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Initiation Effects in the Living Cationic Polymerization of Isobutylene

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ABSTRACT: Isobutylene (IB) polymerization kinetics 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. The measured intensity of this band was found to decrease slightly with increasing temperature (0.42% per 1.0 °C). Polymerizations were initiated using the aromatic difunctional initiator 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC) and a series of monofunctional aliphatic initiators: *tert*-butyl chloride (*t*-BuCl), 2-chloro-2,4,4-trimethylpentane (TMPCl), and 2-chloro-2,4,4,6,6-pentamethylheptane (TIBCl). The co-initiatior was $TiCl_4$, and the Lewis base 2,4-dimethylpyridine (DMP) was used as an electron donor. Polymerizations were performed in methylcyclohexane/methyl chloride (60:40 v/v) cosolvents at temperatures ranging from −80 to −40 °C. Reaction conditions were consistently $[DMP] = 2.00 \times 10^{-3}$ M and $[IB]_0 = 1.0$ M. Initiator concentrations were [TIBCl] = [TMPCl] = [*t*-BuCl] = 2[*t*-Bu-*m*-DCC] = 2.08×10^{-2} M. Co-initiator concentrations ranged from $[TiCl_4] = 7.20 \times 10^{-3}$ to 6.79×10^{-2} M. Inspection of the monomer concentration vs time data revealed a number of deviations from first-order decay, depending on initiator. It was observed that polymerizations initiated with *t*-Bu-*m*-DCC exhibited an initial regime of rapid monomer consumption (RMC), which is accompanied by a significant reaction exotherm. This phenomenon was attributed to a higher ionization equilibrium constant for the *tert*-benzylic chloride initiator relative to *tert*-alkyl chloride PIB chain ends. It was proposed that cations formed from the initiator undergo a number of propagation steps prior to the first ion-pair collapse and that this number yields an estimate of the number of IB units consumed per successful ionization during propagation. This number was observed to decrease with increasing temperature. It was also proposed that the RMC event may offer a means for the experimental determination of the absolute rate constant for IB propagation in $TiCl_4$-co-initiated polymerizations. RMC behavior was completely absent with aliphatic initiators; initiation was extremely slow with *t*-BuCl and sluggish with TMPCl, relative to TIBCl.

Introduction

We have recently become interested in the details of initiation for isobutylene (IB) polymerization using $TiCl_4$ co-initiator in mixed aliphatic hydrocarbon/chlorinated hydrocarbon cosolvents. While there are a significant number of different initiators and Lewis acids employed in IB polymerizations, the greatest focus of work in this area to date has been for BCl_3-mediated systems in chlorinated hydrocarbon solvents. Mayr and co-workers[1,2] have studied the living oligomerization of IB in methylene chloride ($MeCl_2$) using diisobutylene chloride (TMPCl), triisobutylene chloride (TIBCl), cumyl chloride (CC), and mono- and diisobutylene adducts of CC. They have found that, for BCl_3-co-initiated systems, TIBCl reacts nearly 3 times faster than TMPCl. This difference in rates is likely due to increased back strain present in TIBCl.[3] A similar phenomenon was observed for CC type initiators; the diisobutylene adduct is roughly 20−35 times more reactive than the monoisobutylene adduct. Although Mayr and co-workers have investigated $TiCl_4$-co-initiated systems, focusing upon the early stages of polymerization and cation reactivity, these studies were primarily concerned with aliphatic initiators and conducted solely in chlorinated solvents.[4,5]

Our desire to study the details of initiation in $TiCl_4$-co-initiated systems derives from an interesting phenomenon repeatedly observed for IB polymerizations conducted at low monomer/initiator ratios ($M_n \leq 5600$ g/mol) using an aromatic initiator such as 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC) in mixed cosolvents, e.g., methylcyclohexane/methyl chloride (MCHex)/(MeCl), 60/40 (v/v).[6,7] This phenomenon is characterized by a transient period of high polymerization rate, followed by a slower first-order decay in the monomer concentration. In a first-order kinetic plot, this initial period of rapid monomer consumption appears as a positive *y*-intercept if, as is usually the case for gravimetric data, there is a low density of data points at short times. Storey and Choate[8] reported the observance of positive *y*-intercepts in first-order plots of IB polymerizations conducted at −30 °C in 60/40 (v/v) hexane/methyl chloride; their initiation system consisted of *t*-Bu-*m*-DCC/$TiCl_4$ with 2,4-dimethylpyridine present as an electron donor. At the time, this phenomenon was ascribed to a higher apparent rate constant in the initial stage of the polymerization, caused by a higher ionization equilibrium for the *tert*-benzylic chloride initiator and also for short chains still affected by the presence of the aromatic moiety in the polymer backbone. Positive *y*-intercepts were conspicuously absent from polymerizations conducted at lower temperatures ($T \leq -50$ °C); however, the polymerization systems of Storey and Choate were designed such that the [IB]/[*t*-Bu-*m*-DCC] ratio was lowest at −30 °C, and this would have tended to magnify this effect if it were indeed associated with the initiation event.

Faust and co-workers have shown that β-proton expulsion can also result in finite positive *y*-intercepts in first-order kinetic plots.[9] In the course of their investigations, they discovered and conclusively demonstrated that, at temperatures > −40 °C and in the presence of a proton trap such as di-*tert*-butylpyridine,

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spontaneous β-proton expulsion is the primary mechanism of termination of $TiCl_4$-co-initiated IB polymerizations. The β-proton expulsion occurs sufficiently rapidly at these higher temperatures to be easily detectable even at moderately high initiator concentrations. This terminative event is evidenced by downward curvature and eventual flattening of $\ln([M]_0/[M])$ vs time plots (first-order analysis) and was confirmed by ^{1}H NMR spectroscopy by detecting the presence of olefinic resonances at 4.64, 4.84, and 5.15 ppm.[9]

Since the appearance of the Storey and Choate paper,[8] we have observed positive y-intercepts in first-order plots at lower temperatures such as −80 °C, but only in cases when an aromatic initiator is used at high concentration.[7] Terminative β-proton elimination cannot account for this, particularly since the initiator concentration is high. However, further elucidation of this phenomenon using existing gravimetric techniques is virtually impossible due to the high polymerization rates involved under these conditions. Therefore, another method is needed. In the past 2 years, both Puskas et al.[10,11] and Storey et al.[6,12−14] have devoted significant effort to the development of real-time in situ FTIR monitoring for IB and styrene polymerizations. This direct method has been shown to agree well with traditional gravimetry[13] and also provides the speed and sensitivity required to monitor polymerizations such as these, which exceed the limits of the latter method, i.e., polymerizations that have low target degrees of polymerization (X_n) and/or occur on short time scales. This paper describes the application of this new technique to the analysis of the details of initiation for IB polymerizations using $TiCl_4$ co-initiator.

Experimental Section

Materials. Methylcyclohexane (MCHex) (99%+, anhydrous) was used as received from Aldrich Chemical Co. *tert*-Butyl chloride (Aldrich Chemical Co.) was dried and purified prior to use by distillation from calcium hydride. 2-Chloro-2,4,4,6,6-pentamethylheptane (TIBCl) was synthesized using a modified version[15] of the procedure of Mayr.[4] The source and preparation of all other reagents have been previously reported.[8]

Instrumentation. Number-average molecular weights (M_n) 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.[15] 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 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.[13]

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). The initial monomer concentration (1.0 M), cosolvent composition (MCHex/MeCl 60/40, v/v), DMP concentration (2.0×10^{-3} M), chain end concentration ([aliphatic initiator] = 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. A representative polymerization procedure was as follows: the DiComp probe was inserted into a stainless steel scabbard, which was immersed into the −80 °C heptane bath and allowed to thermally equilibrate prior to acquisition of a background spectrum (1024 scans, 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 2.08×10^{-3} mol (0.5975 g) of *t*-Bu-*m*-DCC, 110.5 mL of MCHex, 73.7 mL of MeCl, 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, 1.44×10^{-3} mol (157.9 μL) of $TiCl_4$ (neat and at room temperature) was rapidly injected into the reactor.

The rapid 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 8 or 32 acquisitions collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}, within a time period of less than 3 or 12 s, respectively, with an instrument resolution of 8 cm^{-1}. The rapid acquisition mode differs from standard mode by providing for continuous data collection, but at the sacrifice of simultaneous data observation and processing. This permits quicker acquisition of data; however, display and data analysis can only be performed after the experiment has finished. When standard reaction mode was utilized, each spectrum was the Fourier transformation of 128 scans collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}, with an instrument resolution of 8 cm^{-1}. A single spectrum was acquired each minute; the acquisition required 36 s, with 24 s required for data processing.

Reaction conversion was determined by monitoring the $=CH_2$ wag at 887 cm^{-1} as previously described[13] 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 (or polymer at complete conversion).[13] For reactions that were stopped prior to complete conversion, the peak area measured prior to the addition of IB was used for [IB] = 0.0 M; the error in the calculated conversion thus introduced was <2%. At low conversions (<50%), the error introduced into the calculated value of $\ln([M]_0/[M])$ was <2.8%.[17]

Results and Discussion

The kinetics of $TiCl_4$-co-initiated polymerization of IB were studied to determine the effect of the nature of the initiating species on polymerization. The monomer concentration was measured in real time using in-situ ATR-FTIR spectroscopy.

Aromatic Initiators. We undertook a detailed study of the initiation process as a result of an interesting phenomenon repeatedly observed in the living polymerization of low molecular weight PIB initiated by *t*-Bu-*m*-DCC ($\bar{M}$ = 5600 g/mol).[6,7] A typical monomer concentration profile is shown in Figure 1. One observes an initial, high rate, followed by the expected first-order decay of monomer concentration. The initial regime of rapid monomer consumption (RMC) is accompanied by a significant reaction exotherm; under the conditions in Figure 1, reactor temperature increased by 2.1 °C.

A close inspection of the data in Figure 1 (inset) reveals minor oscillations in the [IB] = 1.0 M data, as well as the [IB] decay profile. These oscillations are spectral artifacts, which result from fluctuations in reactor temperature. As the reactor temperature rises, there is a slight decrease in the measured intensity of the $=CH_2$ wag of IB. This is perceived as a slightly lower monomer concentration. To determine the magnitude

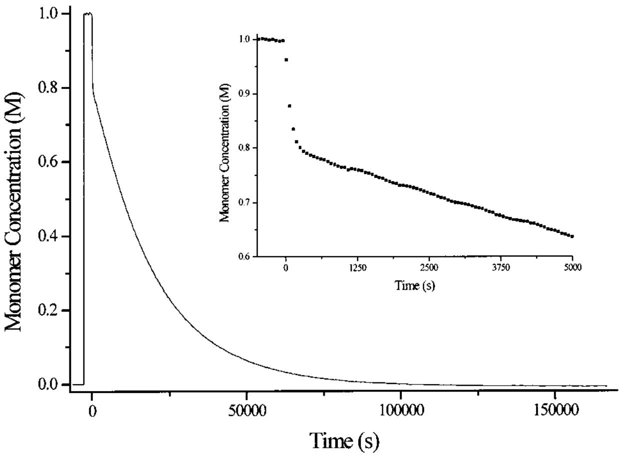

Figure 1. Isobutylene concentration vs time for *t*-Bu-*m*-DCC initiator. $[TiCl_4] = 7.20 \times 10^{-3}$ M; $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 MCHex/MeCl cosolvents (v/v). The inset shows the initial stage of polymerization.

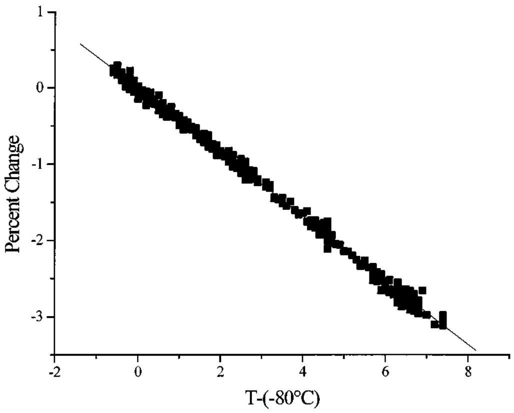

Figure 2. Normalized intensity of the $=CH_2$ wag of IB vs temperature (normalized to −80 °C); $[IB]_0 = 1.0$ M; 60/40 MCHex/MeCl cosolvents (v/v).

of the attenuation, the following experiment was performed: a reactor charged with IB (1.0 M) was monitored while the temperature was varied from −80.6 to −72.6 °C. Figure 2 shows a plot of the percent change in the intensity of the $=CH_2$ wag of IB vs temperature (referenced to −80 °C); the data are perfectly linear and show that the measured intensity decreases 0.42% for each 1 °C rise in temperature. This systematic experimental error is very small (<1% for the ΔT that occurred during the initial exotherm in Figure 1) and is insufficient to account for the initial, rapid decay observed in the 887 cm^{-1} peak.

The data from Figure 1 were plotted as $\ln([M]_0/[M])$ vs time in Figure 3; linearity to nearly six half-lives clearly demonstrates that no termination events, i.e., β-proton elimination, are detectable in this system under these conditions. Notably, the initial rapid monomer consumption event appears as a finite *y*-intercept, reminiscent of the data of Storey and Choate[8] at −30 °C. Unfortunately, it is difficult to have a complete understanding of this initial phenomenon due to the paucity of data describing the event. As can be seen in the Figure 1 inset, the characteristic downward "hook" is defined by only about six data points. For polymerizations much faster than this (Figure 1 represents a relatively slow reaction; $t_{1/2} \approx 3.5$ h), the situation can be even worse, with the first data point possibly occurring after this region of high rate has ended.

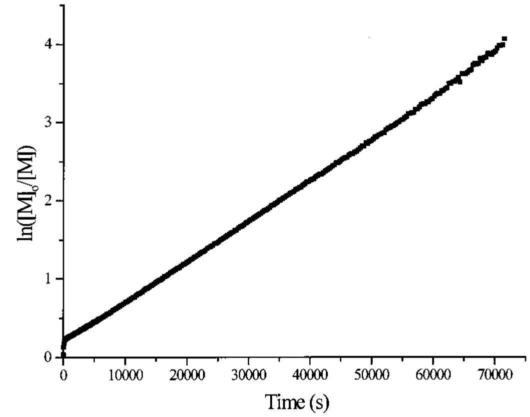

Figure 3. First-order plot for *t*-Bu-*m*-DCC initiator. $[TiCl_4] = 7.20 \times 10^{-3}$ M; $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 MCHex/MeCl cosolvents (v/v).

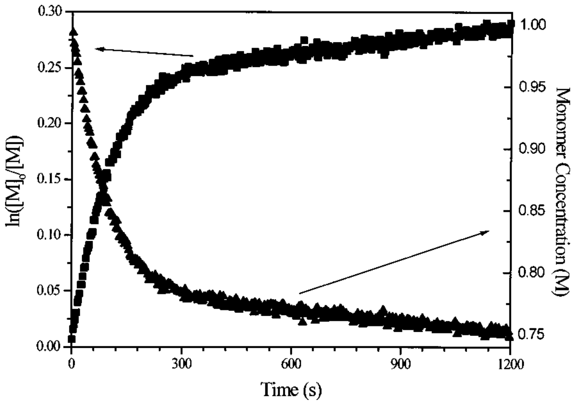

Figure 4. Isobutylene concentration vs time and first-order plot for *t*-Bu-*m*-DCC initiator. $[TiCl_4] = 7.20 \times 10^{-3}$ M; $[IB]_0 = 1.0$ M; [*t*-Bu-*m*-DCC] $= 1.04 \times 10^{-2}$ M; [DMP] $= 2.0 \times 10^{-3}$ M; 60/40 MCHex/MeCl cosolvents (v/v).

To study this phenomenon more closely, the experiment was repeated using the rapid acquisition mode. This afforded the opportunity to increase the rate of data acquisition dramatically since rapid mode provides for continuous scans and defers processing or profiling of data until reaction completion. Additionally, by decreasing the number of scans to eight scans/spectra, the density of discrete data points increased in excess of 20-fold, while only sacrificing a factor of 4 in the signal-to-noise ratio. As we were concerned solely with monitoring the early stages of polymerization, where the signal is quite strong, this is an excellent trade-off.

The IB monomer decay profile and first-order kinetic plot are shown together in Figure 4. The first-order plot displays two linear regions; the first, persisting to about 100 s or so, represents the initial stages of the RMC. After the RMC, the first-order plot is again quite linear, as would be expected under living polymerization conditions. Table 1 lists the slope, equal to the apparent rate constant for polymerization, of each linear region determined by linear regression. The *y*-intercept of the second linear region yields an estimate of the amount of monomer consumed during the RMC. From this was calculated the number of IB units consumed per initiation site during the RMC, i.e., the initiation run number, which is also listed in Table 1. For the −80 °C data in Figure 4, the rate constant during the RMC is about 50 times higher than for the subsequent living polymerization, and the RMC event persists until approximately

Table 1. Kinetic Parameters for IB Polymerizations at Various Temperatures Using *t*-Bu-*m*-DCC Initiator (Figures 4−6)[a]

temp (°C)	k_{app} (s^{-1}) × 10^3 during RMC	k_{app} (s^{-1}) × 10^5 during living polymerization	X_n per initiating site
−80	2.0	4.0	10
−70	1.1	2.1	5.2
−60[b]	1.4	5.9	3.5

[a] $[IB]_0$ = 1.0 M; [*t*-Bu-*m*-DCC] = 2.08 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; [$TiCl_4$] = 7.20 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents v/v. [b] [$TiCl_4$] = 1.24 × 10^{-2} M.

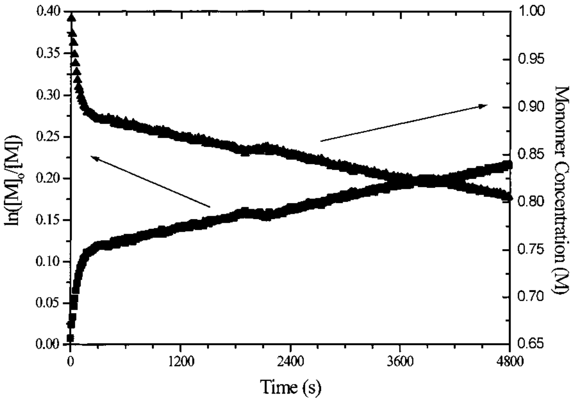

Figure 5. Isobutylene concentration vs time and first-order plot for *t*-Bu-*m*-DCC initiator at −70 °C. [$TiCl_4$] = 7.20 × 10^{-3} M; $[IB]_0$ = 1.0 M; [*t*-Bu-*m*-DCC] = 1.04 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents (v/v).

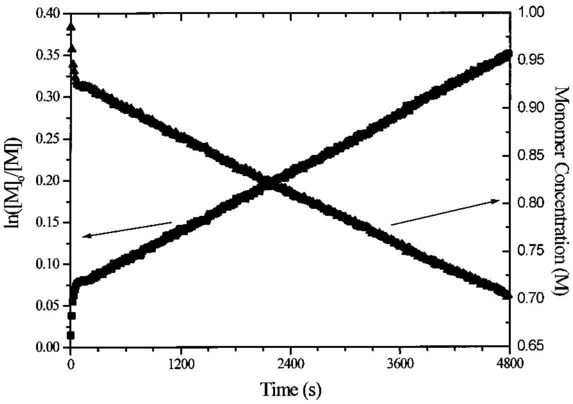

Figure 6. Isobutylene concentration vs time and first-order plot for *t*-Bu-*m*-DCC initiator at −60 °C. [$TiCl_4$] = 1.24 × 10^{-2} M; $[IB]_0$ = 1.0 M; [*t*-Bu-*m*-DCC] = 1.04 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents (v/v).

21% of the monomer has been consumed. This corresponds to an incorporation of approximately 10 IB units per initiation site.

Three additional experiments were performed to determine the effect of temperature (−70, −60, and −40 °C) on the RMC event. $[TiCl_4]_0$ was held constant at 7.20 × 10^{-3} M for the −70 °C run and increased to 1.24 × 10^{-2} M at −60 °C to achieve the desired level of conversion in 4800 s. In a similar fashion, a higher concentration of $TiCl_4$ was used at −40 °C (2.88 × 10^{-2} M). The monomer decay profiles and the first-order plots for the polymerizations conducted at −70 and −60 °C are shown in Figures 5 and 6, respectively. Table 1 lists the kinetic data extracted from these figures. It is readily apparent from inspection of these decay profiles that the RMC event consumes less monomer with increasing reaction temperature. The intercepts obtained from linear regression of the first-order plots indicate that the effect persists until 5.2 IB units are consumed per each initiating site at −70 °C and 3.5 IB units per site at −60 °C (Table 1). It should be noted that the −60 °C experiment was performed at higher $TiCl_4$ concentration, and the effect of Lewis acid concentration on the run number has not been determined.

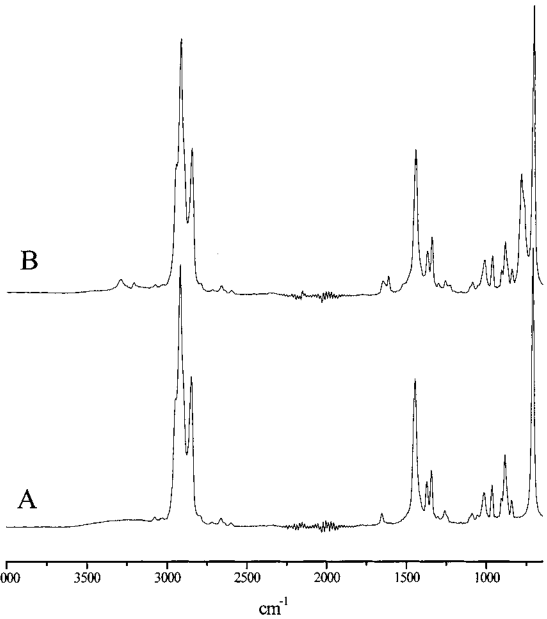

Figure 7. FTIR spectra of polymerization media at −60 °C prior to addition of $TiCl_4$ (A) and at approximately 30% conversion (B).

Kinetic analyses at temperatures in excess of −60 °C are complicated by the appearance of new absorbance bands at 783, 1615, 1649, 3211, and 3292 cm^{-1}, which all increase in intensity with increasing reaction time and increasing reaction temperature. Of these, the band at 783 cm^{-1} is the most intense and, unfortunately, the one most likely to interfere with the monitoring of the $=CH_2$ wag at 887 cm^{-1}. Figure 7 shows spectra acquired at −60 °C for the polymerization system immediately prior to the addition of $TiCl_4$ (A) and at roughly 30% conversion (B). While the new absorbance at 783 cm^{-1} does not interfere with infrared monitoring at −60 °C or below, it is much more intense at −40 °C and significantly overlaps the $=CH_2$ wag at 887 cm^{-1}. Kinetic analysis based upon absorbances other than the $=CH_2$ wag are similarly prevented as the bands at 1649 and 1615 cm^{-1} completely obscure the absorbance due to the C=C stretch at 1656 cm^{-1}. The appearance of these strong absorbances, which increase in intensity over time, makes it extremely difficult, if not impossible, to monitor the IB decay at temperatures higher than about −60 °C for this particular polymerization system, i.e., $TiCl_4$-co-initiated, with MCHex/MeCl cosolvents and 2,4-DMP as the Lewis base. It is interesting to note that Storey and Maggio[14] have not observed any of these new absorbances in BCl_3-co-initiated IB polymerizations at elevated temperatures; thus, they appear to be unique to $TiCl_4$-co-initiated systems. Since $TiCl_4$ and its initial reaction products (complex with DMP and onium salts due to proton scavenging) are not consumed during reaction, the increase in intensity of these bands with reaction time suggests a physical phenomenon. We speculate that these absorbances are due to the insoluble $TiCl_4$·2,4-DMP complex that gradually plates onto the diamond-composite probe surface at higher temperatures. At lower reaction temperatures, the

Table 2. Co-initiator Concentration, Molecular Weight, and IB Conversions for Various Aliphatic *tert*-Chloride Initiators[a]

initiator	[TiCl$_4$] (M) × 10^3	M_n (g/mol)	M_w/M_n	% IB conversion
TIBCl	7.20	1500		22
TMPCl	7.20	1500		14
t-BuCl	7.20			1
t-BuCl	17.6	8700	1.15	16
t-BuCl	67.9	15700	1.16	$\sim$100[b]

[a] Reaction time = 4800 s; [IB]$_0$ = 1.0 M; [initiator] = 2.08 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents v/v. [b] Reaction time 1200 s.

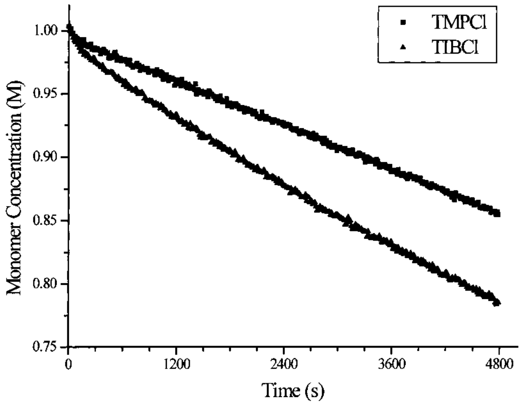

Figure 8. Isobutylene concentration vs time for TMPCl and TIBCl initiators. [TiCl$_4$] = 7.20 × 10^{-3} M; [IB]$_0$ = 1.0 M; [TMPCl] = [TIBCl] = 2.08 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents (v/v).

complex is apparently significantly more soluble in the reaction medium and does not plate. Under these conditions, its concentration is several orders of magnitude less than monomer, and thus its absorbances are of negligible relative intensity.

Aliphatic Initiators. The rapid monomer consumption event described in the previous section represents a higher apparent rate constant in the initial stage of the polymerization. If, as originally proposed by Storey and Choate,[8] this is caused by a higher ionization equilibrium constant for a *tert*-benzylic chloride initiator, no such behavior should be observed in IB polymerizations initiated by aliphatic tertiary chlorides. To determine whether experimental results are consistent with this prediction, the initial stage of IB polymerization was examined for the following three aliphatic initiators: *t*-BuCl, TMPCl, and TIBCl. A relatively low target degree of polymerization (X_n = 48) was selected, such that the initial stage of polymerization (up to about 10 monomer units) corresponded to approximately 20% conversion. Co-initiator concentrations were chosen to optimize real-time FTIR monitoring. The systems studied were tailored to reach the desired level of conversion (10−30%) in approximately 4800 s. Co-initiator concentrations and percent conversion achieved in 4800 s are shown in Table 2.

Figure 8 shows [IB] vs time profiles for TMPCl- and TIBCl-initiated polymerizations. It is apparent that the rate of polymerization is slightly higher for TIBCl. Since the polymer chains derived from these initiators are chemically identical after the addition of one IB unit to TMPCl, it seems highly improbable that there exist any electronic differences between the polymer chains which would cause TIBCl-initiated PIB to propagate at a faster rate. Therefore, the cause must be either dilution of the TMPCl with an impurity, e.g., dehydrochlorinated TMPCl, or inherently slower initiation by TMPCl. ^{1}H NMR confirmed that the TMPCl purity is in excess of 98%; i.e., the olefin content is less than 2%. The same level of impurities was observed for the TIBCl initiator. Therefore, the only remaining probable cause for this behavior is slow initiation by TMPCl relative to TIBCl. Slow initiation in the TMPCl-initiated polymerization can be confirmed by calculating the fractional initiator conversion at some experimental time and comparing it to the same quantity for TIBCl at the same time. GPC analysis of the PIB obtained from these polymerizations showed that both polymers have essentially identical $\bar{M}_n$ (±5%) at 4800 s reaction time (Table 2). Since the monomer conversion at this time was 22% for TIBCl but only 14% for TMPCl, this indicates that the initiator conversion was considerably lower for TMPCl, and thus, TMPCl is slowly initiating relative to TIBCl. It is believed that TMPCl exhibits moderately slow initiation due to the lesser degree of back strain relative to TIBCl,[3] and this is manifested in slightly lower polymerization rates until all the TMPCl molecules have initiated.

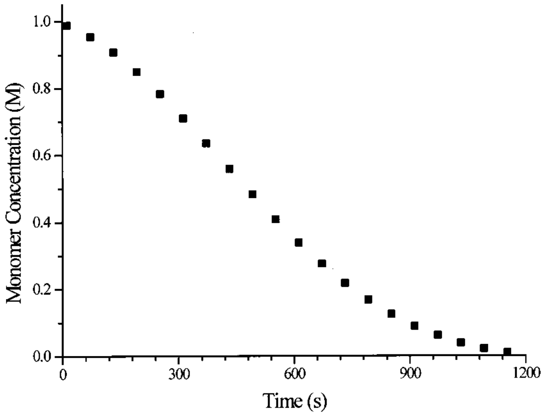

Figure 9. Isobutylene concentration vs time for *t*-BuCl initiator. [TiCl$_4$] = 6.70 × 10^{-2} M; [IB]$_0$ = 1.0 M; [*t*-BuCl] = 2.08 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents (v/v).

Inspection of the [IB] vs time profiles for both TMPCl and TIBCl reveals an initial, slight downward deviation from normal exponential decay. While these deviations are superficially similar to the hook observed in the *t*-Bu-*m*-DCC-initiated system, they in fact are due to the previously described temperature sensitivity of the absorbance intensity of the $=CH_2$ wag at 887 cm^{-1}. Because of the initial exotherm of polymerization, internal reactor temperatures were observed to rise 0.3 and 0.4 °C for the TMPCl and TIBCl systems, respectively, which precisely accounts for the observed downward deviation. It is also important to note that the observed temperature rise is much smaller than the 2.1 °C rise found in the *t*-Bu-*m*-DCC initiated system. This dramatic difference in polymerization exotherms further evidences an initial regime of rapid monomer consumption in systems containing an aromatic initiator.

When *t*-BuCl was used to initiate polymerization under the same conditions as TMPCl and TIBCl, approximately 1% conversion was achieved in the same time period. This was not altogether unexpected since *t*-BuCl is known to be an extremely slow initiator for the cationic polymerization of IB.[18] Figure 9 shows isobutylene concentration vs time for the same system co-initiated with approximately 10 times greater concentration of TiCl$_4$ (6.70 × 10^{-2} M). What is most

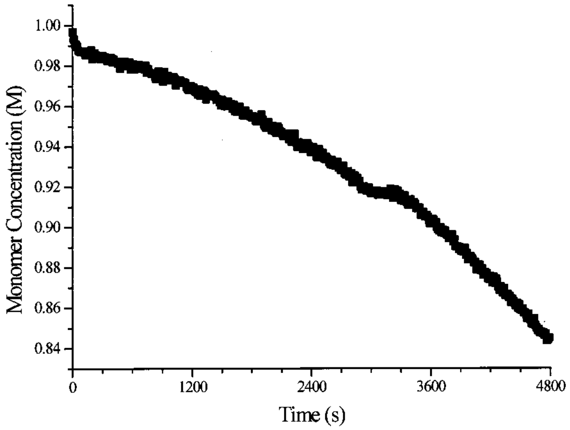

Figure 10. Isobutylene concentration vs time for *t*-BuCl initiator. [TiCl$_4$] = 1.76 × 10^{-2} M; [IB]$_0$ = 1.0 M; [*t*-BuCl] = 2.08 × 10^{-2} M; [DMP] = 2.0 × 10^{-3} M; 60/40 MCHex/MeCl cosolvents (v/v).

interesting about this concentration profile is its significant deviation from the normal first-order decay observed in the living polymerization of IB using initiators such as TMPCl[19] or *t*-Bu-*m*-DCC.[13] A pronounced induction period is observed, which is characteristic of very slow initiation. This interpretation is supported by GPC analysis, which indicated approximately 18% initiation efficiency at complete monomer conversion ($\bar{M}_n$ = 15 700 g/mol).

t-BuCl was again used to initiate polymerization, although using significantly less TiCl$_4$ (1.76 × 10^{-2} M). These reaction conditions yielded a suitable rate of polymerization to observe 10−30% conversion in 4800 s, which facilitated data collection using the rapid acquisition mode of the ReactIR 1000. Figure 10 shows the concentration profile for this experiment, which exhibits the characteristic downward concavity associated with slow initiation, rather than the traditional first-order decay profile associated with the ideal case where initiation rate is faster than or equal to propagation rate. Since for this polymerization, conversion is still quite low after 4800 s, initiation efficiency is considerably worse; GPC analysis indicates efficiency on the order of 6% ($\bar{M}_n$ = 8700 g/mol). It should be noted that, similarly to Figure 8, slight downward curvature is present in the initial few seconds of polymerization, which is caused by the initial polymerization exotherm. An additional spectroscopic artifact is observed at 2900−3300 s; the brief plateau observed at this point in the IB concentration profile represents the point at which the temperature controller delivered liquid nitrogen to the heat transfer bath. The simultaneous temperature monitor of the reactor indicated that the temperature dropped 1.8 °C (from −78.3 to −80.1 °C), which caused a slight increase in the measured intensity of the =CH$_2$ wag of IB. This is perceived as a slightly higher monomer concentration. This systematic experimental error is very small (<1%) and essentially self-correcting; i.e., it averages out over time and the range of thermal fluctuations. When the rate of data acquisition is slower than in the present case, it can hardly be perceived at all.

Reanalysis of Storey and Choate Data.[8] In light of these new findings, it is instructive to revisit the data of Storey and Choate.[8] These authors observed positive *y*-intercepts in first-order plots at −30 °C, which they attributed to an initial period of rapid monomer consumption. They further proposed that this was due to a higher ionization equilibrium constant for the *tert*-benzylic chloride initiator and for short chains in which the ionization reaction can still be affected by the presence of the initiator residue. The present findings support this original hypothesis, except that we now believe that the initiator residue does not affect the reionization of short chains. The persistence of the RMC to finite degrees of oligomerization (e.g., about 10 at −80°) is rather a consequence of the finite run number of the initiating cations. The concept of run number, or the average number of monomer units consumed per ionization event, has been discussed previously by Puskas et al.[20] and is a central feature of the propagation mechanism of living carbocationic polymerizations.

Table 3. *y*-Intercepts and Calculated IB Conversions for *t*-Bu-*m*-DCC Initiated Polymerizations at −30 °C[a] (From Ref 8, Figure 3)

[*t*-Bu-*m*-DCC] (M) × 10^3	*y*-intercept	% IB conversion	X_n per arm
8.0	0.18	16	10
6.0	0.20	18	15
4.0	0.067	6.5	8.1
2.6	0.053	5.2	10
1.9	0.041	4.0	10

[a] [*t*-Bu-*m*-DCC]:[TiCl$_4$]:[DMP] = 1:20:2; [IB]$_0$ = 1.0 M; 60/40 Hex/MeCl cosolvents (v/v).

Table 3 lists the −30 °C data of Storey and Choate (taken from Figure 3 of ref 8), consisting of *y*-intercepts determined by linear regression of first-order kinetic plots, the percent conversion for a given *y*-intercept, and the corresponding degree of polymerization ($\bar{X}_n$) per arm (initiating site). The magnitude of the *y*-intercept varies directly with initiator concentration or rather inversely with target molecular weight. However, the observed X_n's per arm calculated from the sparse gravimetric data average 10.6, which the present data show is far too large to be caused solely by the use of an aromatic initiator; *β*-proton elimination is the most plausible explanation. As Faust et al.[9] recently demonstrated, the resulting curved ln([M]$_0$/[M]) vs time plots could appear to possess a positive *y*-intercept, especially with a limited number of data points.

While *β*-proton elimination explains the data of Storey and Choate[8] at −30 °C, the conspicuous absence of nonzero intercepts in the experiments run at −50 or −80 °C seems unusual given the strong effect reported herein with aromatic initiators. The absence of positive intercepts is easily understood when the initiator concentrations, or more aptly the target $\bar{M}_n$'s, are considered. Storey and Choate[8] studied $\bar{M}_n$'s ranging from 21 500 to 80 000 g/mol at these lower temperatures. For these high molecular weight polymers, the RMC event would consume less than 6% of available monomer. (For a 80 000 g/mol recipe, it would consumes only ~1.4% of the monomer charge at −80 °C.) Given the paucity of data due to gravimetric monitoring and the increasingly smaller magnitude of this effect with increasing molecular weight, it is not surprising that no positive *y*-intercepts were observed.

Mechanistic Interpretation of Rapid Monomer Consumption Event. The rapid monomer consumption (RMC) event that is plainly evident in Figures 4−6 is a result of a higher ionization equilibrium constant for cumyl chloride than for *tert*-alkyl chloride PIB chain ends. The polymerization of IB under these conditions can be viewed as two separate reactions occurring in series: a fast consumption of IB initiated by the first-formed cumyl cations (initiating cations, R_I^+), followed by a slower consumption initiated by PIB cations (R_{PIB}^+). The latter are defined as chains that have added at least one monomer unit and have subsequently undergone at least one ion-pair collapse (reversible termination event); the former (initiating cations) are defined as chains that originate from the ionization of a cumyl chloride initiation site and have yet to undergo one ion-pair collapse. Under these reaction conditions, PIB cations have been shown to exist as paired ions only,[20] carrying dimeric gegenions (i.e., $Ti_2Cl_9^-$).[6-8] Given the high proportion of hydrocarbon solvent in the reaction medium (60 vol %), we believe that the initiating cumyl cations also exist exclusively as ion pairs, but in the absence of experimental evidence, we concede that some degree of dissociation is possible. However, it is widely held that for carbocations free ions and ion pairs possess similar reactivities due to the large size of the counterions (large interionic distance in the ion pair) and strong solvation of the cation.[21,22] Thus, the observed difference in rate is surely due to a difference in concentration, not reactivity, of the active species. The two periods of IB consumption are so dramatically distinct because the initial active species concentration is dictated by the ionization equilibrium constant of the cumyl chloride-type initiator, which is relatively large, whereas the active species concentration at long times is dictated by the ionization equilibrium constant of the PIB chain termini, which is relatively small. Furthermore, it is possible that the ionization equilibrium never becomes established during the RMC under these conditions; in this case, the cation concentration during this period would be a steady-state concentration, which is lower than the equilibrium concentration.

The first-formed cumyl cations add a number of IB units before collapsing for the first time. Persistence of the RMC event to a fairly high degree of oligomerization allows measurement of the run number for the initiating cations. This new capability, made possible by rapid acquisition FTIR, was heretofore impossible with traditional gravimetry. Measurement of the initiation run number is quite significant since the latter provides a direct experimental determination of the run number for living IB propagation. However, interpretation of this value as the run number for IB propagation under these conditions is subject to several cautions. The first derives from the fact that, of the multiple monomer additions involved, the first and to a lesser extent the second involve addition of IB to cations that are dissimilar to the general propagating cation. Second, toward the end of the RMC reionized PIB chains begin to contribute slightly toward propagation, and this causes an overestimation of the general propagation run number. Third, if free ions were present during the RMC, and if they were significantly more reactive than ions pairs, then this would also cause an overestimation of the general propagation run number. Finally, it is conceivable that initiating cations might be terminated by a dual mechanism involving both ion-pair collapse and chain transfer to the initiator. In this interpretation, the RMC event would constitute a transient period that is controlled by an inifer-type mechanism,[24] which rapidly gives way to living polymerization. Obviously, if this were the case, the run number measured in the presence of unreacted initiators would be different from that measured in their absence.

At −80 °C, the RMC persists until about 21% monomer conversion, which translates to a run number of about 10. This agrees remarkably well with run numbers that have been theoretically calculated from experimental molecular weight distributions of PIBs obtained under similar conditions.[20] This supports the conclusion that the initiating and PIB cations are of similar reactivity (ion pair dissociation either does not occur or does not significantly affect reactivity) and that the RMC occurs because of a difference in the concentration of cations.

During the RMC, the concentration of active cations slowly decays as the reservoir of nonionized cumyl chloride initiating moieties is depleted and replaced with an equal number of dormant *tert*-alkyl chloride PIB chain ends. The period of decay ends when essentially all initiating cations have collapsed. Throughout the entire polymerization, the total number of cations, $[R_{TOT}^+]$ is given by the sum of the extant initiating cations, $[R_I^+]$, and the PIB cations, $[R_{PIB}^+]$:

$$[R_{TOT}^+] = [R_I^+] + [R_{PIB}^+] \tag{1}$$

At very short times in the polymerization reaction $[R_{PIB}^+] \approx 0$; at intermediate and long times, $[R_I^+] = 0$.

The $\ln([M]_0/[M])$ vs time data obtained at −80 °C (Figure 4) may now be reconsidered in light of this discussion. The RMC event is defined by the condition $[R_{PIB}^+] \approx 0$. Therefore, the slope of the curve in the limit of $t = 0$ is approximately equal to $k_p[R_I^+]$. The value of this quantity taken from Figure 4 is 2.0×10^{-3} s^{-1} (first nine points, $R^2 = 0.992$). The extended linear region occurring after the RMC, which represents living polymerization, is defined by the condition $[R_I^+] = 0$. The slope that was calculated from the data within the range of 480−4800 s is 4.0×10^{-5} s^{-1}. This value represents $k_p[R_{PIB}^+]$. From this analysis, we may thus conclude that under these conditions the approximate initial concentration of initiating cations is about 50 times higher than the steady-state concentration of PIB cations. Figures 5 and 6 indicate that the RMC event becomes shorter lived as the temperature is increased. This suggests that the run number of the initial ionization is smaller, i.e., that the rate constant for collapse of the initiating cations is larger. Analysis of the −70 °C data in Figure 5 indicates that the concentration of initiating cations is again about 50 times higher than the steady-state concentration of PIB cations. The number of data points defining the RMC event was too small at −60 °C to make a similar estimation at this temperature.

The RMC phenomenon theoretically offers an elegant method for determination of the absolute second-order rate constant for IB propagation and the associated equilibrium constant describing the dormant-active PIB chain end equilibrium. The major impediment, which has so far prevented this experimental determination, is the difficulty of observing PIB cations at very low concentrations using spectroscopy or other means. In contrast, measurement of the concentration of cumyl cations via UV spectroscopy has been recently reported, under conditions typical of polymerizations.[25] Given a value for $k_p[R_I^+]$ measured via real-time FTIR and a value of $[R_I^+]$ obtained through UV spectroscopy, the value of the absolute rate constant of propagation, k_p, could be calculated. For this method to be valid, it must be demonstrated that initiating and PIB cations have essentially the same reactivity; i.e., the possibility for dissociation of the initiating cations into free ions of higher reactivity must be eliminated. This could be accomplished, for example, using a common ion salt additive. Then at least two additional problems must be overcome. As stated earlier, the $[R_I^+]$ during the RMC may be a steady-state rather than an equilibrium value. The latter obviously cannot be obtained from UV measurements of a solution of cumyl chloride and $TiCl_4$ in the absence of monomer. One would have to first equilibrate cumyl chloride and $TiCl_4$ in the absence of monomer and measure the cation concentration using UV spectroscopy. Then monomer could be added and the slope of the RMC determined. If the slope were significantly larger than what is presently observed, this would support the existence of a steady-state concentration of cumyl cations when $TiCl_4$ is added as the last component. The second problem is the low probability that the equilibrium concentration of cumyl cations under these conditions is within the level of detection using current UV spectroscopy. Certainly, if it is only 50 times greater than the PIB cations, then the value for k_p reported by Mayr et al.[4] of 6×10^8 L/(mol s) would predict $[R_I^+] = 3 \times 10^{-12}$ M under the conditions of Figure 4, a value too low to be measured. However, the equilibrium concentration may be quite higher, and in addition, the concentration can be dramatically increased by lowering temperature and/or increasing solvent polarity. This could push the apparent rate of polymerization beyond the time scale of measurement of our current instrument; however, stopped-flow techniques using a quicker, more powerful interferometer could then be brought to bear.

Conclusions

It has been demonstrated that polymerizations initiated with *t*-Bu-*m*-DCC exhibit an initial regime of rapid monomer consumption, which is accompanied by a significant reaction exotherm. This phenomenon was attributed to a higher ionization equilibrium constant for the *tert*-benzylic chloride initiator relative to *tert*-alkyl chloride PIB chain ends. It was proposed that cations formed from the initiator undergo a number of propagation steps prior to the first ion-pair collapse and that this number decreases with increasing temperature. The RMC phenomenon is a direct consequence of the quasiliving nature of carbocationic polymerization. If, upon addition of the co-initiator, all cumyl chloride sites became instantaneously active and the resulting PIB chain ends were all instantaneously active, there could be no RMC, and the concept of run number would have no meaning. Even for a quasiliving polymerization, if the initiator has exactly the same ionization equilibrium constant as the growing chain, then no RMC will be observed. This condition is approximately fulfilled by the aliphatic initiators TMPCl and TIBCl. It is interesting to note that the extremely slow initiation observed in the *t*-BuCl polymerizations (20% efficiency at 100% conversion) is essentially the opposite of the extremely fast initiation observed with cumyl chloride-type initiators. In the *t*-BuCl system, PIB chain ends reionize more rapidly than the initiator. Boundary value analysis of the RMC event, coupled with spectroscopic (UV) determination of the equilibrium concentration of cumyl cations, theoretically provides the opportunity to determine detailed kinetic information about the polymerization of IB, including the second-order rate constant for propagation, k_p.

Additionally, these results have facilitated a more complete understanding of the findings of Storey and Choate.[8] Specifically, the observed finite positive *y*-intercepts are too large to be solely caused by the RMC event; β-proton elimination is clearly the largest contributing factor at −30 °C. The absence of positive intercepts at low temperatures (−50, −80 °C) in the data obtained by Storey and Choate[8] is the direct result of high target $\bar{M}_n$'s, and the low density of kinetic data, due to gravimetric monitoring techniques.

As expected, experiments with the aliphatic initiators confirmed that TMPCl is a slower initiator than TIBCl (a good model for the PIB chain end) for $TiCl_4$-coinitatied IB polymerization. Extremely slow initiation and poor initiation efficiency were observed for *t*-BuCl.

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(17) Addition of 1 M IB dilutes the solvent charge by about 8 vol %. This is irrelevant to the calculation of monomer conversion if the solvent system has no absorbance at 887 cm^{-1} or if the asymptotic peak area at very long reaction times is taken as the reference absorbance corresponding to [IB] = 0.0. However, if the solvent has a finite absorbance at 887 cm^{-1} and the peak area prior to introduction of the monomer is used as the reference absorbance, an overstatement of the actual conversion will occur. The error introduced by this depends on the magnitude of the solvent absorbance at 887 cm^{-1}; e.g., methylcyclohexane is superior to hexane in this regard since it has a much smaller absorbance at this wavenumber. For methylcyclohexane, typical relative absorbance values are 0.03 prior to monomer addition, 1.62 immediately after addition of 1 M IB, and 0.00 at very long reaction times. Use of 0.03 as the reference absorbance yields an error in the calculated conversion of $0.03 \times 100\%/(1.62 - 0.03) = 1.9\%$.

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