# Real-Time Monitoring of Carbocationic Polymerization of Isobutylene via ATR-FTIR Spectroscopy: The *t*-Bu-*m*-DCC/DMP/$BCl_3$ System

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ABSTRACT: The kinetics of isobutylene (IB) polymerization were monitored using real-time, in-situ ATR-FTIR spectroscopic analysis. Polymerization was initiated using the 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)-benzene (*t*-Bu-*m*-DCC)/2,4-dimethylpyridine (DMP)/boron trichloride ($BCl_3$) system in pure methyl chloride (MeCl) solvent, over a range of [$BCl_3$], [IB], and temperatures. Profiles of [IB] as a function of time were obtained by monitoring the absorbance at 887 and/or 1656 $cm^{-1}$, associated with the $=CH_2$ wag and C=C stretch, respectively, of IB. First-order kinetic plots were constructed to obtain the apparent rate constant, $k_{app}$, for polymerization under specific conditions. Over the range of [$BCl_3$] studied, the kinetic order of the reaction with respect to $BCl_3$ was found to be close to unity but was depressed below unity at high [$BCl_3$] due to depression of the overall solvent polarity by $BCl_3$. A similar decrease in polarity of the reaction medium resulted in a decrease in the $k_{app}$ as the initial IB concentration, $[IB]_0$, was increased. Polymerizations conducted in the range −80 to −30 °C revealed a relatively low and positive apparent energy of activation, $E_a$, of 1.7 kcal/mol for the rate of polymerization, which was attributed to the polar 100% MeCl solvent system; the $k_{app}$ of the polymerization increased by 130% as temperature was increased over this range. Over the range of [$BCl_3$], [IB], and reaction temperatures studied, this system produced well-defined, low molecular weight PIB exhibiting extremely narrow molecular weight distribution (PDI = 1.05) and possessing *tert*-chloride chain ends exclusively, with no evidence of direct or moisture initiation or chain termination or transfer occurring during the experimental lifetime.

## Introduction

Because of intense research efforts within the past two decades, advances in carbocationic polymerization techniques have led to a myriad of novel materials spanning a wide range of architectures and potential uses.[1−3] Isobutylene (IB) polymerizations initiated by a cumyl chloride-type initiator (i.e., an inifer) in the presence of $BCl_3$ were among the earliest reported cationic polymerizations yielding well-defined products, in this case telechelic polyisobutylenes (PIB) bearing exclusively *tert*-alkyl chloride end groups.[4,5] Thereafter, $BCl_3$-co-initiated systems were the focus of early, pioneering work concerning the living carbocationic polymerization (LCCP) of IB. Kennedy et al.[6−8] showed that *tert*-alkyl or cumyl ester (or ether)/$BCl_3$ systems could bring about the "truly living" polymerization of IB, although these early systems suffered from slow initiation relative to propagation, which resulted in broad polydispersities (1.3 < MWD < 2.0). The next important development in this field was the use of various externally added electron donors (EDs) to promote LCCP of IB to yield polymers exhibiting narrow molecular weight distribution (1.1−1.2).[9−12] These works demonstrated the synthesis of well-defined polyisobutylene (PIB) via addition of certain types of Lewis bases to the early "conventional" systems that had been developed previously. It was proposed that the addition of a suitable ED served to stabilize the growing carbocations, effectively moderating their reactivity. Although much has been learned about these systems since this innovation, research conducted to date has yet to yield a complete understanding of the role and effect of each of the system components, as well as specific reaction conditions.[13−16] Due to the inherent complexity of LCCP and in large part to the limitations on experimental techniques available to analyze these systems, it is still difficult to produce well-defined materials of a specific architecture without an extensive body of kinetic data for a given system. Thus, there remains a pressing need for continued study of LCCP, especially with regard to the polymerization kinetics of specific systems.

We have recently begun a series of kinetic investigations into the LCCP of IB through the use of real-time in-situ ATR-FTIR spectroscopic analysis. The capabilities and operation of the ReactIR 1000 reaction analysis system have been detailed previously, and we have demonstrated its usefulness in generating accurate kinetic data on IB polymerization.[17,18] We were particularly interested in turning this new method of kinetic analysis to the study of a system facilitating the synthesis of well-defined low molecular weight PIB. In the presence of certain EDs, *tert*-chloride/$BCl_3$ initiating systems have been shown to yield low molecular weight PIB exhibiting polydispersity of ∼1.1.[9,10,19] On the basis of these findings, the present investigation focuses specifically on IB polymerization in methyl chloride (MeCl) solvent utilizing the 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)/2,4-dimethylpyridine (DMP)/boron trichloride ($BCl_3$) initiating system. Although similar systems have been studied, the literature contains very little information concerning the effect of reaction conditions on the apparent rate constant, $k_{app}$, for polymerization of IB, especially utilizing the *t*-Bu-*m*-DCC/DMP/$BCl_3$ initiating system. Therefore, we chose to examine this system by systematically varying the [$BCl_3$], [IB], and the reaction temperature independently to determine their effect on the kinetics of the polymerization and the resulting polymer.

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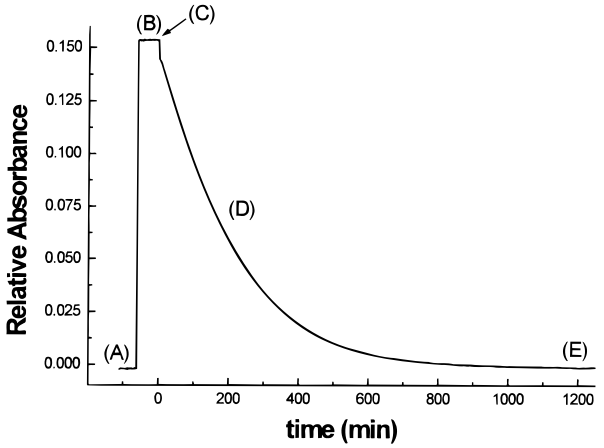

**Figure 1.** Real-time profile of isobutylene monomer depletion over time from analysis of 887 cm$^{-1}$ peak. $[BCl_3]_{eff} = 0.22$ M; $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl; −80 °C.

## Experimental Section

**Materials.** The source and preparation of 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC), methyl chloride (MeCl), isobutylene (IB), 2,4-dimethylpyridine (DMP), and methanol (MeOH) have been previously reported.[20] Boron trichloride ($BCl_3$) was obtained in a cylinder from AIRCO or Matheson Gas Products and freshly condensed into a culture tube immediately prior to use.

**Instrumentation.** Molecular weights and molecular weight distributions were determined using a gel permeation chromatography system equipped with a Wyatt Technology miniDAWN on-line multiangle laser light scattering (MALLS) detector as previously described.[21,22] Polymer samples were run on this system at a concentration of 16 mg/mL in freshly distilled tetrahydrofuran. Solution $^1$H NMR spectra were obtained on a Bruker AC-300 spectrometer using 5 mm o.d. tubes with sample concentrations of 5−15% (w/v) in deuterated chloroform ($CDCl_3$) containing tetramethylsilane as an internal reference. A detailed account of the operation and capabilities of the ReactIR 1000 reaction analysis system has been previously published.[17]

**Polymerization and ATR-FTIR Data Collection Procedure.** All polymerizations were conducted under a dry nitrogen atmosphere in a M Braun Labmaster 130 glovebox equipped with an integral heptane bath maintained at the desired temperature 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).

Temperature and ATR-FTIR data were collected during reagent addition and subsequent polymerization of the isobutylene. The ATR-FTIR data were comprised of spectra collected as the average of either 64, 128, or 1024 scans, over the spectral ranges of 4000−2200 and 1900−650 cm$^{-1}$, with either 4 or 8 cm$^{-1}$ resolution. At 8 cm$^{-1}$ resolution, the acquisition times associated with this number of transients are approximately 18.3, 36.6, and 293 s, respectively. The IB absorbance at a given time was determined by measuring the peak height (peak area yields essentially the same result[17]) at either 887 or 1656 cm$^{-1}$, referenced to either a one- or two-point baseline. Figure 1 shows a typical absorbance vs time profile generated by monitoring the peak height at 887 cm$^{-1}$; the various positions along the profile used to calculate kinetic data are labeled. Region A yields an average value of the baseline absorbance, $A_b$, for the solvent, initiator, and Lewis base (DMP) prior to introduction of IB. After IB has been added, region B yields a new average absorbance value, $A_0$, that is related to the initial monomer concentration, $[IB]_0$. Point C represents the point of introduction of the co-initiator $BCl_3$; thereafter, region D defines the depletion of monomer during living polymerization. The absorbance data were converted to relative IB concentrations using the following relationship,

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

where $[IB]_t$ and $A_t$ are the monomer concentration and relative absorbance, respectively, at time $t$. Alternatively, $A_b$ may be taken as the absorbance at $t = \infty$ (region E), after complete reaction of the monomer.

**Co-initiator Concentration Study.** To ensure solubility of the formed PIB in MeCl and to facilitate analysis by NMR, low molecular weight PIBs were synthesized having a designed number-average molecular weight at full monomer conversion of 4000 g/mol. The following reaction conditions were held constant: temperature = −80 °C; reaction volume = 0.2 L; $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M. The effective $BCl_3$ concentration ($[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0$) was varied as 0.025, 0.055, 0.11, 0.22, 0.30, 0.45, 0.90, or 1.80 M. A representative experimental procedure was as follows: an air background spectrum was obtained by fitting a stainless steel sleeve to the end of the DiComp probe of the ReactIR 1000 and immersing this assembly in the heptane bath at −80 °C. After allowing sufficient time for thermal equilibration, a number of spectra were collected until a relatively constant peak profile was achieved. This spectrum was subtracted from all subsequent spectra to correct for absorbances due to the DiComp probe. From this point forward, the probe remained stationary. The sleeve was removed from the probe and replaced by a 250 mL four-neck round-bottom flask equipped with a mechanical stirrer and platinum resistance thermometer. The flask was then charged with 0.875 g ($3.02 \times 10^{-3}$ mol) of *t*-Bu-*m*-DCC initiator, 181 mL of MeCl (−80 °C), $4.62 \times 10^{-2}$ mL ($4.0 \times 10^{-4}$ mol) of DMP, and 15.9 mL (0.2 mol) of IB (−80 °C). The solution was stirred until thermal equilibration was reached as indicated by the thermometer (~10−15 min), and polymerization was initiated by the rapid addition of the appropriate volume of $BCl_3$ co-initiator (−80 °C). Polymer samples for GPC and NMR analysis were obtained at various reaction times by withdrawing 5−10 mL aliquots from the reaction vessel and immediately adding them to separate scintillation vials containing 10 mL of prechilled (−80 °C) anhydrous MeOH.

**Monomer Concentration Study.** To investigate the effect of monomer concentration, $[IB]_0$ was varied as 0.25, 0.5, 0.75, 1.0, 1.25, 2.0, and 3.0 M, while the following reaction conditions were held constant: reaction temperature = −40 °C; reaction volume = 0.2 L; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[BCl_3]_{eff} = 0.22$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M. The experimental procedure and data collection for this series of polymerizations were the same as described in the previous section.

**Temperature Variation Study.** The effect of temperature on IB polymerization rate was studied over the temperature range −80 to −30 °C. The following reaction conditions were held constant: reaction volume = 0.2 L; $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}] = 1.51 \times 10^{-2}$ M; $[BCl_3]_{eff} = 0.22$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M. Table 1 lists the volume of MeCl, IB, and $BCl_3$ used at each temperature. The experimental procedure was very similar to that described above, with the exceptions that the air background spectra for use in ATR-FTIR analysis were collected at each experimental temperature and MeCl, IB, and $BCl_3$ were chilled to the experimental temperature before addition to the reaction flask.

## Results and Discussion

**Kinetic Data Acquisition and Analysis.** The ReactIR 1000 reaction analysis system was used to generate kinetic data on isobutylene polymerization via real-time ATR-FTIR spectroscopy. This was accomplished by monitoring the intensity of characteristic peaks in the IR spectrum, which reflect the concentration of isobutylene monomer at a given time. Previous kinetic studies of titanium tetrachloride ($TiCl_4$)-co-initiated

**Table 1. Recipes for Isobutylene Polymerizations at Various Temperatures**

| temp (°C) | $[BCl_3]_{eff}{}^a$ (mol/L) | $BCl_3$ (mL) | $[IB]_0$ (mol/L) | IB (mL) | $CH_3Cl$ (mL) | $[I]_0{}^b \times 10^2$ (mol/L) | $[DMP]_0 \times 10^3$ (mol/L) |
|---|---|---|---|---|---|---|---|
| −30 | 0.22 | 3.61 | 1.00 | 17.26 | 179.1 | 1.51 | 2.00 |
| −40 | 0.22 | 3.56 | 1.00 | 16.93 | 179.5 | 1.51 | 2.00 |
| −50 | 0.22 | 3.52 | 1.00 | 16.65 | 179.8 | 1.51 | 2.00 |
| −60 | 0.22 | 3.47 | 1.00 | 16.33 | 180.1 | 1.51 | 2.00 |
| −70 | 0.22 | 3.42 | 1.00 | 16.10 | 180.5 | 1.51 | 2.00 |
| −80 | 0.22 | 3.38 | 1.00 | 15.80 | 180.8 | 1.51 | 2.00 |

[a] $[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0$. [b] $[I]_0 = [t\text{-Bu-}m\text{-DCC}]_0$.

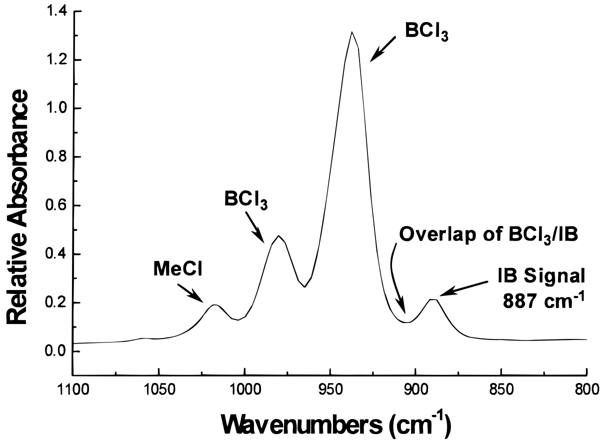

**Figure 2.** Partial ATR-FTIR spectrum of a solution of MeCl, $BCl_3$, and IB illustrating region of overlap near the 887 cm$^{-1}$ IB peak. $[BCl_3] = 1.80$ M; $[IB] = 1.0$ M.

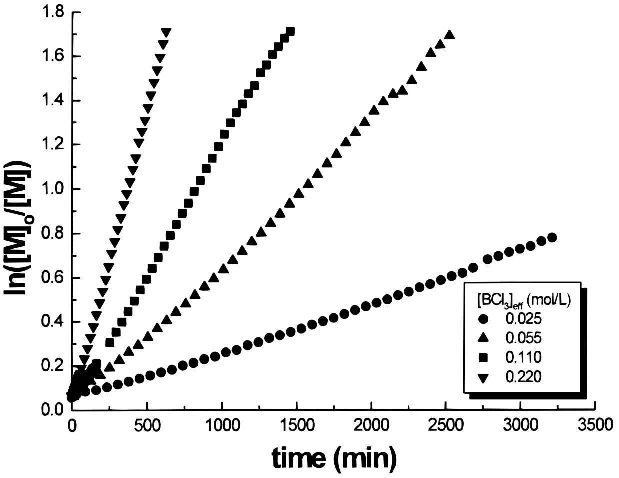

**Figure 3.** First-order kinetic plots for $[BCl_3]_{eff} = 0.025$, 0.055, 0.110, and 0.220 M. $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl; −80 °C.

polymerizations were carried out by monitoring the primary absorbance peak associated with the $=CH_2$ wag of IB located at 887 cm$^{-1}$.[17] However, during this investigation it was determined that an overlap of the $BCl_3$ absorbance with the IB 887 cm$^{-1}$ peak becomes significant at $BCl_3$ concentrations higher than about 0.5 M, as evidenced by the partial ATR-FTIR spectrum, shown in Figure 2, of a solution of $BCl_3$ (1.8 M) and IB (1.0 M) in MeCl. Obviously, this overlap can introduce error into the profile of IB concentration over time. Puskas et al. have demonstrated that the absorbance peak due to the C=C stretch of IB located at 1656 cm$^{-1}$ can also be monitored to obtain kinetic data.[23] Although this peak is less intense than the peak at 887 cm$^{-1}$,[24] it is not influenced by the presence of $BCl_3$, and kinetic data were obtained by analyzing both spectral regions. For experiments conducted at $BCl_3$ concentrations less than 0.5 M, the data were essentially identical regardless of which peak was used for analysis. However, because of the aforementioned spectral overlap, the data were found to differ by as much as 15% when the $[BCl_3]_{eff}$ was equal to or greater than 0.5 M. Consequently, for these high $[BCl_3]_{eff}$ concentrations, kinetic data were obtained exclusively from analysis of the 1656 cm$^{-1}$ peak.

The kinetic data were treated in terms of a quasiliving polymerization in which an equilibrium exists between dormant and active chain ends:

$$P{-}t\text{Cl} + BCl_3 \overset{K_i}{\rightleftharpoons} P^+C^- \overset{K_{diss}}{\rightleftharpoons} P^+ + C^- \qquad (2)$$

P−*t*Cl represents the dormant PIB *tert*-alkyl chloride chain ends, $P^+C^-$ represents the active chain ends in the form of ion pairs, $K_i$ is the ionization equilibrium constant, and $C^+ = BCl_4{}^-$. Equation 2 also shows a dissociation equilibrium, characterized by $K_{diss}$, between ion pairs and free ions, $P^+$. However, the present system contains the strong Lewis base, DMP. Scavenging of protic impurities by the latter creates 2,4-dimethylpyridinium cations, which in the presence of excess $BCl_3$ will possess counteranions that are common with the active chain ends. Under these conditions it is assumed that the active chain ends remain predominantly as paired ions.

The rate of polymerization, $r_p$, is then given by

$$r_p = -\frac{d[M]}{dt} = k_p[P^+C^-][M] = k_{app}[M] \qquad (3)$$

where $k_p$ is the second-order rate constant for propagation, $[P^+C^-]$ is the concentration of ion pairs, [M] is the concentration of monomer, and $k_{app}$ is the apparent rate constant for propagation. Assuming that $K_i$ is small, a combination of eq 3 with the definition for the ionization equilibrium yields, after integration,

$$\ln\frac{[M]_0}{[M]} = k_{app}t = k_pK_i[BCl_3][P{-}t\text{Cl}]_0t \qquad (4)$$

where $[P\text{-}t\text{Cl}]_0$ is the concentration of total chain ends (= 2[*t*-Bu-*m*-DCC]).

**Co-initiator Concentration Study.** The objective of this series of experiments was to determine the apparent kinetic order of the propagation reaction with respect to $[BCl_3]$. To account for losses of $BCl_3$ due to complexation with the Lewis base, an effective $BCl_3$ concentration was used, defined as $[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0$. As presented in Figures 3 and 4, the kinetic data collected from a series of polymerizations conducted at various $[BCl_3]_{eff}$ were used to construct first-order plots according to eq 4. The slopes obtained by performing linear regression on each set of data were taken as the apparent rate constant, $k_{app}$, for polymerization under those conditions and are listed in Table 2.

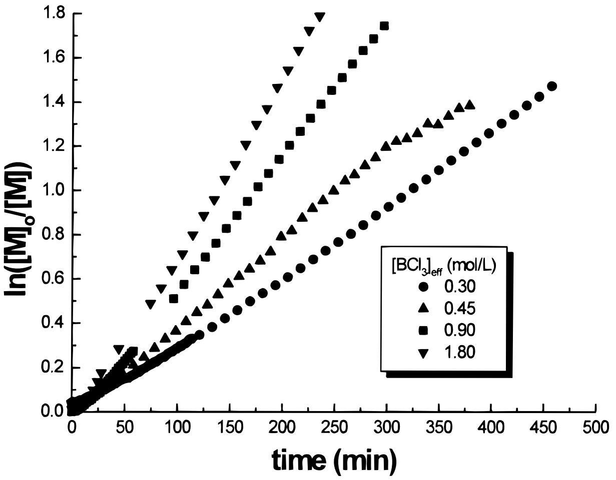

**Figure 4.** First-order kinetic plots for $[BCl_3]_{eff} = 0.30$, 0.45, 0.90, and 1.8 M. $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl; −80 °C.

**Table 2. Apparent Rate Constants for Propagation, $k_{app}$, and $k_{app}$ Normalized to [*t*-Bu-*m*-DCC] and $[BCl_3]_{eff}$, for Various $[BCl_3]_{eff}$[a]**

| $[BCl_3]_{eff}$[b] (mol/L) | $k_{app} \times 10^5$ ($s^{-1}$) | $(k_{app}/[I]_0) \times 10^3$ (L $mol^{-1}$ $s^{-1}$) | $k_{app}/[BCl_3]_{eff}) \times 10^4$ (L $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 0.025 | 0.37 | 0.25 | 1.48 |
| 0.055 | 1.10 | 0.73 | 2.00 |
| 0.11 | 1.97 | 1.30 | 1.79 |
| 0.22 | 4.42 | 2.93 | 2.01 |
| 0.30 | 5.25 | 3.48 | 1.75 |
| 0.45 | 6.47 | 4.28 | 1.44 |
| 0.90 | 10.13 | 6.71 | 1.13 |
| 1.80 | 12.98 | 8.60 | 0.72 |

[a] Reaction Conditions: MeCl; −80 °C; $[IB]_0 = 1.0$ M; $[I]_0 = [t\text{-Bu-}m\text{-DCC}] = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M. [b] $[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0$.

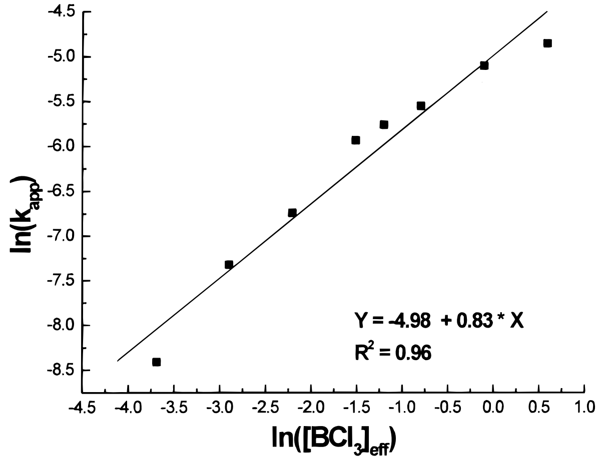

**Figure 5.** Plot of $\ln(k_{app})$ versus $\ln([BCl_3]_{eff})$ to determine order of the reaction with respect to $[BCl_3]_{eff}$.

Whenever possible, the data for each of the polymerizations were analyzed to approximately the same number of half-lives to establish a basis for comparison. From Table 2, it is clear that the $k_{app}$ values increase with increasing $[BCl_3]_{eff}$; however, they are not proportional to $[BCl_3]_{eff}$, as implied by eq 4, since the value of $k_{app}/[BCl_3]_{eff}$ diminishes at high $[BCl_3]_{eff}$.

The apparent kinetic order of the reaction with respect to $[BCl_3]_{eff}$ was determined by plotting $\ln(k_{app})$ versus $\ln([BCl_3]_{eff})$, as shown in Figure 5. Although the data clearly form a curve with continuously decreasing slope, linear regression was performed, and the apparent slope was found to be 0.83. This result agrees well with the value of 0.848 published for a similar system in which $BCl_3$ was the co-initiator.[19]

In a preliminary report involving a more limited data set, we found that the kinetic order of the reaction with respect to $[BCl_3]_{eff}$ was 0.55 over the range $0.22 \le [BCl_3]_{eff} \le 1.8$ M.[25] It was hypothesized that the kinetic order was substantially below unity due to the decrease in polarity of the reaction medium as larger volumes of $BCl_3$ were used. For example, at the highest $[BCl_3]_{eff}$ studied, 1.8 M, $BCl_3$ comprised approximately 14% of the reaction volume; in contrast, at the lowest concentration of 0.22 M it was only about 2 vol %. The reaction medium should be considerably less polar at high $[BCl_3]$, since at −80 °C the dielectric constant of $BCl_3$ is ∼3 while that of MeCl is ∼19.[15,26] A decrease in medium polarity would act to suppress the rate of polymerization by partially offsetting the increase in chain-end ionization expected from increasing Lewis acid concentration. We still feel this hypothesis is correct within the upper range of $[BCl_3]$. However, the present data covering an expanded range of $[BCl_3]_{eff}$ (Table 2 and Figure 5) indicate that curvature is also present within the lower regime of $[BCl_3]_{eff}$ (0.025−0.22 M), where the change in dielectric constant due to changes in $[BCl_3]$ is negligible. Furthermore, the tangent to the curve at the lowest $[BCl_3]_{eff}$ has a slope greater than unity, suggesting the kinetic order may be greater than one in this range. It is doubtful that this reflects involvement of greater than 1 equiv of $BCl_3$ in the ionization equilibrium. If the variation of the apparent order were due to a change in the stoichiometric coefficient for $BCl_3$ in eq 2, the order would be expected to increase, rather than decrease, with increasing $[BCl_3]_{eff}$. Involvement of greater than 1 equiv of $BCl_3$ would also imply the existence of complex counterions of the form $B_nCl_{3n+1}^-$; such counterions would require that boron assume a coordination number of greater than four, which is highly unlikely for a second period element. Therefore, we propose that curvature within the lower range of $[BCl_3]$ is caused by overestimation of $[BCl_3]_{eff}$, due to unaccounted pathways for $BCl_3$ consumption. For example, water scavenging by the Lewis base additive leads to the formation of 2,4-dimethylpyridinium salts with $BCl_3OH^-$ counterions. In the presence of excess $BCl_3$ these counterions disproportionate to form $BCl_4^-$ counterions and the less reactive Lewis acid $BCl_2OH$. Obviously, these losses become fractionally greater as $[BCl_3]_0$ decreases, and this would lead to precisely the behavior observed, i.e., an apparent order greater than one at the lowest concentrations. Despite the slight curvature, when linear regression was performed over the range $[BCl_3]_{eff} \le 0.22$ M (e.g., $[BCl_3]_{eff} < 2$ vol %), the apparent order of the reaction with respect to $BCl_3$ was 1.1 ($r^2 = 0.992$), which is very close to the unit order predicted by eq 4.

Plots of number-average molecular weight ($M_n$) versus percent conversion were also constructed, and data for several $[BCl_3]_{eff}$ are presented in Figure 6. The data are linear and lie close to the theoretical line, demonstrating the absence of bimolecular (direct) chain transfer during the experimental lifetime. However, at low IB conversions the data lie slightly above the theoretical line which may indicate slow initiation but is more likely due to the inherent difficulty of determining accurate values of molecular weight for low molecular weight materials using MALLS. Additionally, as presented in

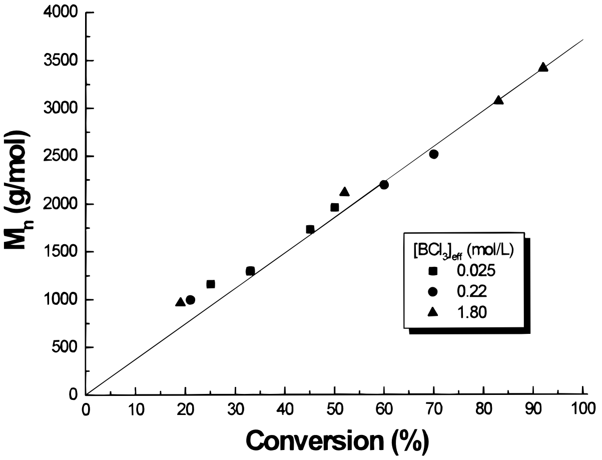

**Figure 6.** $M_n$ versus percent conversion for $[BCl_3]_{eff} = 0.025$, 0.22, and 1.8 M. $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl; −80 °C. Line is theoretical.

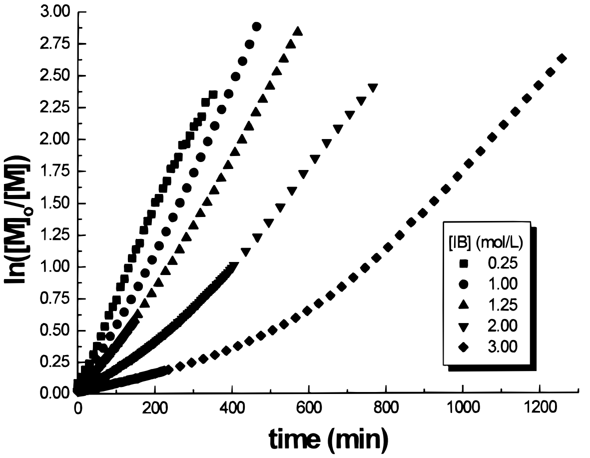

**Figure 7.** First-order kinetic plots for $[IB]_0 = 0.25$, 1.0, 1.25, 2.0, and 3.0 M. $[BCl_3]_{eff} = 0.22$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl; −40 °C.

**Table 3. Apparent Rate Constants for Propagation, $k_{app}$, and $k_{app}$ Normalized to $[I]_0$, for Various $[IB]_0$[a]**

| $[IB]_0$ (M) | $k_{app} \times 10^4$ (s$^{-1}$) | $(k_{app}/[I]_0) \times 10^3$ (L mol$^{-1}$ s$^{-1}$) | $[IB]_0$ (M) | $k_{app} \times 10^4$ (s$^{-1}$) | $(k_{app}/[I]_0) \times 10^3$ (L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|
| 0.25 | 1.13 | 7.48 | 1.00 | 1.05 | 6.95 |
| 0.50 | 1.13 | 7.48 | 1.25 | 0.85 | 5.63 |
| 0.75 | 1.02 | 6.75 | 2.00 | 0.51 | 3.38 |

[a] Reaction conditions: MeCl; −40 °C; $[I]_0 = [t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0 = 0.22$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M.

Figures 3 and 4, the first-order plots constructed according to eq 3 did not exhibit an induction period typical of a system with slow initiation.

**Monomer Concentration Study.** The effect of monomer concentration on the system was investigated by monitoring the kinetics of polymerizations conducted for $[IB]_0 = 0.25$, 0.5, 0.75, 1.0, 1.25, 2.0, and 3.0 M. Figure 7 presents representative data plotted according to eq 3, and the value of $k_{app}$ determined for polymerization at each $[IB]_0$ is listed in Table 3. Since the initiator concentration was held constant for this series, the target molecular weight of the polymers increased with $[IB]_0$. As a consequence, the polymerization carried out at $[IB]_0 = 3.0$ M exceeded the solubility limitations of MeCl (milky-white opacity at moderate conversions), and this may have affected the kinetic data. It should be noted, however, that a previous study on a similar system found that propagation rates were unaffected by precipitation and that monomer diffusion to the active sites was not rate determining.[15]

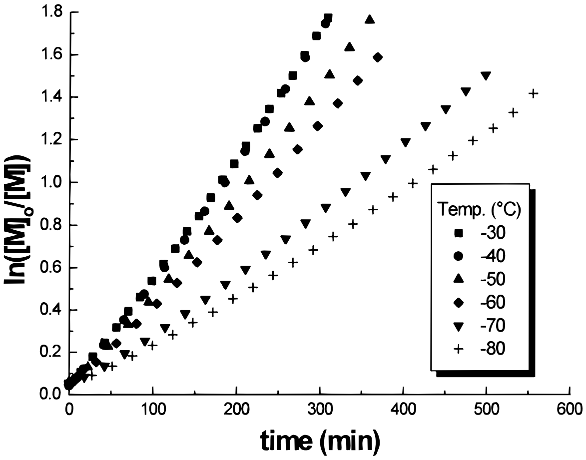

**Figure 8.** First-order kinetic plots for temperatures of −30, −40, −50, −60, −70, and −80 °C. $[BCl_3]_{eff} = 0.22$ M; $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}] = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl.

**Table 4. Apparent Rate Constants for Propagation, $k_{app}$, and $(k_{app})_T/(k_{app})_{-80}$ at Various Temperatures[a]**

| temp (°C) | $k_{app} \times 10^5$ (s$^{-1}$) | $(k_{app})_T/(k_{app})_{-80}$ | temp (°C) | $k_{app} \times 10^5$ (s$^{-1}$) | $(k_{app})_T/(k_{app})_{-80}$ |
|---|---|---|---|---|---|
| −30 | 9.75 | 2.31 | −60 | 6.75 | 1.60 |
| −40 | 9.00 | 2.14 | −70 | 4.91 | 1.17 |
| −50 | 8.18 | 1.94 | −80 | 4.21 | 1.00 |

[a] Reaction conditions: MeCl; $[I]_0 = [t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[BCl_3]_{eff} = [BCl_3]_0 - [DMP]_0 = 0.22$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M.

As listed in Table 3, $k_{app}$ determined from data in Figure 7 is relatively constant for $[IB]_0 \leq 1.0$ M, but for $[IB]_0 > 1.0$ M $k_{app}$ decreases with increasing $[IB]_0$, in agreement with an earlier study.[19] Theoretically, the $k_{app}$ measured for different $[M]_0$ should be the same; however, additional monomer displaces the polar solvent MeCl. At $[IB]_0 = 0.5$ M the monomer accounts for ~4% of the reaction volume, whereas at $[IB]_0 = 2.0$ M, IB occupies ~16% of the reaction volume and significantly decreases the polarity of the reaction medium. Thus, the results can be rationalized in terms of a depression of the ionization equilibrium (eq 2) caused by nonpolar IB. These results are in agreement with Ivan and Kennedy,[15] who also reported that BCl$_3$-coinitiated systems are highly sensitive to the polarity of the reaction medium. For the polymerizations carried out at $[IB]_0 = 2.0$ and 3.0 M, the first-order plot exhibited an upward curvature, indicating that the $k_{app}$ increased significantly as the reaction progressed. This demonstrates that IB monomer is more effective at depressing the reaction medium polarity than the same molar concentration of IB repeat units. The changes in $k_{app}$ during the course of polymerizations carried out over a range of $[IB]_0$ did not affect the plots of number-average molecular weight versus conversion, as they were all linear and passed through the origin.

**Temperature Variation Study.** The effect of temperature on kinetics of the system was investigated over the range from −80 to −30 °C. First-order kinetic plots from data collected on this series of reactions are shown in Figure 8. Table 4 lists the values of $k_{app}$ obtained by performing linear regression on the data for each

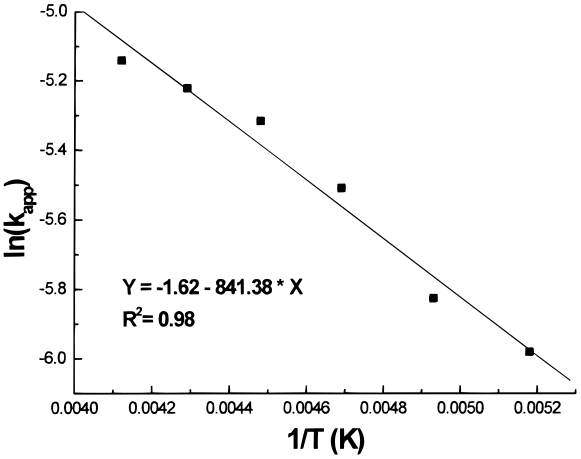

**Figure 9.** Arrhenius plot of $\ln(k_{app})$ versus $1/T$ to determine apparent energy of activation, $E_a$.

temperature; once again, as a basis of comparison the data were analyzed to approximately the same number of half-lives. Comparison of the $k_{app}$'s showed that the rate increased as the reaction temperature was increased, in contrast to IB polymerizations co-initiated by $TiCl_4$ which display negative apparent activation energies for polymerization.[14,20] While the increase in rate was not dramatic, the rate more than doubled going from −80 to −30 °C.

Figure 9 presents an Arrhenius plot of the data as $\ln(k_{app})$ versus $1/T$; from the slope, the apparent activation energy, $E_a$, was calculated to be 1.7 kcal/mol. This positive and relatively low $E_a$ is the product of two competing effects of temperature. The pure rate constant for propagation increases with increasing temperature. However, in the case of living cationic polymerization, the overall rate of polymerization is largely affected by the temperature-dependent ionization equilibrium shown in eq 2. Since $K_i$ is believed to be very small, the chain ends remain predominantly in the dormant state. This equilibrium can be shifted to the right to favor the active state by decreasing reaction temperature or increasing the polarity of the reaction medium. Thus, the generally accepted explanation for the negative $E_a$ oftentimes observed in controlled/living isobutylene polymerization is that an increase in reaction temperature negatively impacts the polymerization rate by decreasing the fraction of chain ends in the active state. Additionally, since an increase in temperature decreases the dielectric constant of a liquid, higher reaction temperatures also decrease the polarity of the reaction medium, further shifting the ionization equilibrium to the dormant state and negatively impacting the rate of polymerization. However, this same decrease in the polarity of the reaction medium is expected to increase the true rate constant of propagation.[27] In the present case, the data suggest that increasing reaction temperature sufficiently increases the true rate constant for propagation so as to more than completely compensate for the shift in the ionization equilibrium.

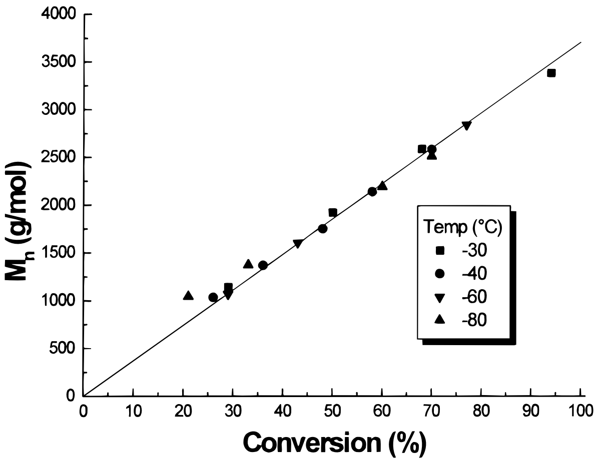

**Figure 10.** $M_n$ versus percent conversion for temperatures of −30, −40, −60, and −80 °C. $[BCl_3]_{eff} = 0.22$ M; $[IB]_0 = 1.0$ M; $[t\text{-Bu-}m\text{-DCC}]_0 = 1.51 \times 10^{-2}$ M; $[DMP]_0 = 2.0 \times 10^{-3}$ M; MeCl. Line is theoretical.

A further comparison can be made between $TiCl_4$-co-initiated IB polymerizations, which are typically conducted in relatively nonpolar solvent systems, e.g., 60/40 hexanes/MeCl, and the present $BCl_3$-co-initiated systems, which are run in 100% MeCl. The apparent activation energy is approximately the sum of the ionization equilibrium enthalpy, $\Delta H_i°$, which is negative, and the activation enthalpy for the bimolecular propagation reaction, $\Delta H_p^‡$, which is positive.[28] Increasing solvent polarity is well-known to decrease the former and increase the latter.[27] Two separate laboratories have obtained a value of −8.5 kcal/mol for the apparent activation energy for $TiCl_4$-co-initiated IB polymerization in 60/40 hexanes/MeCl.[20,28] Fodor et al. additionally reported an $E_a$ of −6.9 kcal/mol for the slightly more polar solvent system, 40/60 hexanes/MeCl.[28] This suggests that, upon increasing solvent polarity, the magnitude of the increase in $\Delta H_p^‡$ is larger than the magnitude of the decrease in $\Delta H_i°$, at least in $TiCl_4$-co-initiated systems. This effect on the activation parameters may be a general one, in which case it is logical that the present systems, conducted in 100% MeCl, would have an activation energy that had been increased to the point of being positive.

Plots of number-average molecular weight ($M_n$) versus percent conversion were also constructed, and data for various reaction temperatures are presented in Figure 10. The data were linear and close to the theoretical line, indicating the absence of bimolecular (direct) chain transfer even at relatively high (−30 °C) polymerization temperature. Thus, the data indicate that for the synthesis of low molecular weight PIB this system affords control over molecular weight and molecular weight distribution even at −30 °C.

**Effect of Reaction Conditions.** It is generally accepted that for a polymerization system to be considered living it is both necessary and sufficient that the $\ln([M]_0/[M]_t)$ versus time and $M_n$ versus conversion plots both be linear.[29] In the present case, the relatively high initiator concentration diminishes the practical consequences of termination, and thus the system will be quite well controlled even if slow terminative chain transfer were operating, i.e., spontaneous $\beta$-proton expulsion followed by rapid onium salt formation with the ED. First-order plots presented in Figures 3, 4, 7, and 8 do in fact exhibit linearity, thus demonstrating the absence of measurable chain termination even at the highest temperatures studied. The $M_n$ versus conversion plots at various $[BCl_3]$ (Figure 6), [IB], and reaction temperatures (Figure 10) are also linear and lie close to the theoretical line, indicating that bimolecular (direct) chain transfer is not occurring during the experimental lifetime. In addition, GPC data on aliquots collected during this study indicated that the

PIB formed possessed a molecular weight distribution on the order of the theoretical Poisson distribution and was considerably more narrow (PDI ~1.05) than materials produced under similar reaction conditions using $TiCl_4$ as the co-initiator (PDI ~ 1.2). Propagation run number (average number of monomer units added per successful ionization) is responsible for this difference; the run number for IB propagation is lower in $BCl_3$-co-initiated systems relative to $TiCl_4$-co-initiated systems.[16,18] Narrow molecular weight distributions also support the assumption that the rate of initiation is fast relative to the rate of propagation, in accordance with the kinetic treatment of this system. Further evidence for the validity of this assumption is that our recent research utilizing in-situ ATR-FTIR analysis has revealed that, under certain conditions, a higher rate of IB consumption occurs during the very early stages of the reaction.[18] This rapid monomer consumption event can be seen in Figure 1, point C, as an initial drop in the relative absorbance due to IB upon addition of the Lewis acid co-initiator. We are currently investigating this newly observed phenomenon as part of our continuing studies of controlled/living IB polymerization.

It has been demonstrated in nearly all cases that the living carbocationic polymerization of isobutylene via a purposefully added *tert*-chloride initiator results in PIB containing exclusively *tert*-chloride chain ends.[1,2] In the case of low molecular weight PIB (<8000 g/mol), the occurrence of side reactions such as protic or direct initiation[30] and/or $\beta$ proton expulsion is readily visible by NMR. Integration of $^1H$ NMR spectra indicated that, under all the reaction conditions studied, the PIB was initiated by the purposefully added initiator and possessed *tert*-chloride chain ends, with no evidence of olefin formation or direct or moisture initiation.

## Conclusions

Real-time in-situ ATR-FTIR spectroscopy was used to monitor the living carbocationic polymerization of IB initiated by the *t*-Bu-*m*-DCC/DMP/$BCl_3$ system in MeCl. The effect of [$BCl_3$], [IB], and reaction temperature on the kinetics of the polymerization was studied. Profiles of the rate of monomer consumption over time were constructed, and the data were interpreted by applying the first-order kinetic rate law for a quasi-living polymerization with fast initiation. From plots of $\ln([M]_0/[M])$ versus time were obtained the apparent rate constants of the polymerization, $k_{app}$, under specific conditions. At low [$BCl_3$] (<0.22 M), the kinetic order of the reaction with respect to $BCl_3$ was found to be approximately unity. A reduction in the polarity of the reaction medium was proposed to be responsible for a shift to lower kinetic order with respect to $BCl_3$ at higher [$BCl_3$]. A similar decrease in polarity of the reaction medium occurred as the $[IB]_0$ was increased, resulting in a decrease in the $k_{app}$ due to a shift in the ionization equilibrium.

An Arrhenius plot of the data from the temperature variation study revealed a relatively low and positive apparent energy of activation for the polymerization of 1.7 kcal/mol. An increase in reaction temperature is believed to lower the ionization equilibrium but more strongly increase the bimolecular rate constant for propagation. As a result, the $k_{app}$ of the polymerization was seen to increase as temperature increased, ultimately doubling over the temperature range −80 to −30 °C. This finding is in direct contrast to $TiCl_4$-co-initiated IB polymerizations, which are generally conducted in less polar media and exhibit a negative apparent energy of activation for polymerization.

First-order kinetic plots, along with $M_n$ versus IB conversion plots, demonstrated that IB polymerization initiated by the *t*-Bu-*m*-DCC/DMP/$BCl_3$ system in MeCl meets the criteria for a living polymerization over a range of conditions, including fairly high temperatures (to −30 °C). This finding is of practical significance, since $BCl_3$-co-initiated IB polymerizations are quite slow; for example, they are significantly slower than $TiCl_4$-co-initiated polymerizations. Thus, the higher temperatures may be used to maximize polymerization rate without compromising the desired degree of control over molecular weight, molecular weight distribution, or *tert*-chloride chain end functionality. Although excellent control in this system is promoted by the relatively high initiator concentration, $BCl_3$ has proven to be the co-initiator of choice for the synthesis of well-defined, low molecular weight PIB (<4000 g/mol) possessing *tert*-chloride chain ends exclusively. In the presence of an initiator and an ED, there is no evidence of direct or moisture initiation, or terminal olefin formation, and the resulting PIBs display molecular weight distributions much more narrow (MWD ~ 1.05) than those for similar systems employing $TiCl_4$ as co-initiator.

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