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Effect of Reaction Conditions on the Kinetics of Living Isobutylene Polymerization at High Initiator/$TiCl_4$ Ratios

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ABSTRACT: The kinetics of isobutylene (IB) polymerization initiated by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ in methylcyclohexane (MeCHx)/methyl chloride (MeCl) or hexane (Hx)/MeCl 60/40 v/v at −80 °C were investigated in the range of $[TMPCl]_0/[TiCl_4]_0 > 1$ using a real-time fiber-optic mid-IR monitoring technique. The rate of IB consumption was monitored by following the disappearance of the 1655 cm^{-1} IR band, characteristic of the C=C stretching vibration. Both the area and the height of the 1655 cm^{-1} band were found to be directly proportional to IB concentration under the conditions investigated. From polymerization rate data the overall rate constant $k_p' = k_pK_{eq}$ was calculated, where k_p is the rate constant of propagation and $K_{eq} = k_1/k_{-1}$ is the equilibrium constant for the dormant/active equilibrium characteristic of living IB polymerization. The investigation revealed that k_p' was very sensitive to solvent quality. $k_p' \approx 0.5-1.7$ L^2 mol^{-2} s^{-1} was found using MeCHx, while $k_p' \approx 1.7-3.4$ L^2 mol^{-2} s^{-1} was obtained using Hx from different providers and/or with and without further purification. GC analysis and real-time IR monitoring revealed the presence of carbonyl contaminants in the solvents, which were found to form a complex with $TiCl_4$. Regardless of solvent quality, the reaction order in $TiCl_4$ was found to be invariably 1 under the conditions investigated. Monomer concentration and temperature were found to have a profound effect on the polymerization; k_p' increased exponentially with an increase of $[IB]_0$ or a decrease in temperature. The apparent activation enthalpy of propagation was found to be $\Delta H_a = -26.4$ kJ/mol.

Introduction

Since the development of living carbocationic polymerization of olefins such as isobutylene (IB), unraveling the mechanism and kinetics of polymerizations has been a major theoretical challenge. In fact, the large majority of living IB polymerizations can be characterized as quasi-living polymerizations with a dynamic equilibrium between active (living and propagating) and dormant (inactive and nonpropagating) species:[1,2]

$$P_n{-}X + MtX_m \overset{k_1}{\underset{k_{-1}}{\longleftrightarrow}} P_n^{+}//^{-}MtX_{m+1} \overset{k_2}{\underset{k_{-2}}{\longleftrightarrow}} P_n^{+} + {}^{-}MtX_{m+1} \qquad (1)$$

Kinetic investigations showed that living isobutylene polymerization co-initiated by $TiCl_4$ proceeds via ion pairs[3−5] and that the ionization equilibrium is shifted toward the covalent species (see eq 1). The following kinetic equations were developed:[4]

$$\ln([I]_0/[I]) = k_1[\,TiCl_4]_0t \qquad (2)$$

$$\ln([M]_0/[M]) = k_p'[TiCl_4]_0t \qquad (3)$$

where $k_p' = K_1k_p = (k_1/k_{-1})k_p$, and the reaction order in [I], [M], and $[TiCl_4]$ is unity. The reaction kinetics of living isobutylene polymerization were studied extensively. While the various systems investigated differ in the nature of initiator (I), additives (electron pair donor (electron pair donor) or proton trap), and solvents, the kinetic order with respect to initiator was found to be invariably 1. The reaction order in monomer was found to be 1 in most cases, but apparent zero-order monomer dependence has also been reported.[6−11] Most research groups investigated $TiCl_4$-co-initiated systems and reported a second-order dependency on $TiCl_4$ concentration. $TiCl_4$ shows a tendency to form dimers at high concentrations[12] and/or at cryogenic temperatures:[13]

$$2TiCl_4 \leftrightarrow Ti_2Cl_8 \qquad (4)$$

However, first-order dependence in $TiCl_4$ under certain conditions was also claimed.[4,14−16] Coexistence of monomeric and dimeric counterions in living IB polymerizations has been suggested.[5,17,18] Subsequently, it was shown that second-order dependence involving dimeric $Ti_2Cl_9^-$ counteranions can only be explained by the reaction of additional $TiCl_4$ with monomeric counteranions, not by direct ionization of chains by neutral dimeric Ti_2Cl_8:[5]

$$P_n^{+}//TiCl_5^{-} + TiCl_4 \leftrightarrow P_n^{+}//Ti_2Cl_9^{-} \qquad (5)$$

Recently, a comprehensive mechanistic scheme, which accommodates both first- and second-order dependence, was introduced by our team[15] and is shown in Figure 1. First-order dependence at $[I]_0 > [TiCl_4]_0$ was verified in our group but is challenged by other groups.[19] Thus, the $TiCl_4$ order is still controversial and will be one of the subjects of the present study.

The dormant-active equilibria in eq 1 were shown to be affected by solvent polarity; less polar medium will favor less dissociated species. It was shown that the equilibrium constant K_1 decreased exponentially with decreasing solvent polarity. Interestingly, recent reports revealed substantial differences between hexane (Hx) and methylcyclohexane (MeCHx) when used as nonpolar components of the mixed solvents routinely used in carbocationic polymerization. Also, the living cationic polymerization of α-methylstyrene with BCl_3 as a co-initiator was much faster when Hx was used as the nonpolar component in the solvent mixture, compared to the case of MeCHx.[20] The rate constant of ionization

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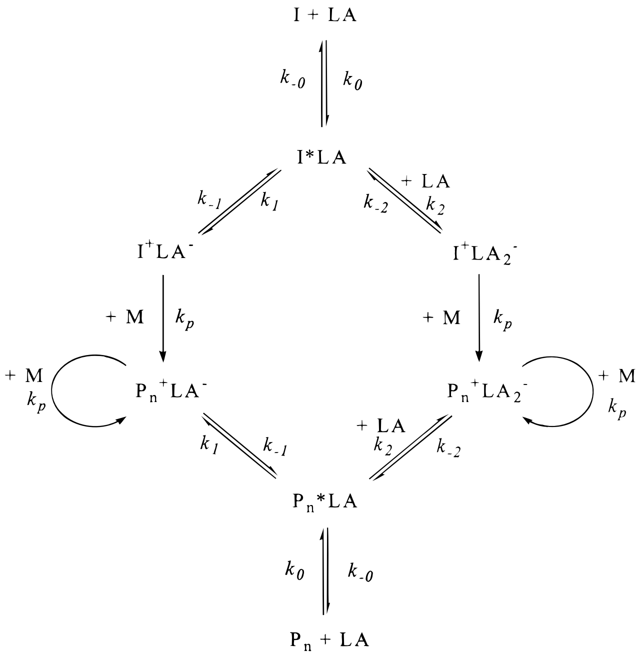

Figure 1. Comprehensive mechanism proposed for the living carbocationic polymerization of IB.[15]

(k_1 in eq 1) in living IB polymerization initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ was shown to be 10 times higher in Hx than in MeCHx.[15] No explanation has been given for these phenomena, and this will be another topic of the present investigations.

The role of certain additives in living carbocationic polymerization is also debated.[14,17,21−26] Common ion salts were demonstrated to shift the ionic equilibria toward less dissociated species, but the role of added nucleophiles (also termed electron pair donors, ED) and proton traps such as 2,6-di-*tert*-butylpyridine (D*t*BP) is still obscure. In the case of IB polymerization the effectiveness of EDs in preventing side reactions such as protic initiation or electrophilic aromatic substitution, and improving initiator efficiencies by reducing the overall propagation rate relative to initiation, was classified according to their Gutmann donor number,[8] defined as the molar enthalpy value of the interaction of the donor with the reference acceptor $SbCl_5$.[27] The most effective EDs such as dimethylacetamide or dimethyl sulfoxide have high Gutmann donor numbers. It was suggested that the role of additives is merely proton scavenging.[22,28] In fact, some additives were used as colorimetric indicators of effective proton scavenging.[29] At the same time, EDs were found to reduce the rate of IB polymerization.[5,26,30,31] The reaction order in 2,4-dimethylpyridine, which gives a soluble complex with $TiCl_4$, was found to be 0.25, similarly to pyridine, which forms an insoluble complex.[5] The proton trap D*t*BP was found to cause proton elimination and subsequent chain coupling.[32,33] It was demonstrated that in the presence of Lewis bases chain coupling and carbocation rearrangement occurred simultaneously. D*t*BP participated in bimolecular proton abstraction, producing exclusively *exo*-olefin end groups at higher temperatures. Complexing bases such as 2,6-dimethylpyridine produced both *exo*- and *endo*-olefins.[34,35] Since the role of additives is not clear, in our investigations we will use only D*t*BP as a noncomplexing proton trap.

This paper will investigate the effect of $[I]_0/[TiCl_4]_0$ ratio, solvent quality, monomer concentration, and temperature on the kinetics of IB polymerizations at $[I]_0 > [TiCl_4]_0$. Because of ambiguities, and in line with our previous reports, we will use only D*t*BP to eliminate protic initiation, and the effect of D*t*BP on the rate of IB polymerization will be investigated. The kinetic investigations will utilize real-time monitoring by a fiber-optic mid-IR technique, developed in collaboration with Remspec, Inc. In the course of our kinetic studies we recognized a need for a convenient, real-time method of monitoring IB consumption. The first reports of real-time monitoring of carbocationic polymerization using a fiber-optic ATR and a conduit-type ATR IR technique have been published simultaneously.[36,37] Recently, a report appeared on the real-time monitoring of living radical polymerization using a conduit IR technology.[38] While the fiber-optic cable cannot be used below 1000 cm^{-1}, the flexible cable allows for easy maneuverability, and the probe is immersed directly in the reaction vessel. The conduit technology[37] was used to monitor the disappearance of the 887 cm^{-1} wag of the $=CH_2$ group of IB in $TiCl_4$-co-initiated polymerizations. In BCl_3-co-initiated polymerizations, however, this band was found to overlap with the BCl_3; thus, the C=C double bond stretching at 1656 cm^{-1} was monitored.[19] The fiber-optic technique followed the disappearance of the C=C double bond stretching at 1656 cm^{-1} and the C−H bending in the CH_3 group of IB at 1375 cm^{-1}. In addition, the appearance of the doublet characteristic of the C−H bending in the *tert*-butyl groups of the forming PIB at 1365 and 1390 cm^{-1} was also monitored.[36] In this paper, the C=C double bond stretching at 1656 cm^{-1} will be monitored with the redesigned ATR probe, which is more robust and not sensitive to freeze fracture.

Experimental Section

Materials. Hexane (Hx) and methylcyclohexane (MeCHx), (Caledon, Aldrich) were distilled from calcium hydride just prior to use or used as received where specified. Methyl chloride (MeCl) and isobutylene (IB) (Matheson) were dried by passing the gaseous material through in-line gas purifier columns packed with $CaCl_2$/BaO. They were condensed in the cold bath of the glovebox prior to use. 2-Chloro-2,4,4-trimethylpentane was synthesized as described.[39] 2,6-Di-*tert*-butylpyridine (D*t*BP) (Aldrich) was used as received. Degassed methanol was used to quench the reactions.

Procedures. a. Polymerizations. Polymerizations were carried out under a dry nitrogen atmosphere (H_2O, <1 ppm; O_2, <5 ppm) in a Mbraun LabMaster 130 glovebox at −80 °C. The moisture content was monitored and kept at the desired level (H_2O, <1 ppm). The hexane bath was cooled by liquid nitrogen and maintained at −80 °C with an FTS Flexi Cool immersion cooler. A 500 mL three-neck round-bottom flask, equipped with an overhead stirrer and a thermocouple, was charged with the cosolvents (MeCHx/MeCl or Hx/MeCl, 60/40 v/v). The reaction volume was 250 mL. The addition sequence of the reactants was as follows: TMPCl, D*t*BP, and IB. The reaction was started by the rapid addition of a chilled stock solution of $TiCl_4$ in Hx or MeCHx, depending on the cosolvent system used. For gravimetric conversion analysis, aliquots were subsequently taken at specified times and quenched in chilled culture tubes containing methanol. The reactions were quenched after completion as indicated by IR, by addition of prechilled methanol. MeCl was evaporated, and the polymer was dissolved in Hx. The solution was washed with distilled water, dried over $MgSO_4$, filtered, precipitated into a large excess of methanol, and dried in a vacuum oven for 1 week.

b. IR Monitoring. The polymerization reactions were monitored in real time using an attenuated total reflectance (ATR) fiber-optic probe. The IR probe (Remspec Inc.), with its

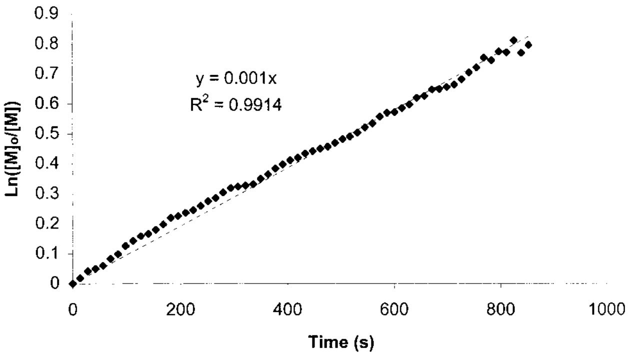

Figure 2. A typical $\ln([M]_0/[M]_t)$ vs time plot by IR monitoring. $[IB]_0 = 2.00$ mol/L; $[I]_0 = 0.054$ mol/L; [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80$ °C.

source and receiver cables, is interfaced with a Bio-Rad FTS 175C FTIR unit, to which a mid-IR fiber-optic liquid nitrogen cooled 0.5 × 0.5 mm MCT detector is attached. The cable bundle is fed into the drybox through a port, and the probe is immersed into the reactor. The cable ends are aligned manually. Optimum signal/noise ratios were obtained when the center burst maximum (negative peak on the on-screen display) was about −5 to −7 V at an amplifier gain between 1 and 3 within the ±10 V signal range. The signal resolution was 8 cm^{-1}. Background spectra was taken before the addition of IB into the polymerization mixture. IR spectra (64 acquisitions each) were taken every 14 s and collected into one multifile (150−250 spectra) by the Bio-Rad Win-IR software. The kinetic data were evaluated with the REMPAEK software package (Remspec Inc.) This software application for GRAMS/32 is designed to take a large set of spectral data and calculate the area of an individual peak in each spectrum. To evaluate the kinetic data, the main multifile was split into individual subfiles via the application program *mfutils* within GRAMS/32. The peak areas were calculated using the Lorentzian curve fit in REMPAEK. Calibration demonstrated proportionality between IB concentration and both the area and the height of the 1656 cm^{-1} band, characteristic of the C=C stretch in IB. Semilogarithmic first-order monomer consumption plots were obtained by ratioing the 1656 cm^{-1} peak area at any given time to the area at time = 0, i.e., prior to the addition of $TiCl_4$.

c. Solvent Analysis. MeCHx and Hx were analyzed by UV−vis spectroscopy using a Varian UV−vis Cary 50 spectrophotometer and by GC-MS using a Varian 3400 GC equipped with a DB5 30 m column and a Finnigan MAT 8200 detector.

Results and Discussion

Effect of the $[I]_0/[TiCl_4]_0$ Ratio and Solvent Quality. In the recent publication of our group,[15] Kaszas's experiments[4] were repeated, and $k_p' = 0.53$ and 0.55 $L^2/(mol^2\ s)$ were found for $[I]_0/[TiCl_4]_0 = 1$ and 4, respectively. In line with Kaszas' original claim, these results were considered to verify $n = 1$ for high $[I]_0/[TiCl_4]_0$ ratios. These results were challenged;[19] thus, we embarked on a thorough investigation of the $TiCl_4$ reaction order. $[TiCl_4]_0$ was varied between 20 and 40 mmol/L, while all other concentrations were kept constant. The reactions were followed by fiber-optic IR monitoring, and k_p' values were obtained from semilogarithmic monomer consumption plots. A typical plot is shown in Figure 2. Table 1 list data obtained in MeCHx/MeCl mixtures where the MeCHx was purified by distillation from CaH_2. To our surprise, $k_p' = 1.4$−1.7 $L^2/(mol^2\ s)$ was consistently found under these conditions. We then repeated the experiments using 99% anhydrous MeCHx as specified by Storey et al.[2] The data show that $k_p' = 0.3$−0.7 $L^2/(mol^2\ s)$ was found. While the k_p' values are different for the purified and unpurified solvent, they are not affected by the change in $[TiCl_4]_0$ in the range of $[I]_0/[TiCl_4]_0 > 1$ within experimental error.

Table 1. k_p' **Values in MeCHx/MeCl = 60/40 v/v by IR for** $[I]_0/[TiCl_4]_0 > 1$[a]

	k_p', $L^2/(mol^2\ s)$	
$[TiCl_4]_0$, mol/L	MeCHx[b]/MeCl	MeCHx[c]/MeCl
0.02	1.5	0.6
	1.6	0.4
0.025		0.5
		0.3
0.03	1.6	0.7
	1.4	0.5
0.04	1.5	0.6
	1.6	0.5
	1.7	

[a] $[IB]_0 = 2$ mol/L; $[TMPCl]_0 = 0.054$ mol/L; [D*t*BP] = 0.008 mol/L; $T = -80$ °C. [b] MeCHx distilled off CaH_2 before use (Aldrich, reagent grade). [c] MeCHx used as received (Aldrich anhydrous).

Table 2. k_p' **Values in Hx/MeCl 60/40 v/v by IR for** $[I]_0/[TiCl_4]_0 > 1$[a]

	k_p', $L^2/(mol^2\ s)$	
$[TiCl_4]_0$, mol/L	hex[b]/MeCl	hex[c]/MeCl
0.02	1.5	3.5
	1.6	
0.025	1.6	
0.03	1.6	3.1
0.04	1.5	3.7
	1.7	
0.05		4.1

[a] $[IB]_0 = 2$ mol/L; $[TMPCl]_0 = 0.054$ mol/L; [D*t*BP] = 0.008 mol/L; $T = -80$ °C. [b] Hx distilled off CaH_2 before use (Caledon, reagent grade). [c] Reference 15, Hx distilled off CaH_2 before use (Aldrich, reagent grade).

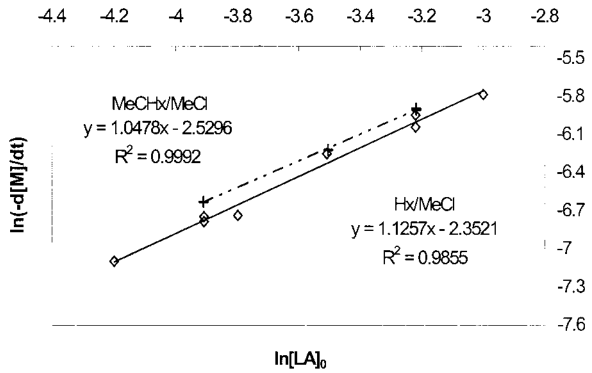

Figure 3. $\ln(-d[M]/dt)$ vs $\ln[TiCl_4]_0$ plot of IB polymerizations $[I]_0/[TiCl_4]_0 > 1$. $[IB]_0 = 2.0$ mol/L; $[I]_0 = 0.054$ mol/L; [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; Hx/MeCl = 60/40 v/v; $T = -80$ °C.

Based on these curious results and on literature data indicating differences between MeCHx and Hx,[15,20] a series of polymerizations were conducted using Hx as the nonpolar ingredient. There is no significant difference between the dielectric constant of Hx and MeCHx ($\epsilon = 1.8865$ and 2.0240, respectively);[40] thus, theoretically no differences would be expected. Table 2 lists data obtained using Hx from two different suppliers, both of them distilled from CaH_2 before use. The differences are striking. Comparison of Tables 1 and 2 reveals that nearly identical rates were obtained in Aldrich MeCHx and Caledon Hx distilled from CaH_2 prior to use.

Figure 3 shows $\ln\{-d[M]/dt\}$ versus $\ln[TiCl_4]_0$ for all the data combined in Tables 1 and 2. The slopes for MeCHx ($n = 1.04$) and Hx ($n = 1.13$) verify that the

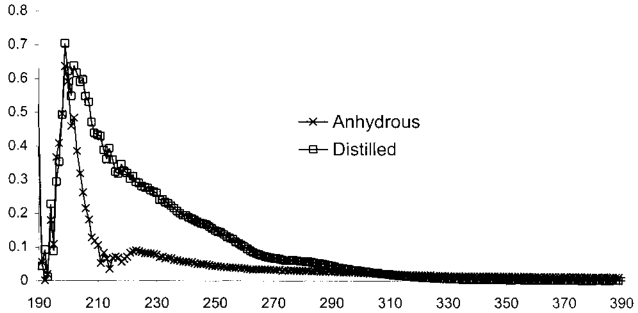

Figure 4. UV of anhydrous MeCHx (Aldrich, used as received) and MeCHx and Hx (Aldrich) distilled from CaH_2 before use.

Table 3. GC-MS Analysis of Solvents: Possible Matches

MeCHx[a]	Hx[b]
2-hexynol	2-methylpropyl ester or cyanic acid
cyclooctanone	1-(ethenyloxy)-2-methyl-butane
7-oxabicyclo(4,1,0)heptane	2-nitrobutane
3-hexanal	
3-ethylcyclopentanone	
cyclohexanone	

[a] MeCHx distilled off CaH_2 before use (Aldrich, reagent grade) and MeCHx used as received (Aldrich anhydrous). [b] Hx distilled off CaH_2 before use (Aldrich, reagent grade).

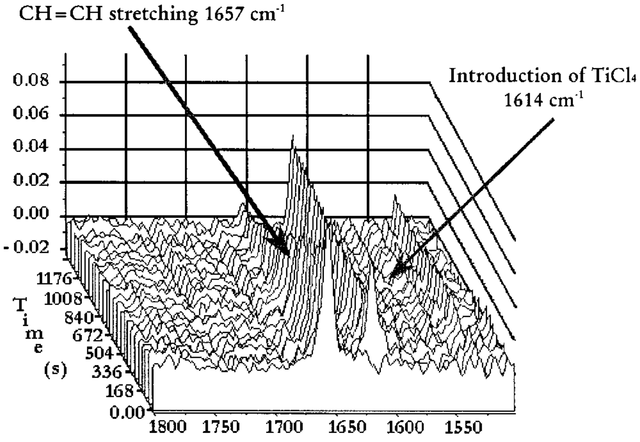

Figure 5. Waterfall IR plot of an IB polymerization displaying the C=C stretch signal at 1656 cm^{-1} and the strong 1614 cm^{-1} signal upon $TiCl_4$ addition. $[IB]_0 = 2.0$ mol/L; $[TMPCl]_0 = 0.054$ mol/L; $[TiCl_4]_0 = 0.04$ mol/L, $[DtBP] = 0.008$ mol/L, MeCl/MeCHx = 40/60 v/v, MeCHx used as received (Aldrich anhydrous).

Table 4. Effect of $[IB]_0$ on k_p' by IR for $[I]_0/[TiCl_4]_0 > 1$[a]

$[IB]_0$ (mol/L)	k_p' ($L^2/(mol^2\ s)$)	$[IB]_0$ (mol/L)	k_p' ($L^2/(mol^2\ s)$)
1.5	1.80	3.5	0.70
2	1.47	4	0.55
2.5	1.10	4.5	0.45
3	0.86	5	0.37

[a] $[TMPCl]_0 = 0.054$ mol/L; $[TiCl_4]_0 = 0.04$ mol/L; $[DtBP] = 0.008$ mol/L; MeCHx/MeCl 60/40 v/v, $T = -80$ °C.

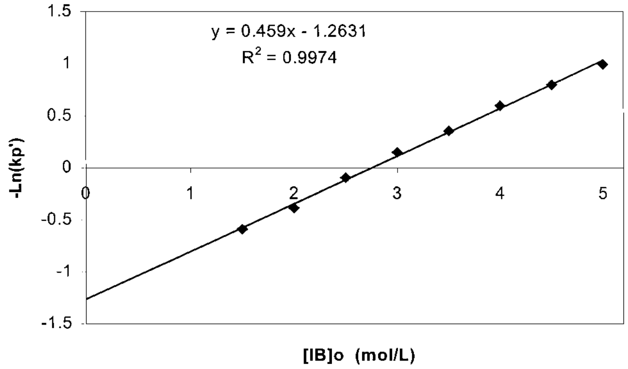

Figure 6. $-\ln k_p'-[IB]_0$ plot in IB polymerizations. $[TMPCl]_0 = 0.054$ mol/L; $[TiCl_4]_0 = 0.04$ mol/L; $[DtBP] = 0.008$ mol/L; MeCHx/MeCl = 60/40 v/v; $T = -80$ °C.

reaction order in $TiCl_4$ is nearly one under the conditions investigated. While the reaction order was found to be consistently one in various solvents, the strikingly different k_p' values prompted us to take a closer look of the solvents. UV/vis spectroscopy revealed the presence of contaminants absorbing in the 190−300 cm^{-1} region, as shown in Figure 4, and GC-MS analysis revealed the presence of various carbonyl-containing contaminants in the solvent. The possible matches are listed in Table 3. More carbonyl contaminants were found in MeCHx than in Hx; the total amount of the impurities was as high as 2% in certain samples. During our polymerization experiments, we noticed the appearance of a strong IR absorption at 1614 cm^{-1} upon the addition of $TiCl_4$ into the polymerization charge. Figure 5 shows a “waterfall” display of the appearance of this peak. The height of this peak was found to vary from solvent to solvent and was mainly present when using MeCHx (99%, Aldrich anhydrous). Carbonyl compounds were shown to form complexes with $TiCl_4$, lowering the carbonyl frequencies and displaying strong IR absorptions. For instance, cinnamic aldehyde, with a carbonyl absorption at 1676 cm^{-1}, was shown to form 1:1 and 1:2 complexes with $TiCl_4$, absorbing at 1607 and 1610 cm^{-1}, respectively.[41] The 1647 cm^{-1} carbonyl absorption of 2-(*N*,*N*-diethylaminovinyl)cyclohexan-1-one was found to shift to 1617 cm^{-1} upon complexation with $TiCl_4$.[42] The presence of cyclohexanone was identified in MeCHx. Carbonyl compounds are complexing EDs, which can explain the slower rates in this solvent.

In summary, the results presented here demonstrate that the living carbocationic polymerization of IB displays first-order dependence in $TiCl_4$ at $[I]_0/[TiCl_4]_0 > 1$ under the conditions investigated. Since at $[I]_0/[TiCl_4]_0 < 1$ second order dependence was found, our proposed mechanism of competing reaction paths with monomeric and dimeric counteranions,[15] shown in Figure 1, seems to be a very feasible mechanism. Our investigations demonstrate the sensitivity of path A of living carbocationic IB polymerizations toward solvent quality. Comparisons between results of various research groups should take this into consideration.

Monomer Concentration Effect. The effect of initial monomer concentration on the rate of IB polymerization was studied using the following conditions: MeCHx/MeCl in a 60/40 volume ratio, $[TMPCl]_0 = 0.054$ mol/L, $[DtBP] = 0.008$ mol/L, and $[TiCl_4]_0 = 0.04$ mol/L. The results are presented in Table 4 and Figure 6. Figure 6 clearly shows a negative exponential dependence of k_p' on $[IB]_0$ (k_p' is proportional to $[IB]_0^{-0.46}$). The plot in Figure 6 allows the prediction of k_p' values for a given $[IB]_0$. This also must be kept in mind when comparing experiments at different $[IB]_0$. With increasing $[IB]_0$ the polarity of the system decreases and subsequently affects the dormant/active equilibrium. A similar effect has been reported when *n*-pentane was used to reduce the polarity of the reaction medium.[10]

Effect of Temperature. Similarly to previous studies presented by other research teams for $[I]_0/[TiCl_4]_0$

Table 5. Effect of Temperature on k_p' by IR for $[I]_0/[TiCl_4]_0 > 1$[a]

temp (°C)	k_p' ($L^2/(mol^2\ s)$)	temp (°C)	k_p' ($L^2/(mol^2\ s)$)
−80	1.5	−50	0.2
−70	0.8	−40	0.1
−60	0.4		

[a] $[IB]_0 = 2$ mol/L, $[TMPCl]_0 = 0.054$ mol/L, $[TiCl_4]_0 = 0.04$ mol/L, [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v, MeCHx used as received (Aldrich anhydrous).

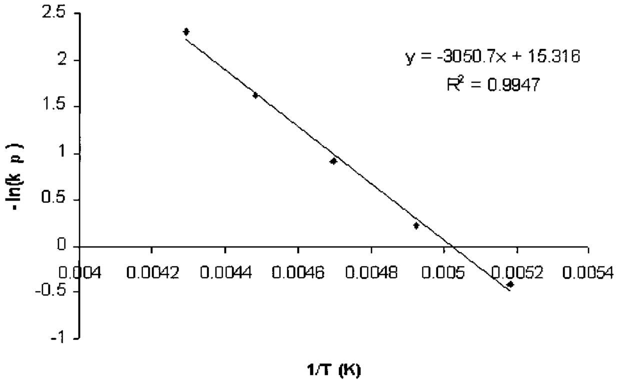

Figure 7. −ln k_p' vs 1/*T*, $[IB]_0 = 2$ mol/L, $[TMPCl]_0 = 0.054$ mol/L, $[TiCl_4]_0 = 0.04$ mol/L, [D*t*BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v, MeCHx used as received (Aldrich anhydrous).

Table 6. Effect of D*t*BP on k_p' by IR for $[I]_0/[TiCl_4]_0 > 1$[a]

	k_p' ($L^2/(mol^2\ s)$)	
[D*t*BP] (10^{-3} mol/L)	MeCl/MeCHx[b]	MeCl/Hx[c]
4	1.6	2.2
8	1.5	2.1
12	1.6	2.1
16	1.7	2.2

[a] $[IB]_0 = 2$ mol/L; $[TMPCl]_0 = 0.054$ mol/L; $[TiCl_4]_0 = 0.04$ mol/L; MeCHx/MeCl or Hx/MeCl = 60/40 v/v; *T* = −80 °C. [b] Hx distilled off CaH_2 before use (Caledon, reagent grade). [c] Hx distilled off CaH_2 before use (Aldrich, reagent grade).

< 1,[5,43] we observed a substantial increase of the polymerization rate with decreasing temperature for $[I]_0/[TiCl_4]_0 > 1$ as well. Table 5 lists k_p' values obtained at various temperatures. Figure 7 displays the Arrhenius plot. The apparent enthalpy of activation was found to be $\Delta H_a = -26.4$ kJ/mol, close to those published earlier for $[I]_0/[TiCl_4]_0 < 1$ (−33.5 kJ/mol in Hx/MeCl 60/40 v/v and −28.9 kJ/mol in Hx /MeCl 40/60 v/v).[5,43] The values seem to indicate that the solvent quality may have an effect on the apparent activation enthalpy as well. This phenomenon requires further studies.

Effect of D*t*BP Concentration. A series of experiments were conducted with varying the concentration of D*t*BP at − 80 °C in MeCHx/MeCl and Hx/MeCl 60/40 v/v, while keeping all other concentrations constant ($[IB]_0 = 2$ mol/L, [TMPCl] = 0.054 mol/L, $[TiCl_4]_0 = 0.04$ mol/L); the results are listed in Table 6. At this temperature and these concentrations, D*t*BP had no effect on k_p'.

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