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Kinetic Study of the Living Cationic Polymerization of Isobutylene Using a Dicumyl Chloride/TiCl$_4$/Pyridine Initiating System

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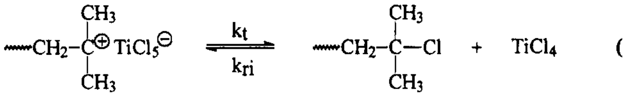
ABSTRACT: A kinetic study of the living carbocationic polymerization of isobutylene using a 1,4-bis(2-chloro-2-propyl)benzene (dicumyl chloride) (DCC)/TiCl$_4$ initiating system in conjunction with pyridine as an externally added Lewis base, in mixed hexane/methyl chloride cosolvents was conducted utilizing a wide variety of conditions. The investigation revealed that at −80 °C the rate of polymerization was first-order in monomer concentration, first-order in the concentration of the initiator DCC, and second-order in coinitiator (TiCl$_4$) concentration and was proportional to the −0.28 power of the pyridine concentration. In addition, the rate of polymerization was found to decrease with increasing temperature and to increase with increases in solvent polarity. It was also revealed that only ion-paired chain carriers participate in propagation. These results are consistent with a mechanism in which propagation is a simple bimolecular reaction between active polyisobutylene (PIB) chain ends and monomer, and the concentration of active PIB chains is determined by an equilibrium between active and dormant species.

Introduction

The development of living cationic polymerization of isobutylene (IB) may be traced to the early 1980s for polymerizations employing the so-called "quasiliving" polymerization technique, that was reported for a number of cationically polymerizable monomers including α-methylstyrene[1] and IB.[2] This method was carried out under conditions of monomer starvation and, for the case of IB, involved one of several reported initiators, TiCl$_4$ as coinitiator, and 60/40 (v/v) hexane/methylene chloride as cosolvents.[2] Living characteristics were attributed to rapid initiation, suppression of chain transfer to monomer, and reversibility of termination, as shown below, where k_t and k_{ri} are the rate constants for termination and reionization, respectively. The importance of these early systems is underscored by the fact that this equilibrium between dormant and active chain ends (in various reported forms, e.g., tight ion pairs, polar covalent, etc.) has become a hallmark of living IB polymerizations specifically and living carbocationic polymerizations in general.



$$\sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\,TiCl_5^{\ominus} \underset{k_{ri}}{\overset{k_t}{\rightleftharpoons}} \sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + TiCl_4 \qquad (1)$$

Later it was found that certain initiators could produce living characteristics without the use of monomer starvation. For instance, living IB polymerization was obtained when 1,4-bis(2-methoxy-2-propyl)benzene (*p*-dicumyl methyl ether) was used in conjunction with TiCl$_4$ in a 60/40 (v/v) hexane/methyl chloride cosolvent system at −80 °C.[3] The living nature of this polymerization was attributed by Kaszas et al.[4] to the formation of an *in situ* electron donor (ED), namely TiCl$_3$OCH$_3$, which serves to reduce unwanted side reactions, resulting in the formation of narrow molecular weight distribution (MWD) polymers. This mechanism also featured an equilibrium between dormant *tert*-alkyl chloride end-capped polymers and active species; however, the active species were said to be stabilized by complexation with the *in situ* ED. The idea of cation stabilization by EDs, i.e., Lewis bases, was extended by investigating the effect of deliberately added ("external") EDs on the polymerization of IB. EDs such as dimethyl sulfoxide and dimethylacetamide were found to cause a significant decrease in the rate of polymerization, a suppression of chain transfer and termination reactions, and a narrowing of product MWD, when used in conjunction with a cationogen-type initiator and a Lewis acid coinitiator such as TiCl$_4$.[5] In addition, these EDs were found to eliminate uncontrolled initiation by protic impurities and intramolecular alkylation of aromatic initiators, preventing indanyl structures. Stabilization of these systems by an externally added ED has been ascribed to the interaction of an ED/Lewis acid complex with the growing chain end.[4–6] The proposition that the cation-stabilizing species is an ED/Lewis acid complex can be attributed to the fact that the molar concentration of Lewis acid is usually 2–20 times the sum of the initiator plus ED concentrations, and that TiCl$_4$, as well as BCl$_3$, rapidly form well-defined complexes with O-, S-, and N-containing compounds.[7]

Recently, the concept of carbocation stabilization by EDs has been challenged. Faust et al.[8] have suggested that the main function of externally added EDs is to react with protic impurities in the polymerization system. Thus with uncontrolled, protic initiation eliminated, according to these authors, the polymerization of IB coinitiated with TiCl$_4$ is living due to the absence of chain transfer and the presence of reversible termination. Evidence for this proposition follows primarily from the observation that the polymerization of IB at −80 °C using a 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (*t*-Bu-*m*-DCC)/TiCl$_4$ initiating system in 60/40 (v/v) hexane/methyl chloride in the presence of di-*tert*-butylpyridine (DtBuP) shows a linear increase of M_n with conversion and linearity of first-order rate plots with $k_p[M^+]$ independent of the concentration of DtBuP. According to these authors, since DtBuP is incapable of a nucleophilic interaction with either carbocations or Lewis acids due to steric hinderance around the nitrogen atom, but exhibits great specificity toward protons

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due to its very high basicity, living characteristics cannot be the result of carbocation stabilization.

We have investigated and utilized a system for the living cationic polymerization of isobutylene consisting of 1,4-bis(2-chloro-2-propyl)benzene (dicumyl chloride) (DCC) as the initiator, $TiCl_4$ as the coinitiator, and pyridine as the electron donor in a 60/40 (v/v) hexane/methyl chloride cosolvent system.[9] This system has been used very successfully for the synthesis of polyisobutylene (PIB) telechelic ionomers possessing a narrow MWD between ionic groups,[10] block copolymers,[11-13] and block copolymer ionomers.[14] Furthermore, it has proven to be suitable for the synthesis of nearly monodisperse PIBs with molecular weights as high as 100 000 g/mol.[9] To better understand this polymerization system, a complete kinetic study was undertaken. This paper describes the results of studies aimed at determining the effect each component of the system exerts on the rate of polymerization, as well as the effects of solvent polarity and temperature. Facilitating the studies is the fact that the pyridine-based system produces only one type of ED, namely the pyridine:$TiCl_4$ complex, since DCC contains no heteroatoms such as O, N, or S which could produce competing *in situ* EDs. Complicating the study is the fact that the pyridine:$TiCl_4$ complex is at least partially insoluble in the polymerization medium, and therefore the concentrations of pyridine and $TiCl_4$ must be viewed critically with this in mind. Finally, the results of these studies were interpreted in terms of the mechanisms for living cationic polymerization that have been presented in the literature.

Experimental Section

Materials. DCC was prepared from 1,4-bis(2-hydroxy-2-propyl)benzene (dicumyl alcohol) (Goodyear Tire and Rubber Co.) by reaction with gaseous HCl, using a modification of a procedure described previously.[9] Hexane (Aldrich Chemical Co.) was dried prior to use by distillation from calcium hydride. Methyl chloride and isobutylene (Linde Division, Union Carbide Corp.) were dried by passing the gaseous material through a column packed with BaO and $CaCl_2$. $TiCl_4$, pyridine, and anhydrous methanol were used as received from Aldrich Chemical Co.

Procedures. Polymerizations were carried out in a glovebox under dry nitrogen. Specific reaction conditions are listed in the figure captions and tables. A representative polymerization procedure used to construct a single first-order plot was as follows: 400 mL of methyl chloride, 1.09 mol of IB, 1.0×10^{-3} mol of DCC, 600 mL of hexane, and 3.1×10^{-3} mol of pyridine were added sequentially to a chilled 2000 mL three-necked round-bottomed flask, equipped with a mechanical stirrer. Methyl chloride and IB were condensed into chilled graduated cylinders before addition to the flask. The mixture was stirred for 0.5 h; then 50 mL portions of the solution were transferred to chilled, 25 × 250 mm culture tubes *via* a 50 mL volumetric pipet. With vigorous shaking, 9.1×10^{-4} mol of $TiCl_4$ was rapidly injected into each stoppered culture tube to commence polymerization. Polymerizations in the various tubes were terminated at differing times, as dictated by experimental design, by the injection of 10 mL of prechilled methanol.

The fractional yield (Y) of polymer was determined gravimetrically, and the quantity $[M]_0/[M]$ was calculated as $1/(1 - Y)$.

Results and Discussion

Initial investigations of the polymerization of IB using a *t*-Bu-*m*-DCC or 1,3,5-tris(2-chloro-2-propyl)benzene (tricumyl chloride)/$TiCl_4$/pyridine initiating system showed that PIBs with narrow MWD values ($M_w/M_n \cong 1.1$) and M_n values as high as 100 000 g/mol could be prepared with quantitative initiation efficiency.[9] The living nature of the polymerization was demonstrated by the linearity of molecular weight *vs* conversion plots and first-order kinetic plots. The blocked difunctional initiator, *t*-Bu-*m*-DCC, was used in this initial investigation to ensure the absence of cycloalkylation of the initiator (formation of indanyl structures), a side reaction often encountered with cumyl chloride or DCC.[15] Since this initial investigation, it has been found that DCC, which is more easily synthesized, can be used in place of *t*-Bu-*m*-DCC. At −80 °C using typical reagent concentration ratios, such as $[DCC]/[pyr]/[TiCl_4] = 1/2/20$, little or no cycloalkylation was detected in polymers formed under these conditions, as indicated by GPC.

The kinetics of the living cationic polymerization of IB using the DCC/$TiCl_4$/pyridine initiating system were determined by monitoring the amount of polymer produced as a function of reaction time. In all polymerizations, the concentration of IB was 1.0 M, the total volume of the reaction mixture was 50 mL, and $TiCl_4$ was added as the last component. It should be noted that although the polymerization mixtures were apparently homogeneous with regard to initiator, monomer, and growing polymer chains, they were heterogeneous with regard to the $TiCl_4$/pyridine complex, which could be observed throughout the polymerization as a yellow precipitate. Therefore, the kinetic results involving $TiCl_4$ have been interpreted using both the nominal $TiCl_4$ concentration, $[TiCl_4]$, and the effective $TiCl_4$ concentration defined as $[TiCl_4]_{eff} = [TiCl_4] - [ED]$. This quantity is the amount of free $TiCl_4$ that is available to coinitiate the polymerization, assuming a 1/1 Lewis acid/ED complex. It should be noted that if [ED] ≥ [protic impurities], then it is not necessary to consider protic impurities in the calculation of $[TiCl_4]_{eff}$ since reaction of a protic impurity with $TiCl_4$ causes the consumption of one molecule of ED via onium salt formation (this neglects possible further losses of $TiCl_4$ due to disproportionation between complex counterions, e.g., $onium^+TiCl_4OH^- + TiCl_4 \rightleftharpoons onium^+TiCl_5^- + TiCl_3OH$).

Initiating System Concentration. In our investigations, it has been standard practice to treat the initiator, coinitiator, and ED as a unitized initiating system. Thus, using a pyridine concentration equivalent to the concentration of initiating species, $[I]_o$ ($=2[DCC]_o$), and a $TiCl_4$ concentration equal to $10[I]_o$, the kinetics of IB polymerization were determined as a function of the concentration of the unitized initiating system, i.e., DCC/$TiCl_4$/pyridine, at −80 and −50° C. The data were interpreted in terms of the kinetic rate law for a living polymerization with fast initiation:

$$r_p = -\frac{d[M]}{dt} = k_p[R^+][M] = k_{app}[M] \qquad (2)$$

where r_p is the rate of polymerization, k_p is the rate constant for propagation, $[R^+]$ is the concentration of actively growing chains (constant), and k_{app} is the apparent rate constant for propagation. The −80 °C data are plotted in Figure 1 using the integrated form of eq 2 and is representative of the general behavior. The polymerizations follow first-order kinetics with respect to monomer, and the number of actively growing chains remains invariant during a given polymerization. The slope of each plot yields k_{app} for a given set of conditions. The k_{app}'s measured in this way for the unitized initiating system at −80 and −50 °C in 60/40 hexanes/MeCl and at −50 °C for a number of solvent compositions have been listed in Table 1.

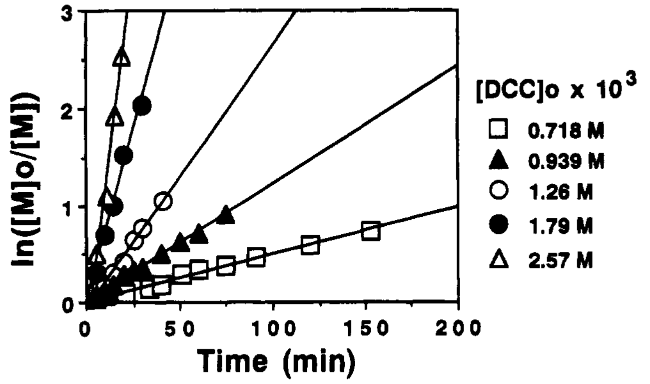


Figure 1. Effect of initiator system concentration ([DCC/$TiCl_4$/pyridine]) on the rate of polymerization of IB at −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $2[DCC]_o = [pyr] = [TiCl_4] \times 10^{-1}$.

Table 1. Apparent Rate Constants for IB Polymerizations Employing the Unitized Initiating System DCC/$TiCl_4$/Pyr[a]

T (°C)	Hex/MeCl (v/v)	10^{-3}[DCC] (M)	10^{-2} k_{app} (min^{-1})
−80	60/40	0.718	0.483
		0.939	1.21
		1.26	2.72
		1.79	7.05
		2.57	14.81
−50	60/40	1.29	0.126
		1.77	0.343
		2.49	0.700
		3.77	1.91
		5.64	3.51
	70/30	2.45	0.105
	60/40	2.49	0.700
	50/50	2.45	1.84
	40/60	2.45	3.95
	30/70	2.45	8.46

[a] [IB] = 1 M; $2[DCC]_o = [pyr] = [TiCl_4] \times 10^{-1}$.

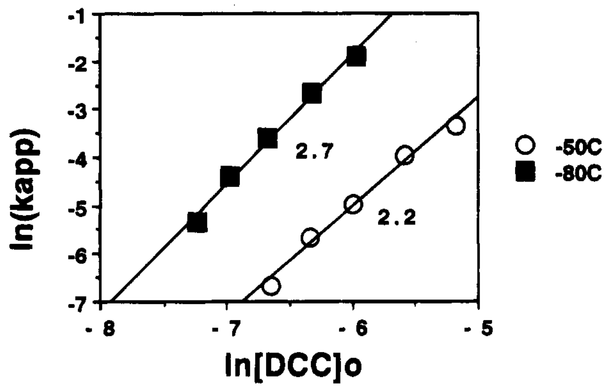


Figure 2. Reaction order of initiator system concentration ([DCC/$TiCl_4$/pyridine]) for polymerization of IB at −50 and −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $2[DCC]_o = [pyr] = [TiCl_4] \times 10^{-1}$.

Figure 1 and the k_{app} data in Table 1 show that the rate of polymerization is strongly affected by the concentration of the initiation system; i.e., k_{app} is a function of $[I]_o$, $[TiCl_4]$, and [pyr]. The functional dependency of rate on concentration of the initiation system can be determined by plotting ln(k_{app}) vs ln $[DCC]_o$, as shown in Figure 2. It should be borne in mind that although the x-axis of Figure 2 only plots ln $[DCC]_o$, the other two components of the initiation system were also changed in direct proportion to $[DCC]_o$. The slopes of these lines show that the rate of polymerization is proportional to the 2.7 power of the initiation system concentration at −80 °C and to the 2.2 power at −50 °C. The power 2.7 has been reproduced for a related initiation system (2-chloro-2,4,4-trimethylpentane/$TiCl_4$/pyridine) also at −80 °C;[16] however, no other corroborating results have thus far been generated at −50 °C. The contribution of each component in the initiation system to the observed 2.7 initiation system reaction order at −80 °C will be discussed individually in the following sections.

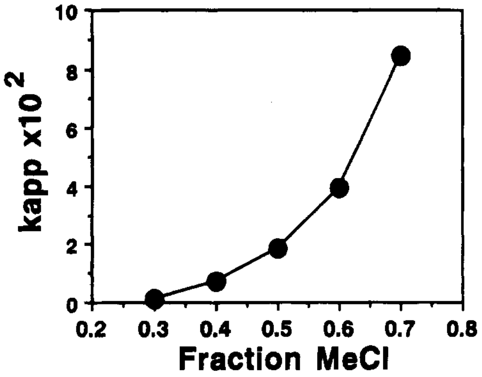


Figure 3. Dependence of apparent rate constant, k_{app} (min^{-1}), of the polymerization of IB at −50 °C on the fraction of methyl chloride in the solvent system. $[IB]_o = 1$ M; $2[DCC]_o = [pyr] = [TiCl_4] \times 10^{-1} = 4.90 \times 10^{-3}$ M.

Effect of Temperature on the Rate of Polymerization. The data in Table 1 illustrate the effect of temperature on the rate of polymerization. For example, comparison of k_{app} at −80 °C using an initiator concentration of 1.79×10^{-3} M to that at −50 °C using an initiator concentration of 1.77×10^{-3} M indicates that the polymerization at −80 °C is about 20 times faster than the polymerization at −50 °C. The increasing rate of polymerization with decreasing temperature indicates that the activation energy associated with the apparent rate constant is negative. Clearly $[R^+]$ is not governed solely by the initiator and co-initiator concentrations, but also by a temperature-dependent equilibrium between dormant and active chain carriers, as shown in eq 1, i.e., $[R^+] \cong K_{eq}[I]_o[TiCl_4]$, where the equilibrium constant $K_{eq} = k_i/k_{ri}$ is numerically small but increasingly favors active chain carriers as the temperature is lowered. Equilibria of this type between dormant and active chain carriers have been previously cited in the literature for both isobutylene[17] and vinyl ethers,[18] and it appears likely that the existence of such an equilibrium is a necessary feature of living carbocationic polymerizations.

Effect of Solvent Polarity on the Rate of Polymerization. The effect of solvent polarity on the rate of polymerization at −50 °C was investigated by varying the hexane/methyl chloride ratio in the polymerization while keeping the concentrations of IB, DCC, pyridine, and $TiCl_4$ constant. The results, listed in Table 1, indicate that the polymerization rate increases with increasing solvent polarity, i.e., increasing concentration of methyl chloride. Figure 3, a plot of k_{app} vs the fraction of methyl chloride in the solvent system, shows that a reduction in the relative amount of methyl chloride in the solvent system below a 50/50 (v/v) hexane/methyl chloride ratio has only a slight effect on the rate of polymerization when compared to an increase above this ratio. Although the dielectric constants of these solvent compositions were not determined, Imanishi et al.[19] have determined the dielectric constants of similar solvent systems composed of hexane and methylene chloride. They found that for hexane/methylene chlo-

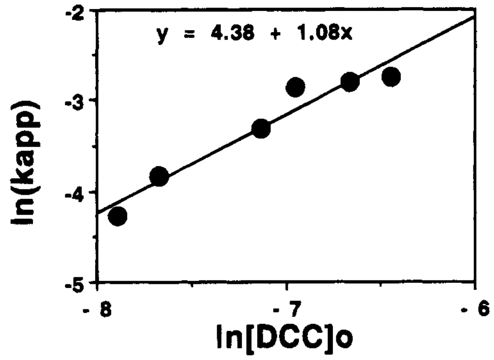


Figure 4. Reaction order of dicumyl chloride (DCC) concentration for polymerization of IB at −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $[Pyr] = 2.5 \times 10^{-3}$ M; $[TiCl_4] = 4.0 \times 10^{-2}$ M.

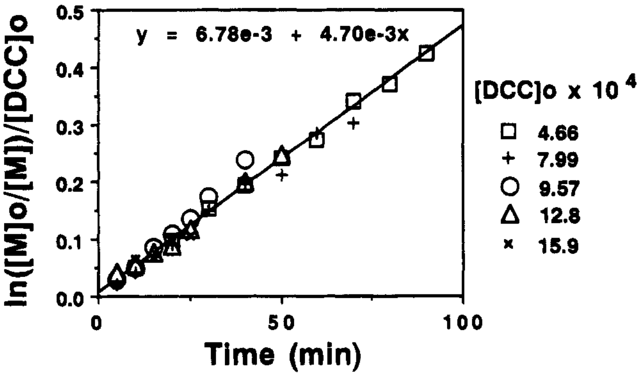


Figure 5. ln $([M]_o/[M])/[DCC]_o$ vs time for the polymerization of IB using various dicumyl chloride (DCC) concentrations at −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $[Pyr] = 2.5 \times 10^{-3}$ M; $[TiCl_4] = 4.0 \times 10^{-2}$ M.

ride at −78 °C, the dielectric constant increased from 3.95 for a 75/25 (v/v) mixture, to 6.53 for a 50/50 mixture, to 10.65 for a 25/75 mixture. Thus, the dielectric constant increases nonlinearly with the fraction of methylene chloride in the solvent system. This same type of nonlinear behavior in dielectric constant with the fraction of polar component in the mixture may be responsible for the increased sensitivity of the rate of polymerization with increasing methyl chloride content above a 50/50 mixture.

Effect of DCC Concentration on the Rate of Polymerization. The dependence of the rate of polymerization on the concentration of DCC at −80 °C was determined by measuring the first-order kinetic behavior of polymerizations conducted using various concentrations of DCC while keeping the concentration of IB and the nominal concentrations of pyridine and $TiCl_4$ constant at 1.0, 2.50×10^{-3}, and 4.00×10^{-2} M, respectively. The resulting first-order plots were linear and passed through the origin, and the k_{app}'s obtained from the slopes are listed in Table 2. It is clear that the rate of polymerization increases as the concentration of DCC increases. By plotting $\ln(k_{app})$ vs ln $[DCC]_o$, as shown in Figure 4, it was found that the rate of polymerization varies with the first power of DCC concentration. This validates the assumption that the rate of polymerization, as expressed in eq 2, is first-order in growing chain ends, provided that $[R^+]$ is proportional to $[I]_o = 2[DCC]_o$ over the entire range of DCC concentrations. The latter condition can be qualified by plotting ln $([M]_o/[M])/[DCC]_o$ vs time for several DCC concentrations, as shown in Figure 5. The fact that all lines coincide shows that $[R^+]$ is indeed proportional to $[DCC]_o$ at a given temperature, and that only ion-paired species are present. Polymerizations in which propagation occurs through both ion pairs and free ions, typically yield an increase in $k_{app}/[I]_o$ with decreasing $[I]_o$, as has been reported for classical, living anionic polymerizations in polar solvents.[20,21] The conclusion that only ion-paired species participate as chain carriers was also reached by Puskas et al.[22] for a similar isobutylene polymerization system.

Table 2. Apparent Rate Constants for IB Polymerizations: Effect of [DCC], [TiCl$_4$], and [Pyr] in Isolation[a]

10^{-3}[DCC] (M)	10^{-2}[TiCl$_4$] (M)	10^{-3}[pyr] (M)	10^{-2} k_{app} (min^{-1})
0.373	4.0	2.5	1.39
0.466			2.16
0.799			3.59
1.28			6.02
1.78	1.09	3.56	0.361
	1.82		1.26
	2.91		3.34
	5.46		9.87
1.0	4.0	0.335	11.27
		1.00	8.39
		4.90	5.68
		10.00	4.80
		15.10	3.53

[a] [IB] = 1 M; hexanes/MeCl (v/v) = 60/40; −80 °C.

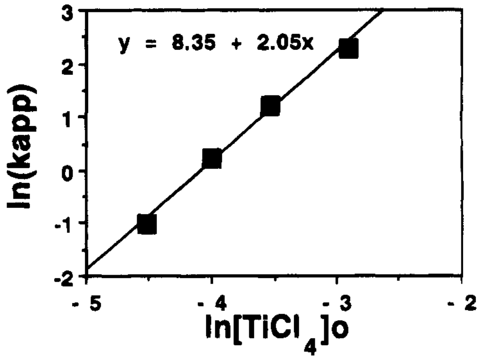


Figure 6. Reaction order of $[TiCl_4]$ for polymerization of IB at −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $2[DCC]_o = [pyr] = 3.56 \times 10^{-3}$ M.

Effect of TiCl$_4$ Concentration on the Rate of Polymerization. The dependence of the rate of polymerization on the concentration of $TiCl_4$ was determined by measuring the first-order kinetic behavior of polymerizations conducted using various concentrations of $TiCl_4$ while keeping the concentration of IB, DCC, and pyridine constant at 1.0, 1.78×10^{-3}, and 3.56×10^{-3} M, respectively. The lowest concentration of $TiCl_4$ studied was 1.09×10^{-2} M, which is approximately 3 times the concentration of pyridine. This lower limit for $[TiCl_4]$ was chosen to ensure that sufficient free Lewis acid was present to coinitiate the polymerization, and to yield $[TiCl_4]_{eff}$, as defined earlier, approximately equal to $[TiCl_4]$, thus minimizing the effect on the kinetics of the loss of a portion of the $TiCl_4$ through complexation. Nevertheless, both $[TiCl_4]_{eff}$ and $[TiCl_4]$ were considered in analyzing the kinetic order of $TiCl_4$.

Table 2 lists k_{app}'s of polymerizations at −80 °C for which only $[TiCl_4]$ was varied. It may be seen that $[TiCl_4]$ exerts a strong effect on the rate of polymerization. From the slope of a plot of $\ln(k_{app})$ vs ln $[TiCl_4]$, shown in Figure 6, it was found that the kinetic order of the reaction with respect to $TiCl_4$ was 2, which accounts for the largest part of the dependency of the overall initiation system. Second-order dependence

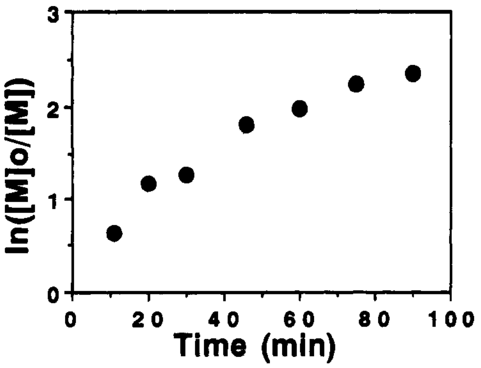


Figure 7. First-order rate plot for polymerization of IB at −80 °C in 60/40 hexane/methyl chloride, constructed using a [pyr]/[CE] (chain end) ratio of 0.20. $[IB]_o = 1$ M; $[DCC] = 1.0 \times 10^{-3}$ M; $[TiCl_4] = 4.0 \times 10^{-2}$ M.

with respect to $[TiCl_4]$ was also observed by Faust for the polymerization of IB[8] using a ring-substituted dicumyl methyl ether/$TiCl_4$/(hexane:methyl chloride) (60:40, v:v)/proton trap polymerization system at −80 °C, as well as for the polymerization of styrene[23] under similar conditions. Second-order behavior with this system was described as being the result of the formation of dimers of $TiCl_4$ *via* chlorine bridges.[7] If $[TiCl_4]_{eff}$ instead of $[TiCl_4]$ is used in the calculation, a kinetic order of 1.7 is obtained, which is still close to 2. The kinetic order with respect to $TiCl_4$ at −50 °C was not determined, and one must speculate whether the measured overall order of the initiation system of 2.2 (Figure 2) is indicative of a decreasing $TiCl_4$ kinetic order with increasing temperature.

Effect of Pyridine Concentration on the Rate of Polymerization. The effect of the concentration of pyridine on the rate of polymerization was determined by measuring the first-order kinetic behavior of polymerizations conducted using various concentrations of pyridine while keeping the concentration of IB, DCC, and $TiCl_4$ (nominal) constant at 1.0, 1.00×10^{-3}, and 4.00×10^{-2} M, respectively. Several pyridine concentrations were investigated, ranging, in terms of the ratio of moles of pyridine to moles of chain ends ($2[DCC]_o$), from 0.067 to 15 [pyr]/[chain ends]([CE]). Among the [pyr]/[CE] ratios investigated, those below 0.33 yielded a deviation from linearity of first-order plots, which occurred at low conversions, as illustrated in Figure 7 for polymerization using a [pyr]/[CE] ratio of 0.20, indicating a decrease in the number of propagating chains due to irreversible chain termination. At a [pyr]/[CE] ratio of 0.067, complete nonliving behavior was observed, as evidenced by scatter in the first-order kinetic plot. In addition, GPC traces of polymers produced using these low [pyr]/[CE] ratios exhibited bimodal MWDs. Figure 8 shows GPC traces of polymer samples produced using (a) 0.20 and (b) 0.067 [pyr]/[CE] ratios. Both traces are bimodal, and it may be seen that the high molecular weight peak became larger as [pyr] was decreased. Bimodality can be attributed to simultaneous initiation by the intended initiator (low molecular weight peak) and adventitious protic impurities (high molecular weight peak), and it is noteworthy that even at vanishingly low [pyr], trace b, both peaks remained. Supporting these conclusions, a control experiment run in the absence of both pyridine and DCC yielded only the high molecular weight peak (69% IB conversion after 15 min).

Table 2 lists k_{app}'s for polymerizations conducted at −80 °C using various pyridine concentrations above a 0.33 [pyr]/[CE] ratio. From the data it may be seen that the rate of polymerization decreases with increasing pyridine concentration. The dependence of the rate of polymerization on pyridine concentration at −80 °C was determined to be −0.28 by plotting $\ln(k_{app})$ vs ln [pyr] (not shown). Other than the fact that it is negative, which is consistent with the retarding effects of pyridine, and that it correlates well with the overall dependency of the unitized initiation system, the specific value of this fractional negative power does not appear to have any obvious mechanistic interpretation, other than the fact that it is dictated by the degree to which [pyr] is a significant fraction of $[TiCl_4]$.

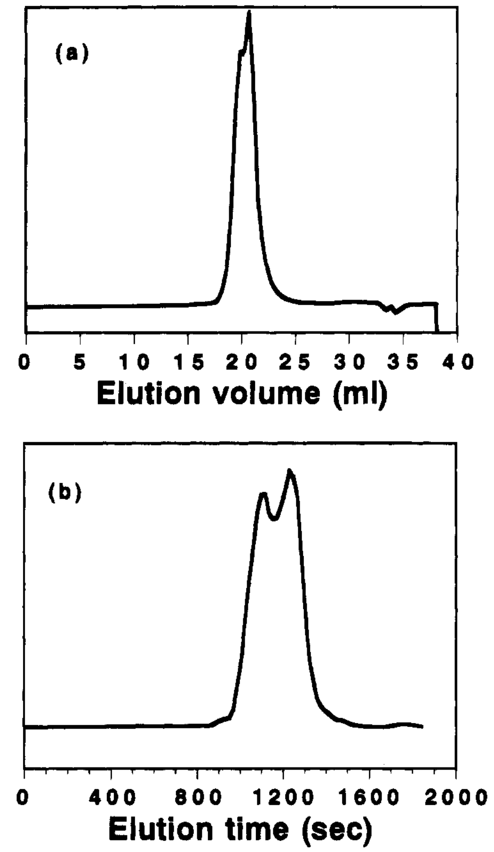


Figure 8. GPC traces of PIB produced using 1/5 (a) and 1/15 (b) [pyr]/[CE] ratios.

Another way to view the problem is to consider a model in which pyridine simply scavenges $TiCl_4$ from the system. In this case, changes in [pyr] are treated as changes in $[TiCl_4]_{eff}$; this is reasonable considering the observation of an insoluble complex. Thus, the data in Table 2 were plotted as $\ln(k_{app})$ vs ln $[TiCl_4]_{eff}$, as shown in Figure 9. The points appear to form a straight line except for the point representing the highest $[TiCl_4]_{eff}$ (lowest [pyr]). The significant increase in rate for this point may be logically attributed to fast initiation and propagation by chains initiated by protic impurities, since for this point [pyr] < [protic impurities]. Linear regression of the remaining four points yields a slope of 1.8, which is approximately the kinetic order of the reaction with respect to $TiCl_4$, suggesting that the retarding effect of pyridine is approximately what one would predict simply on the basis of the decrease in $TiCl_4$ concentration.

Mechanistic Considerations. All of the polymerizations, conducted under a wide variety of conditions, were first-order with respect both to IB and DCC concentration. This indicates that propagation occurs through a simple bimolecular reaction between active chains and monomer. In addition, the maintenance of

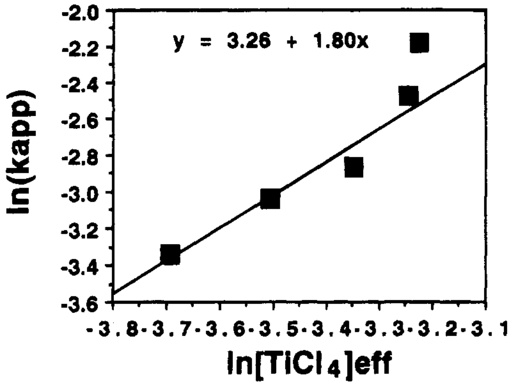
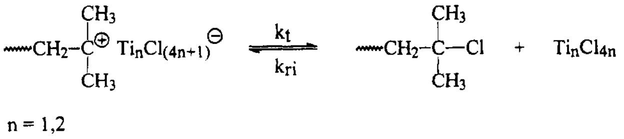


Figure 9. Reaction order of $[TiCl_4]_{eff}$ for polymerization of IB at −80 °C in 60/40 hexane/methyl chloride. $[IB]_o = 1$ M; $[DCC]_o = 1.0 \times 10^{-3}$ M; $[TiCl_4] = 4.0 \times 10^{-2}$ M.

linearity of first-order plots to relatively high monomer conversion indicates that the concentration of active species remains constant with reaction time or that absolute termination is absent. Further, the fact that the polymerization is first-order in DCC concentration and the plots of ln $([M]_o/[M])/[DCC]_o$ vs time for several DCC concentrations all lie on the same line indicates that only ion-paired active species are responsible for chain propagation; i.e., free ions are not operating.

A common theme of the mechanisms of inifer,[24] quasiliving,[2] and truly living[4] polymerization of IB, all of which utilize $TiCl_4$ or BCl_3 as the coinitiator, is the presence of reversible termination, causing the simultaneous existence of active and dormant chains which are in rapid equilibrium with each other (eq 1). Evidence for this equilibrium follows from the observations that, regardless of the initiator or quenching agent, *tert*-alkyl chloride end-capped PIBs are obtained[25] and well-characterized, preformed *tert*-alkyl chloride end-capped PIBs can be used as initiators for the polymerization of IB.[4] For the DCC/$TiCl_4$/pyridine system under investigation, the very slow rate of polymerization, as well as the observation of a negative activation energy associated with the apparent rate constant, indicate that $[R^+]$ is governed by an equilibrium such as shown in eq 1. If the existence of the equilibrium is accepted, then $[R^+] \simeq K_{eq}[I]_o[TiCl_4]$ if K_{eq} is ≪1, and a simple first-order kinetic dependency on $TiCl_4$ should be observed, similarly to Kamigaito et al.[18]



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ Ti_nCl_{(4n+1)}^{\ominus} \underset{k_{ri}}{\overset{k_t}{\rightleftharpoons}} \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + Ti_nCl_{4n} \tag{3}$$

n = 1,2

To attempt to rationalize the approximately second-order dependence of the rate of polymerization on $[TiCl_4]$ that was actually observed, we can consider that the ionization and propagation of chains may involve either free $TiCl_4$ or dimeric Ti_2Cl_8, as shown in eq 3. Additionally, there is strong precedence in the literature for halogenated titanium compounds to form dimers, as shown below.[26]

$$2TiCl_4 \overset{K_{D0}}{\rightleftharpoons} Ti_2Cl_8 \tag{4}$$

$$TiCl_5^- + TiCl_4 \overset{K_{D1}}{\rightleftharpoons} Ti_2Cl_9 \tag{5}$$

Griffiths[27] has suggested that $TiCl_4$ forms chlorine-bridged dimers as shown in eq 4, while Kistenmacher et al.[28] have confirmed the existence and structure of $Ti_2Cl_9^-$. Second-order dependence on $[TiCl_4]$ of the rate of polymerization will result if two conditions hold: (1) the majority of propagation is carried out by chains which are activated with dimeric species (Ti_2Cl_8 and $Ti_2Cl_9^-$), and (2) the equilibrium constants for dimer formation, both K_{D0} and K_{D1}, are ≪1.0. If these conditions are only marginally met, for example, if significant propagation proceeds with both monomeric and dimeric counterions, the external kinetic order for $TiCl_4$ will be decreased toward unity. This could readily explain the observation of orders fractionally between 1 and 2, e.g., the order of 1.7 calculated for $[TiCl_4]_{eff}$ at −80 °C, and the expected lower kinetic order for $TiCl_4$ at −50 °C (based on the calculated order of 2.2 for the unitized initiation system).

Of particular interest was the effect on the rate of polymerization of the electron donor, pyridine, since the ED is the key component that provides living characteristics to what would otherwise be a transfer- and/or termination-dominated nonliving polymerization. In addition, the exact role of the ED is at present in dispute. Faust et al.[8] have proposed that EDs bring about living polymerization of IB by trapping protons. In the mechanism proposed by Kaszas et al.[4] the main function of the Lewis acid/ED complex is to interact with and to stabilize a carbocation. The latter view has recently been upheld by Majoros, Nagy, and Kennedy[29] who maintain that EDs are able to convert highly reactive species, i.e., ionic species, into less reactive species capable of yielding living polymerization. The proton trapping theory of Faust et al. is attractive in its simplicity and difficult to refute due to the fact that protic impurities are typically present at a concentration which is of the same order as the concentration of the purposefully added initiator. It also makes the most sense for an insoluble complex; it is difficult to envision stabilization of growing carbocations, which appear to be soluble, by a solid complex which has precipitated from the reaction.

It is possible that both theories are operationally correct, although perhaps only proton trapping is functionally responsible for converting the nonliving system to a living system. The solubility of the Lewis acid/ED complex in the polymerization medium may be a key point in attempting to understand this question. For the case of an insoluble complex, the ED forms onium salts with protic impurities, as shown below for the case of water.

$$ED{:}TiCl_4 + H_2O{:}TiCl_4 \rightleftharpoons EDH^+TiCl_4OH^- + TiCl_4 \tag{6}$$

$$EDH^+TiCl_4OH^- + TiCl_4 \rightleftharpoons EDH^+TiCl_5^- + TiCl_3OH \tag{7}$$

(The position of the disproportionation equilibrium, eq 7, and thus the question of whether ED plus H_2O removes one or two molecules of $TiCl_4$, depends on the relative solubility of the two onium salts, among other factors.) However, after depletion of all the protic impurities, excess ED is scavenged by formation of an insoluble complex with the Lewis acid and therefore can only influence the rate of polymerization by changing the concentration of free Lewis acid. This scenario indeed seems to fit the limited data, shown in Figure 9, in which the decrease in rate with increasing [pyr] is accounted for in terms of $[TiCl_4]_{eff}$. A full test of this hypothesis would involve measurement of the rates of two polymerizations with identical $[TiCl_4]_{eff}$, but which were formulated with two different combinations of [TiCl] and [pyr]. We have no data at present for this comparison, but this will be the subject of future experiments. We can say, however, that for the case of an ED that forms a largely soluble complex, e.g., 2,4-dimethylpyridine, the $TiCl_4$/ED complex does cause an easily measurable retardation of the polymerization rate.[30] Even though this seems to qualify as "carbocation stabilization", it is unclear whether it actually contributes materially to "livingness" in view of the equal effectiveness of an ED such as pyridine that forms an insoluble complex.

Conclusions

The kinetics of the DCC/$TiCl_4$/pyridine system for initiation of IB polymerization at −80 °C have been shown to be first-order in IB concentration, first-order in the concentration of initiating sites, approximately second-order in $TiCl_4$ concentration, and a negative fractional order with respect to the pyridine concentration. These results show that propagation is a simple bimolecular reaction between the active species and IB, and that rate of polymerization is simply equivalent to the rate of propagation, indicating rapid initiation. However, the concentration of active species and hence the rate of polymerization is a complicated function of the concentration of all of the components present in the polymerization mixture. The influence of these components on the rate of polymerization can be adequately explained by the existence of an equilibrium, between active and dormant chains, whose position is affected by changes in the concentration of any of the components, i.e. DCC, $TiCl_4$, or pyridine. In addition, temperature and solvent effects also indicate the presence of this equilibrium. With regard to the nature of the active species, it was shown that only unimolecular, ion-paired species, as opposed to free ions, participate in chain propagation.

With regard to the two mechanisms proposed for ED-mediated carbocartion polymerization, one involving carbocation stabilization by Kaszas et al.[4] and the other involving proton trapping by Faust et al.,[8] the present kinetic results cannot fully distinguish between the two; however, the fact that pyridine forms an insoluble complex with $TiCl_4$ suggests that even in cases where carbocation stabilization takes place, it may be proton trapping that actually causes livingness. Further experiments that explore the concept of effective Lewis acid concentration, with both soluble and insoluble complexes, are needed to fully resolve this issue.

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References and Notes

(1) Faust, R.; Fehervari, A.; Kennedy, J. P. *J. Macromol. Sci., Chem.* **1982−83**, *A18*, 1209.
(2) Puskas, J.; Kaszas, G.; Kennedy, J. P.; Kelen, T.; Tudos, F. *J. Macromol. Sci. Chem.* **1982−83**, *A18*(9), 1229.
(3) Kaszas, G.; Puskas, J.; Kennedy, J. P. *Polym. Bull.* **1987**, *18*, 123.
(4) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Macromolecules* **1990**, *23*, 3909.
(5) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Chen, C. C. *J. Macromol. Sci., Chem.* **1989**, *A26*(8), 1099.
(6) Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1989**, *21*, 5.
(7) Faust, R.; Ivan, B.; Kennedy, J. P. *J. Macromol. Sci., Chem.* **1991**, *A28* (1), 1.
(8) Gyor, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci., Chem.* **1992**, *A29*, 639.
(9) Storey, R. F.; Lee, Y. K. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29* (11), 1017.
(10) Storey, R. F.; Lee, Y. K. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 317.
(11) Storey, R. F.; Chisholm, B. J.; Lee, Y. *Polymer* **1993**, *34* (20), 4330.
(12) Storey, R. F.; Chisholm, B. J. *Macromolecules* **1993**, *26*, 6727.
(13) Storey, R. F.; Chisholm, B. J.; Choate, K. R., Jr. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31* (8), 969.
(14) Storey, R. F.; Chisholm, B. J.; Lee, Y. K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 184.
(15) Kennedy, J. P.; Smith, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1523.
(16) Storey, R. F.; Shoemake, K. A. Unpublished results.
(17) Kaszas, G.; Puskas, J. E. Private communication.
(18) Kamigaito, M.; Yamaoka, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6400.
(19) Imanishi, Y.; Higashimura, T.; Okamura, S. *J. Polym. Sci.* **1965**, *A3*, 2455.
(20) Geacintov, C.; Smid, J.; Swarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 1253; **1962**, *84*, 2508.
(21) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley: New York, 1968; p 408.
(22) Puskas, J. E.; Kaszas, G.; Litt, M. *Macromolecules* **1991**, *24*, 5278.
(23) Fodor, Z.; Gyor, M.; Wang, H.-C.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30* (5), 349.
(24) Santos, R.; Kennedy, J. P.; Walters, M. *Polym. Bull.* **1984**, *11*, 261.
(25) Faust, R.; Kennedy, J. P. *J. Macromol. Sci., Chem.* **1990**, *A27* (6), 649.
(26) Rytter, E.; Kvisle, S. *Inorg. Chem.* **1985**, *24*, 640.
(27) Griffiths, J. E. *J. Chem. Phys.* **1968**, *49* (2), 642.
(28) Kistenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* **1971**, *10* (1), 122.
(29) Majoros, I.; Nagy, A.; Kennedy, J. P. *Adv. Polym. Ser.* **1994**, *112*, 1.
(30) Storey, R. F.; Choate, K. R., Jr. *ACS Symp. Ser.*, submitted for publication.

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