Notes

Effect of Reaction Conditions on Apparent $TiCl_4$ Reaction Order in Quasiliving Isobutylene Polymerization at High [Initiator]/[$TiCl_4$] Ratios

Quinn A. Thomas and Robson F. Storey*

The University of Southern Mississippi, School of Polymers and High Performance Materials, Box 10076, Hattiesburg, Mississippi 39406

Received May 30, 2003

Revised Manuscript Received August 29, 2003

Introduction

The kinetic and mechanistic study of quasiliving carbocationic polymerization of isobutylene (IB) continues to be the focus of research in many groups.[1−6] The term quasiliving[7,8] denotes that the growing chain ends exist in equilibrium between dormant (nonpropagating) covalent species (*tert*-alkyl chloride, R−Cl) and actively propagating ion pairs ($R^{+\,-}Ti_nCl_{4n+1}$), as illustrated in eq 1 for systems in which $TiCl_4$ is the Lewis acid co-initiator. Control in quasiliving IB polymerizations is gained by the addition of Lewis bases (LB) and/or proton traps, typically pyridine derivatives, that eliminate initiation by protic contaminants[9] and suppress free ion propagation via the common ion effect.[3,10] These actions yield polyisobutylenes (PIB) with predictable molecular weights (MWs) and narrow molecular weight distributions (MWDs).

$$R{-}Cl + nTiCl_4 \underset{}{\overset{K_{eq}}{\rightleftharpoons}} R^{+\,-}Ti_nCl_{4n+1} \qquad (1)$$

This paper is focused upon the propagation reaction order with respect to Lewis acid co-initiator for IB polymerizations co-initiated with $TiCl_4$. We seek to define the value of n in eq 1, the number of equivalents of $TiCl_4$ involved in chain end ionization. Our motivation arises from a continuing controversy over this issue in the literature. Most researchers agree that under most conditions n assumes a value of 2;[2,5,9,11−14] however, Puskas et al. have consistently reported a value of unity for systems where $[I]_0 > [TiCl_4]$.[1,15−17] The value of n is determined experimentally using the kinetic model for cationic chain polymerization, eq 2, where k_p is the absolute, second-order rate constant of propagation, $[R^{+\,-}Ti_nCl_{4n+1}]$ is the concentration of active species for a polymerization co-initiated by $TiCl_4$, and [M] is monomer concentration. The apparent first-order rate constant of propagation, k_{app}, can be redefined in terms of the equilibrium constituents in eq 1, according to eq 3, and the value of n will determine the kinetic order of propagation with respect to $TiCl_4$ co-initiator.

$$\text{rate} = -\frac{d[M]}{dt} = k_p[R^{+\,-}Ti_nCl_{4n+1}][M] = k_{app}[M] \qquad (2)$$

$$k_{app} = k_pK_{eq}[R{-}Cl][TiCl_4]^n \qquad (3)$$

The observation of a kinetic order for $TiCl_4$ of 2 has been ascribed to the predominance in propagation of cations possessing dimeric counterions, i.e., ion pairs of the structure $R^{+\,-}Ti_2Cl_9$, and is consistent with the known tendency of halogenated titanium compounds to form dimers,[18−20] as shown in eqs 4 and 5. It is significant that studies reporting propagation reaction order with respect to BCl_3 co-initiator, which does not form dimers, universally agree that the order is unity.[6,21,22]

$$2TiCl_4 \overset{K_{D0}}{\rightleftharpoons} Ti_2Cl_8 \qquad (4)$$

$$TiCl_5^- + TiCl_4 \overset{K_{D1}}{\rightleftharpoons} Ti_2Cl_9^- \qquad (5)$$

Equations 4 and 5 suggest two possible ways to arrive at dimeric counterions. Storey and Choate[13] performed an analysis of these two pathways and concluded that K_{D0} must be small and consequently that $[TiCl_4] \gg [Ti_2Cl_8]$, and dimerization must occur through reaction of a monomeric counterion with $TiCl_4$. However, recent studies have shown that the addition of IB[5,23] and styrene[11,24] to active chain ends is at or near the diffusion limit, $k_{p(IB)} \sim 7 \times 10^8$ and $k_{p(S)} \sim (1.5{-}3) \times 10^9$ M^{-1} s^{-1}, respectively. Since addition of a second molecule of $TiCl_4$ after ionization of the chain end can be at most diffusion-controlled, one would expect significant propagation by active chains carrying monomeric counterions, and the order with respect to $TiCl_4$ would be depressed toward one. However, second-order dependence is generally observed, and the conclusion was made that chain ionization must involve neutral Ti_2Cl_8.[5] This conclusion is consistent with the fact that Ti_2Cl_8 is a stronger Lewis acid than $TiCl_4$,[25] and it is further supported by molecular modeling studies of $TiCl_4$ and Ti_2Cl_8, which found the weakly bound van der Waals dimer to be lower in energy than the monomer and a negative free energy of dimerization at low temperatures.[26]

Puskas et al.[1,15] have proposed a mechanism to account for shifting orders in $TiCl_4$, depending on the $[I]_0/[TiCl_4]$ ratio. Their mechanism involves preequilibrium between PIB *tert*-alkyl chloride chain ends (or *tert*-alkyl chloride initiator) and $TiCl_4$ to form a nonpropagating complex. The complex may either (1) spontaneously decompose into a propagating ion pair with monomeric counterion or (2) react with a second molecule of $TiCl_4$ with simultaneous decomposition into a

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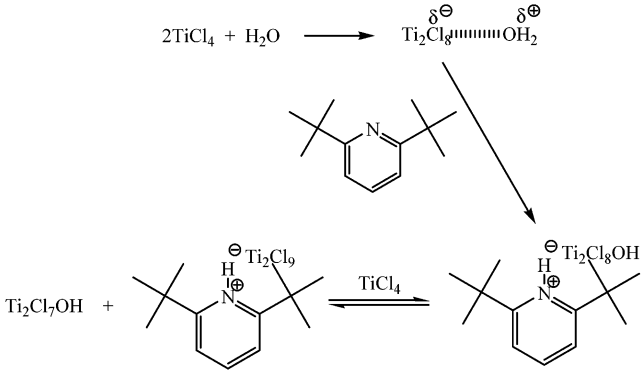

Figure 1. $TiCl_4$ consumption: salt formation.

propagating ion pair carrying a dimeric counterion. According to the authors, if $[I]_0/[TiCl_4]$ is high, route 1 dominates due to a “shortage” of $TiCl_4$, and unit order is observed; if $[I]_0/[TiCl_4]$ is low, route 2 dominates and an order of 2 is observed. This mechanism is appealing in that it accounts for shifting orders and allows for the two-step formation of dimeric counterions, as originally proposed by Storey and Choate,[13] despite near-diffusion-limited propagation rate constants. Its weakness, however, is the lack of spectroscopic evidence and/or literature precedence for the proposed complex. Moreover, since the concentration of ion pairs must be very low in these polymerizations ($10^{-13\pm1}$ M under typical conditions), and if the equilibrium constant for complex formation is small, scarcity of $TiCl_4$ is not a convincing argument for direction of the mechanism along route 1; if the equilibrium constant is large, then reaction would become zero-order in chain ends (for $[I]_0 > [TiCl_4]$), which has not been observed. Wu et al.[27] have also reported shifting orders in $TiCl_4$ depending on the strength of the LB additive, although experiments conducted with a given LB resulted in an order that was consistently one or two.

Contributing to the controversy is the fact that conditions involving low $[TiCl_4]$ are particularly ill-suited for careful kinetic/mechanistic investigation and necessitate corrections to $[TiCl_4]$ and k_{app} so that an accurate propagation reaction order in $TiCl_4$ can be measured. When $[TiCl_4]$ is low and similar to the [LB] (~concentration of protic impurities, HA, $\sim 2 \times 10^{-3}$ M),[28] it is difficult to accurately assign the effective concentration of $TiCl_4$ due to its loss through the proton trapping function, as shown in Figure 1, and possible complexation with LB. The true $[TiCl_4]$ is known with greater certainty when it is high relative to [LB] and [HA]. To meet this goal and satisfy the condition $[I]_0 > [TiCl_4]$, $[I]_0/[LB]$ must be high as well, possibly resulting in large reaction exotherms and poor temperature control. Large initial reaction exotherms suppress the k_{app} measured for a given nominal reaction temperature, due to the apparent negative activation energy of propagation, E_A, for IB polymerizations co-initiated with $TiCl_4$.[2,3] The resulting underestimation of k_{app} becomes increasingly more severe as $[TiCl_4]$ increases, and this results in a more shallow $\ln(k_{app})$ vs $\ln[TiCl_4]$ plot and an underestimation of the $TiCl_4$ reaction order.

Because the mechanism of ionization of PIB chain ends by $TiCl_4$ is still uncertain, and due to the aforementioned issues associated with the $[I]_0 > [TiCl_4]$ condition, it is imperative that we once more study this subject closely. Apparent rate constants for IB propagation were measured under various conditions using real-time FTIR reaction monitoring to follow monomer conversion. Initial experiments more or less reproduced the most recent results obtained by Puskas et al.[1] However, faithful reproduction of these authors' polymerization conditions resulted in massive initial exotherms and thus was not conducive for mechanistic interpretation, which is the goal of study in this area. With this in mind, both spectroscopic and Arrhenius temperature corrections were made to calculate accurate apparent rate constants of propagation when temperature was not controlled. We report polymerizations carried out under milder, more appropriate conditions, while studying the effect of reaction temperature on the order with respect to $TiCl_4$ under the conditions where $[I]_0 > [TiCl_4]$.

Experimental Section

Materials. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by reacting excess dry HCl gas (continuous sparge) with neat 2,4,4-trimethylpentene (99%, Aldrich) at 0 °C. The product was filtered through anhydrous $MgSO_4$ and $NaHCO_3$ just prior to use. Isobutylene and methyl chloride (Matheson Gases) were dried by passing the gas through a column packed with $CaSO_4$ or $CaSO_4$/4Å molecular sieves, respectively. $TiCl_4$ (99.9%, Aldrich), methylcyclohexane (MeCHex, 99%+ anhydrous, Aldrich), and 2,6-di-*tert*-butylpyridine (D*t*BP) (99%, Aldrich) were used as received. Pyrene (99%, Aldrich) was recrystallized in ethanol.

Instrumentation. 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, Stanford, CT) was used to collect infrared spectra of the polymerization components and monitor reactor temperature in real time as previously described.[29] Fluorescence emission spectra from 360 to 450 nm were measured at −80 °C with an Edinburgh FS900CDT T-Geometry fluorimeter with a delay of 0.5 s and step of 0.5 nm. The excitation wavelength was 350 nm.

Procedures. Polymerizations were carried out within an MBraun Labmaster 130 glovebox, equipped with an integral, cryostated hexane/heptane bath. The following procedure was typical: The DiComp probe was fitted into a 250 or 500 mL four-necked round-bottom flask equipped additionally with a mechanical stirrer and RTD and introduced to the cold bath (−80 °C), where it was allowed to thermally equilibrate with stirring of the N_2 gas atmosphere prior to acquisition of a background spectrum (512 scans, 8 cm^{-1} resolution). To the chilled flask was added 245 mL of a 0.98 L stock solution (designed for four reactions) consisting of 158 mL of IB (2.0 mol), 9.18 mL of TMPCl (0.054 mol), 1.8 mL of D*t*BP (8.0 mmol), 480 mL of MeCHex, and 332 mL of MeCl. The reaction mixture was stirred until the solution reached thermal equilibrium as indicated by the RTD. Subsequently, 5 mL of a 2 M $TiCl_4$ solution in MeCHex, prechilled to −80 °C, was rapidly poured into the reactor.

The rapid acquisition mode of the ReactIR 1000 was used to collect IR spectra of the reaction medium; the disappearance of IB was followed by monitoring the decrease in the integrated peak area (referenced to a two-point baseline) of the absorbance centered around 887 cm^{-1}, associated with the $=CH_2$ wag.[29] Spectra were collected for 100 s (2.8 spectra/s, 1 scan/spectrum, 4 cm^{-1} resolution) after monomer addition to obtain an absorbance value, A_0, for the initial monomer concentration, $[M]_0$. The peak area at approximately 100% conversion, A_r, was used as the absorbance value for $[M] = 0.0$ M. The use of this value for $[M] = 0.0$ M accounted for the volume dilution, and thus the solvent absorbance reduction, caused by subsequent addition of monomer and $TiCl_4$ solution. Spectra of the polymerization medium were then acquired where acquisition times varied between 400 s (0.7 spectra/s, 4 scans/spectrum,

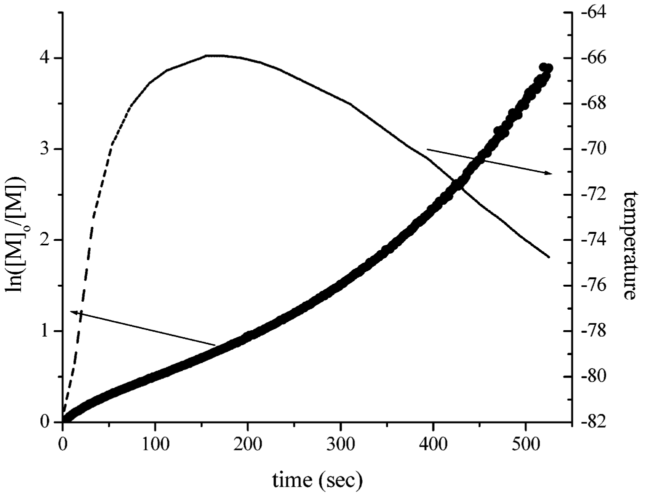

Figure 2. First-order kinetic plot and temperature vs time plot for IB polymerization. Condition A: [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), −80 °C; for [TiCl$_4$] = 0.04 M.

4 cm^{-1} resolution) and 1900 s (0.31 spectra/s, 9 scans/spectrum, 4 cm^{-1} resolution) depending on reaction conditions. TiCl$_4$ was added at 10 s into data acquisition. Each spectrum was collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}. Temperature data were taken manually.

Isobutylene monomer absorbance is known to decrease with increasing temperature by a factor of ~0.42%/°C.[4] To account for reaction exotherm during the polymerization, a spectroscopic correction for temperature was made. Thus, absorbance data were converted to relative monomer concentrations using eq 6, where $[M]_t$ and A_t are the monomer concentration and absorbance, respectively, at time t, and ΔT is the difference between the actual temperature of the reactor contents and the nominal temperature of the experiment.

$$\frac{[M]_0}{[M]_t} = \frac{A_0 - A_r}{(A_t - A_r)(1 + 0.0042\Delta T)} \qquad (6)$$

Fluorescence samples were prepared, transferred to, and sealed in a gastight cuvette inside the glovebox. The cuvette was removed from the glovebox and immersed in a dry ice/acetone bath until placed in the fluorimeter. Three 50 mL solutions termed "solvent", "prereaction mixture", and "polymer" were prepared. The "solvent" solution consisted of pure cosolvents, MeCHex/MeCl 60/40 (v/v). The "prereaction mixture" solution consisted of [IB] = 2.0 M, [TMPCl] = 0.054 M, and [D*t*BP] = 0.008 M, in MeCHex/MeCl 60/40 (v/v). The "polymer" solution contained clean, dry PIB, at an IB repeat unit concentration of 2 M, and [D*t*BP] = 0.008 M, dissolved in MeCHex/MeCl 60/40 (v/v). The PIB was obtained from a polymerization conducted under the following conditions: [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, and [TiCl$_4$] = 0.04 M in MeCHex/MeCl 60/40 (v/v). All samples contained [pyrene] = 2.5 × 10^{-5} M to avoid excimer formation.

Table 1. Average Observed and Temperature-Corrected Apparent Rate Constants and Average Exotherms

condition[a]	temp (°C)	[TiCl$_4$] (M)	raw $k_{app} \times 10^3$ (s^{-1})	corr $k_{app} \times 10^3$ (s^{-1})	exotherm (°C)
A	−80	0.020	1.7	2.7	8.7
		0.025	2.5	6.0	12
		0.030	3.0	6.8	12
		0.040	4.2	13	15
B	−80	0.010	0.46	0.51	1.8
		0.020	2.4	3.3	4.8
		0.030	7.0	16	8.8
		0.040	8.6	19	9.4
C	−80	0.010	0.24	0.27	1.2
		0.015	0.76	1.0	2.0
		0.020	1.8	2.4	4.1
		0.025	3.2	5.2	5.7
	−70	0.010	0.23	*b*	0.50
		0.015	0.42	*b*	1.5
		0.020	0.88	1.0	2.5
		0.025	1.3	3.0	3.2
	−60	0.010	0.04	*b*	0.25
		0.015	0.21	*b*	0.35
		0.020	0.40	*b*	0.83
		0.025	0.67	*b*	1.5
	−50	0.010	0.02	*b*	0.00
		0.015	0.09	*b*	0.00
		0.020	0.21	*b*	0.20
		0.025	0.27	*b*	0.30

[a] A: [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 60/40 (v/v). B: [IB] = 1.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 63/37 (v/v). C: [IB] = 1.0 M, [TMPCl] = 0.025 M, [D*t*BP] = 0.002 M, MeCHex/MeCl 60/40 (v/v). [b] Temperature correction unnecessary, isothermal conditions.

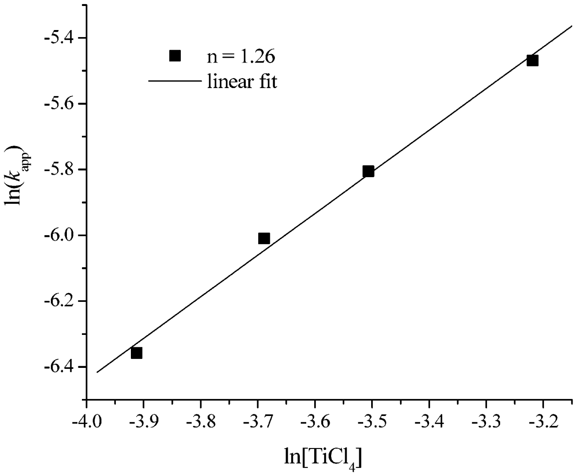

Figure 3. ln(k_{app}) vs ln[TiCl$_4$] for IB polymerization. Condition A: [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), −80 °C.

Results and Discussion

To understand why different research groups have reported different orders of propagation rate with respect to TiCl$_4$, particularly where $[I]_0 > [TiCl_4]$, we conducted IB polymerizations under identical conditions to those used by Puskas et al. in a recent publication[1] where the order was reported to be unity. The conditions were as follows: [IB] = 2.0 M, [TMPCl] = 0.054 M, and [D*t*BP] = 0.008 M, in MeCHex/MeCl 60/40 (v/v), at −80 °C, where [TiCl$_4$] = 0.02−0.04 M (condition A). The first-order kinetic plot for [TiCl$_4$] = 0.04 M is plotted in Figure 2 along with the reaction temperature as a function of time. A significant exotherm, causing a temperature rise of about 16 °C, occurred in the reaction within seconds of initiation. This warming caused a depression in the rate of propagation that is evidenced by a depression in the slope of the first-order plot (decrease in the apparent rate constant, k_{app}) beginning around 30 s. This depression persisted until the reaction temperature began to decrease. The observed k_{app} was extracted from the first extended region of linearity in the original raw first-order plot (e.g., 50−200 s in Figure 2). Using condition A, several polymerizations were conducted, and the observed k_{app}'s were averaged for each [TiCl$_4$]. These average raw k_{app}'s are listed in Table 1 and plotted as ln(k_{app}) vs ln[TiCl$_4$] in Figure 3. The slope was found to be 1.26, which does not exactly equal the finding of Puskas et al.[1] of 1.04 but is closer to unity

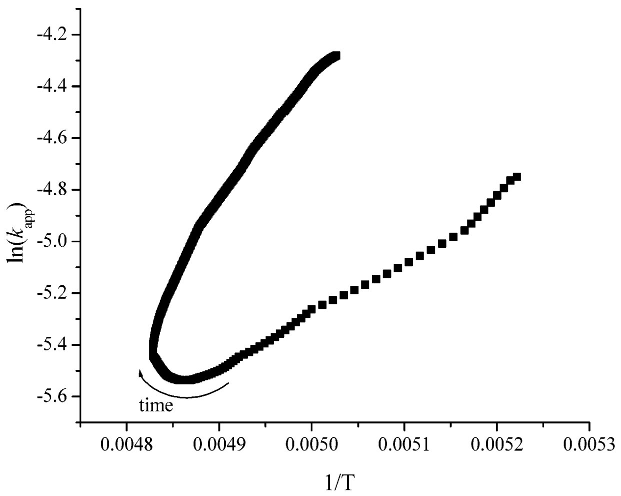

Figure 4. ln(k_{app}) vs 1/T plots for [IB] = 2.0 M. [TMPCl] = 0.054 M, [DtBP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), −80 °C; for [$TiCl_4$] = 0.04 M.

than 2. Obviously, however, this apparent order cannot be accepted at face value in view of the poor temperature control inherent in these fast reactions.

To better understand the effect of temperature, k_{app} (instantaneous slope) was extracted at each point along the first-order plot in Figure 2 and plotted as ln(k_{app}) vs 1/T in Figure 4. Here it can be seen that the instantaneous k_{app} indeed decreases as the temperature increases. This change in the rate with change in reaction temperature demonstrates the need for rate-activated (Arrhenius) temperature corrections to be made to the measured k_{app}'s if they are to be used in determining the $TiCl_4$ order. However, Figure 4 also reveals that as temperature peaks and then falls, k_{app} does return along the same path; rather, the rate of reaction at a given temperature is higher during the later stage of the reaction (longer reaction times). As nonpolar monomer is converted to nonsolvating polymer, an increase in the overall polarity of the system leads to faster polymerization rate later in the polymerization, and this effect is exacerbated by the high initial [IB]. This point will be discussed in more detail in a later section.

Effect of Reaction Temperature on Observed $TiCl_4$ Order. Because the polymerizations carried out under the aforementioned conditions exhibit such large initial exotherms, kinetic data cannot be compared at a single temperature and meaningful conclusions cannot be drawn. Two methods of temperature correction have been developed. First, spectroscopic corrections were made to the data according to eq 6. The second, and more important, temperature-related correction was an Arrhenius correction, carried out according to eq 7, where T_0 and T_{avg} are the original reaction temperature and the average temperature of the period of reaction from which the apparent rate constant is determined, respectively, corr k_{app} and raw k_{app} are the apparent rate constants at T_0 and T_{avg}, respectively, E_A is the apparent activation energy for propagation determined from reactions under milder conditions (−7.20 kcal/mol, discussed later), and R is the gas constant (0.001 986 kcal mol^{-1} K^{-1}).

$$\text{corr } k_{app} = \text{raw } k_{app} e^{(E_A/R)(1/T_0 - 1/T_{avg})} \tag{7}$$

Average temperature-corrected k_{app}'s as well as the average observed exotherms for polymerizations under condition A are listed in Table 1. The open circles in Figure 5 are a plot of ln(k_{app}) vs ln[$TiCl_4$] for condition A, where the k_{app}'s for reactions have been temperature corrected; for comparison, Figure 5 also shows the uncorrected (raw) data shown earlier in Figure 2. Clearly, the actual $TiCl_4$ order is approximately 2 within the regime $[I]_0 > [TiCl_4]$, when the data are corrected for temperature. Figure 5 shows how uncontrolled reaction exotherms systematically skew the data to yield an underestimation of the kinetic order of $TiCl_4$. This process occurs due to the moderately large negative apparent activation energy for $TiCl_4$-co-initiated polymerizations of IB. Uncorrected (raw) and temperature-corrected $TiCl_4$ orders are listed in Table 2 for several reaction conditions including condition A.

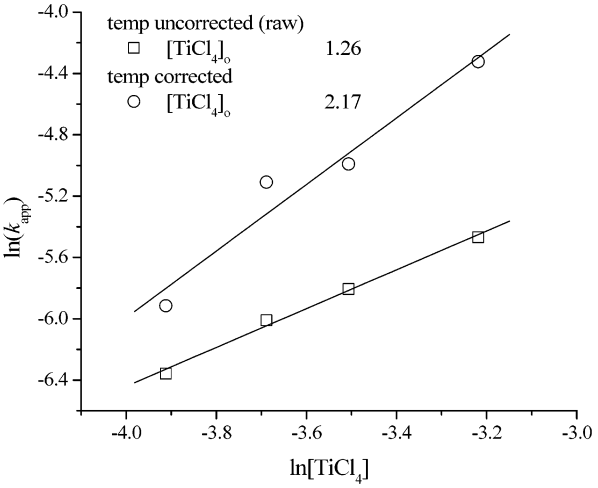

Figure 5. Temperature-corrected and uncorrected (raw) ln(k_{app}) vs ln[$TiCl_4$] for IB polymerization where [IB] = 2.0 M, [TMPCl] = 0.054 M, [DtBP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), and [$TiCl_4$] = 0.02−0.04 M at −80 °C.

Table 2. Order of IB Propagation Rate with Respect to $TiCl_4$

	apparent $TiCl_4$ order		
		temperature-corrected data	
temp[a] (°C)	raw data	[$TiCl_4$]	$[TiCl_4]_{eff}$[b]
−80 (A)	1.26	2.17	1.86
−80 (B)	2.20	2.76	2.12
−80 (C)	2.85	3.23	2.35
−70 (C)	1.93	2.71	1.95
−60 (C)	2.98	2.98[c]	2.12
−50 (C)	2.72	2.72[c]	1.99

[a] A: [IB] = 2.0 M, [TMPCl] = 0.054 M, [DtBP] = 0.008 M, [$TiCl_4$] = 0.02−0.04 M, MeCHex/MeCl 60/40 (v/v). B: [IB] = 1.0 M, [TMPCl] = 0.054 M, [DtBP] = 0.008 M, [$TiCl_4$] = 0.01−0.04 M, MeCHex/MeCl 63/37 (v/v). C: [IB] = 1.0 M, [TMPCl] = 0.025 M, [DtBP] = 0.002 M, [$TiCl_4$] = 0.01−0.025 M, MeCHex/MeCl 60/40 (v/v). [b] $[TiCl_4]_{eff}$ = [$TiCl_4$] − 2[HA] = [$TiCl_4$] − 0.004 M. [c] Temperature correction unnecessary, isothermal conditions.

Effect of Reaction Medium Polarity Changes on Apparent Rate Constant. To illustrate the effect of monomer conversion on reaction medium polarity, and consequently on propagation rate constant, Figure 6 exhibits raw and temperature-corrected (spectroscopic and Arrhenius) k_{app} values with respect to IB conversion for the reaction described earlier in Figure 2 (condition A, [$TiCl_4$] = 0.04 M) using an apparent activation energy for propagation of E_A = −7.2 kcal/mol. The plot shows that even when temperature is corrected there is a linear increase in k_{app} with IB conversion. This effect

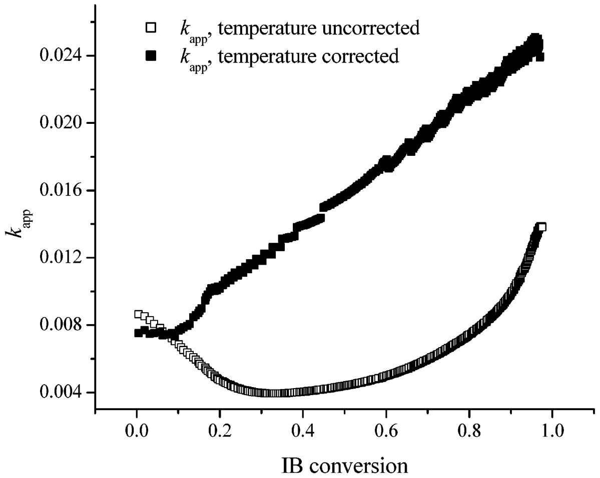

Figure 6. Uncorrected and temperature-corrected k_{app} vs IB conversion plots. Condition A: [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), −80 °C; for [TiCl$_4$] = 0.04 M.

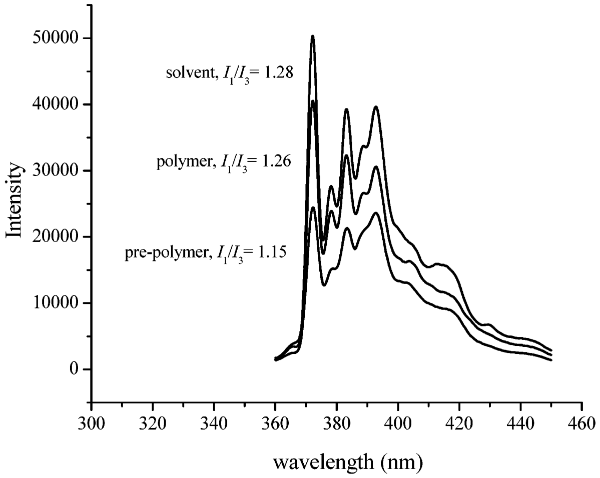

Figure 7. Pyrene fluorescence spectra for solvent, prepolymer, and polymer solutions, where [IB] = 2.0 M, [TMPCl] = 0.054 M, [D*t*BP] = 0.008 M, MeCHex/MeCl 60/40 (v/v), and [pyrene] = 2.5 × 10^{-5} M at −80 °C.

was also reported earlier for IB polymerizations using TiCl$_4$[14] and BCl$_3$[6] co-initiators.

To qualitatively determine reaction medium polarity changes during conversion of monomer to polymer, we measured variations in the vibrational fine structure in pyrene monomer fluorescence spectra. The highest energy 0−0 vibrational band (I_1) intensity shows a strong solvent dependence while that of the 0−2 band (I_3) does not. Thus, the ratio of these band intensities was used to determine the relative polarity of the local environment of pyrene in dilute solutions.[30,31] Winnik et al. have shown that I_1/I_3 ranges from 0.58 for hexane to 1.87 for water.[32] For our purpose, three solutions were made—solvent, prereaction, and polymer—and I_1/I_3 was measured to establish qualitative changes in polarity between the solutions. The solvent sample consisted of MeCHex/MeCl (60/40 v/v); the prereaction and polymer samples were designed to simulate polymerization reactions of condition A, prior to TiCl$_4$ addition and at complete conversion of the monomer, respectively. Each solution contained [pyrene] = 2.5 × 10^{-5} M. A pyrene emission spectrum for each solution is shown in Figure 7, where I_1/I_3 is 1.15, 1.26, and 1.28 for prereaction, polymer, and solvent solutions, respectively. As expected, the most polar solution was that of the solvent, 60/40 MeCHex/MeCl, and the least polar was that of the prereaction solution, made up of 66% hydrocarbon (IB + MeCHex). The polymer solution was only slightly less polar than the solvent solution, illustrating that as monomer is converted, the overall polarity of the solution increases, approaching that of pure solvent. The number of nonpolar molecules, exclusive of MeCHex (~5 M), decreases from 2 to 0.054 M as the polymerization progresses, resulting in a solution that is very similar in polarity to the solvent solution.

Effect of Lewis Base Concentration on Observed TiCl$_4$ Order. As reported previously,[2] when isothermal conditions are achieved or kinetic data have been temperature-corrected, the observed TiCl$_4$ order is usually higher than 2 when the [TiCl$_4$] is low and not significantly greater than the concentration of protic impurities, [HA]. As shown in Figure 1, proton scavenging by the LB consumes two TiCl$_4$ equivalents per protic impurity, and this quantity is approximately constant from reaction to reaction. Thus, the amount consumed is a larger fraction of the total TiCl$_4$ as [TiCl$_4$] is decreased. This causes an increase in the apparent slope of the ln(k_{app}) vs ln[TiCl$_4$] plot, and the effect becomes more pronounced at low [TiCl$_4$]. Orders higher than 2 were observed herein after temperature corrections (center column, Table 2) and are a result of this effect. The concentration of protic impurities has been previously determined to be typically about 0.002 M;[28] therefore, a correction was made to yield an effective TiCl$_4$ concentration, [TiCl$_4$]$_{eff}$ = [TiCl$_4$] − 2[HA], where [HA] = 0.002 M, which was used for subsequent reaction order analyses. For condition A, the TiCl$_4$ order after this correction was slightly less than two, i.e., 1.86 (right column, Table 2).

Effect of Monomer Concentration on Observed TiCl$_4$ Order. The most obvious difference between the experimental conditions of Storey et al.[2] and those of Puskas et al.[1] is initial IB concentration. Puskas et al. generally used [IB] = 2.0 M; Storey et al. consistently used [IB] = 1.0 M.[2,12,13] Thus, a series of polymerizations was carried out under condition B, which was identical to condition A except that the monomer concentration was reduced to [IB] = 1.0 M and the volume fraction of methylcyclohexane in the cosolvent mixture was enriched to MeCHex/MeCl 63/37 (v/v) to maintain constant polarity of the polymerization medium by compensating for the lower volume fraction of IB. The range of TiCl$_4$ used for condition B, [TiCl$_4$] = 0.01−0.04 M, was also slightly broader compared to condition A. Table 1 lists the average observed and temperature-corrected k_{app}'s as well as observed exotherms; Table 2 lists the TiCl$_4$ order results for this series before and after temperature and [TiCl$_4$]$_{eff}$ corrections. The order of propagation with respect to TiCl$_4$ was indeed higher at lower [IB]. In fact, the observed (raw data) order was close to 2, although it was lower than the order for TiCl$_4$ found in previous studies[2] carried out where [I]$_0$ > [TiCl$_4$] and [IB] = 1.0 M. As stated above, an obvious result of the higher monomer concentration used is higher propagation rates with correspondingly higher polymerization exotherms.

To further this study, several series of polymerizations were carried out under conditions designed to give low reaction rates and thus negligible exotherms. The study consisted of polymerizations carried out at four reaction temperatures: −80, −70, −60, and −50 °C, where [IB] = 1.0 M, [TMPCl] = 0.025 M, [D*t*BP] = 0.002

M, MeCHex/MeCl 60/40 (v/v), and $[TiCl_4] = 0.01-0.025$ M (condition C). The low [IB], [I], and $[TiCl_4]$ ensure little to no temperature rise due to polymerization exotherm, especially for the warmer reaction temperatures of −60 and −50 °C. Table 1 lists the average observed and temperature-corrected k_{app}'s for each reaction. Table 2 lists the $TiCl_4$ orders obtained from $\ln(k_{app})$ vs $\ln[TiCl_4]$ plots for each temperature before and after temperature and $[TiCl_4]_{eff}$ corrections. At high temperatures and low $[TiCl_4]$, temperature corrections are not required, and the raw rate data can be used to calculate the reaction order with respect to $TiCl_4$. The data in Table 2 clearly show that the order with respect to $TiCl_4$ is overwhelmingly 2 at these milder conditions, even though $[I]_0 > [TiCl_4]$. Most importantly, the plots for −60 and −50 °C, where no temperature corrections were required, indicate that the order is very close to two after the $[TiCl_4]_{eff}$ is taken into account. Apparent activation energies were calculated for $[TiCl_4] = 0.01$ and 0.015 M, i.e., those $[TiCl_4]$ with the smallest exotherms. The average value was found to be −7.2 kcal/mol.

Conclusions

The best experimental conditions for accurate kinetic studies, including measurements of reaction order, are slow polymerizations for which the rate of heat generation is well within the capacity of the cooling apparatus. Thus, a dilute system is best (low [IB] and low [I]). It is appropriate to apply spectroscopic and activated-rate corrections to attempt to account for temperature rises, but more accurate results are obtained when temperature control problems are avoided. The accuracy to which the real concentration of $TiCl_4$ is known within a given polymerization is also a matter of concern. The best conditions for accurate measurements of reaction order are those in which $[TiCl_4]$ is much higher than the concentration of bases in the system (or appropriate corrections for effective $[TiCl_4]$ are made) and when thermal control of the reaction is achieved. The first set of conditions outlined in this paper (condition A) and the raw data workup fail to meet these guidelines. It is thus not surprising that consensus regarding the kinetic order under these conditions has been elusive, whereas under conditions that do follow the precautions above, there has been nearly universal agreement that the true kinetic order of $TiCl_4$ in IB polymerizations is two over any range of $[I]_0/[TiCl_4]$.

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MA030298O