatic changes in the k_{app}'s due to side reactions of the $TiCl_4$ with the ED and HA. The complexity of these side reactions is made quite apparent from the *N*th-order kinetic analyses. When one accounts for $TiCl_4$-depletion mechanisms related to proton scavenging by the ED, namely the formation of onium salts with counterions of the form $Ti_2Cl_8OH^-$ or $Ti_2Cl_9^-$, reaction orders of approximately 2 are consistently obtained. This provides strong evidence that propagation proceeds through cations that are paired with counterions of the type $Ti_2Cl_9^-$. These results are contradictory to those of Puskas et al.,[20,21] who report kinetic orders near 1 under similar conditions. However, their data set is quite limited and was determined by gravimetry, which is very difficult to perform accurately under these conditions.

While the nature of the initiating species does not appear to affect k_{app}, TMPCl is slightly slowly initiating, whereas *t*-Bu-*m*-DCC exhibits a region of extremely fast monomer consumption at the onset of polymerization. It is believed that this increased rate behavior is due to a higher ionization equilibrium for the *tert*-benzylic chloride initiator.

Although the data set is limited, polymerizations affected using MCHex as the hydrocarbon diluent appeared to be slightly faster than those that utilize Hex as the diluent. In addition, when the noncomplexing DTBP was used in lieu of DMP, polymerizations were consistently faster. There is a greater quantity of free $TiCl_4$ available to participate in propagation reactions, since there is no $TiCl_4$ bound to the excess free ED. The difference in rate between DTBP and DMP became more pronounced as $[TiCl_4]$ decreased; the fractional difference in the amount of free $TiCl_4$ in the polymerization medium is greater at lower Lewis acid concentrations.

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