Effect of Temperature, Solvent Polarity, and Nature of Lewis Acid on the Rate Constants in the Carbocationic Polymerization of Isobutylene

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ABSTRACT: The absolute rate constant of propagation for ion pairs ($k_p^{\pm}$) was determined by the diffusion clock method in the living carbocationic polymerization of isobutylene at different solvent polarity and temperature in conjunction with $TiCl_4$, Me_2AlCl, and BCl_3 as Lewis acids. The $k_p^{\pm}$ ($(3.6-5.7) \times 10^8$ L mol^{-1} s^{-1} in hexanes/MeCl 60/40, v/v) was independent of temperature and nature of Lewis acid and increased moderately with increasing solvent polarity to a nearly diffusion-limited value ($\sim 1.7 \times 10^9$ L mol^{-1} s^{-1}) in pure MeCl. A similar $k_p^{\pm}$ ($\sim(5-6) \times 10^8$ L mol^{-1} s^{-1}) value was obtained in the nonliving polymerization of isobutylene in conjunction with $EtAlCl_2$ in hexanes/MeCl 60/40 (v/v) at −80 °C, indicating that living and nonliving polymerizations proceed on identical propagating centers. The apparent equilibrium constant of ionization (activation) K_i^{app} ($= K_iK_{D0}$, where K_i is the absolute equilibrium constant of ionization and K_{D0} is the equilibrium constant of $TiCl_4$ dimerization) was calculated from the apparent and absolute rate constant of propagation. The rate constant of deactivation, k_{-i} was determined from the conversion vs polydispersity plots. From K_i^{app} and k_{-i}, the apparent values of k_i ($k_i^{app} = k_iK_{D0}$, where k_i is the absolute rate constant of ionization) were also calculated. On the basis of the results, the observed large differences in the overall polymerization rates with different solvent polarity and temperature can be attributed solely to the changes in the active center concentration, which decreases with decreasing solvent polarity and increasing temperature. From the temperature dependence of K_i^{app}, the apparent standard enthalpy ($= \Delta H_i° + \Delta H_{D0}°$) and entropy ($= \Delta S_i° + \Delta S_{D0}°$) of ionization, and from the temperature dependence of k_i^{app} and k_{-i}, the apparent activation enthalpy and entropy of the activation/deactivation process were calculated.

Introduction

A complete mechanistic understanding of cationic polymerization is not possible without knowledge of the rate and equilibrium constants involved in the polymerization process. It is also fundamental for overall control in polymer synthesis and in new catalyst development. The rate constants of carbocationic polymerization, however, are still controversial. For the propagation step of the cationic polymerization of isobutylene (IB), values differing 5 orders of magnitude from about 10^3 to 10^8 L mol^{-1} s^{-1} have been reported. Despite this large variation, 10^3-10^4 L mol^{-1} s^{-1} were previously accepted values for the rate constant of propagation (k_p).[1] Recent results, however, revealed that these values are seriously underestimated.[2,3] Very recently, we reported on the propagation rate constant for ion pairs ($k_p^{\pm}$) determined using two different diffusion clock methods in the polymerization of IB in conjunction with $TiCl_4$ in hexanes (Hex)/methyl chloride (MeCl) 60/40 (v/v) at −80 °C.[3] The first method involved on-line UV−vis monitoring of the diffusion-limited addition of the π-nucleophiles 1,1-bis(4-methylphenyl)ethylene (DTE), 1,1-bis(4-*tert*-butylphenyl)ethylene, and 2-phenylfuran (2-PhFu) to hydrochlorinated IB *n*-mers. The second diffusion clock method involved competition experiments, i.e., polymerization carried out in the presence of a π-nucleophile, which stops short of completion when all chain ends are capped. From the limiting conversion (x_∞^{IB}) or from the limiting number-average degree of polymerization ($DP_{n\infty}$) and the rate constant ratio ($k_p^{\pm}/k_c^{\pm}$), and when the rate constant of the addition of a π-nucleophile to a polymer cation, $k_c^{\pm}$, is known, $k_p^{\pm}$ can be calculated (eqs 1 and 2).[3]

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \quad (1)$$

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - DP_{n\infty}[PIBCl]_0/[IB]_0)}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \quad (2)$$

In eqs 1 and 2, $[PIBCl]_0$, $[\pi Nu]_0$, and $[IB]_0$ are the initial chain end, π-nucleophile, and IB concentration, respectively.

Both methods yielded similar $k_p^{\pm}$ values ranging from 0.3×10^9 to 1.0×10^9 L mol^{-1} s^{-1} for the polymerization of IB in Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C in conjunction with $TiCl_4$ coinitiator.

Solvent, temperature, and strength of Lewis acid greatly affect the overall rate of cationic polymerization.[4] Although the propagation rate constant is predicted to be lower in more polar solvent, faster ionization and slower termination generally result in higher overall polymerization rates. The effect of temperature is more complex, and the overall effect varies for different monomers. For IB and some other monomers the polymerization is faster at lower temperature; i.e., the activation energy for the polymerization is apparently negative.[5−7]

Polymerizations are almost always faster with the stronger Lewis acid;[4] however, it is not known how the separate elementary reactions are affected. In this

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article we report on the effect of solvent polarity, temperature, and the nature of Lewis acid on the rate constants of propagation, ionization (activation), and reversible termination (deactivation) in the carbocationic polymerization of IB.

Experimental Section

Materials. Titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%), boron trichloride (BCl_3, Aldrich, 99.9%), ethylaluminum dichloride ($EtAlCl_2$, Aldrich, 97%), and dimethylaluminum chloride (Me_2AlCl, Aldrich, 97%) were used as received. 2-Chloro-2,4,4-trimethylpentane (TMPCl),[8] 2-phenylfuran (2-PhFu),[9] and 1,1-di-*p*-tolylethylene (DTE)[10] were prepared according to the literature. Methyl chloride (MeCl), isobutylene (IB), hexanes (Hex), and methanol have been purified as described previously.[11]

General Polymerization Procedure. All polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 25 mL. The polymerization mixture was quenched with excess prechilled methanol. Polyisobutylene (PIB) was recovered and purified two times by precipitation from Hex/methanol. Monomer conversions were determined by gravimetric analysis. In all experiments the volume of IB was deducted from that of hexanes; thus, the Hex/MeCl ratio indicates always the (Hex + IB)/MeCl ratio. Compensating this way for the solvent polarity change upon addition of IB is especially important when high IB concentrations are used.

Example for Competition Experiment. In a representative experiment the polymerization was carried out in Hex/MeCl 60/40 (v/v) at −80 °C using the following concentrations: $[\text{TMPCl}] = 0.002$ mol L^{-1}, $[\text{DTBP}] = 0.006$ mol L^{-1}, $[\text{DTE}] = 0.003$ mol L^{-1}, $[\text{IB}] = 2.0$ mol L^{-1}, and $[TiCl_4] = 0.036$ mol L^{-1}. Into a 75 mL culture tube at −80 °C 7.9 mL of Hex, 9.2 mL of MeCl, 1.0 mL of DTBP stock solution in Hex (0.15 mol L^{-1}), 1.0 mL of TMPCl stock solution in Hex (0.05 mol L^{-1}), 1.0 mL of DTE stock solution in Hex/MeCl 60/40 (v/v) (0.075 mol L^{-1}), and 3.9 mL of IB were added and mixed thoroughly. The polymerization was started by the addition of 1.0 mL of $TiCl_4$ solution (0.9 mol L^{-1}, in Hex/MeCl 60/40 (v/v)). After 1 h the solution was mixed with 5 drops of prechilled methanol. The polymer was precipitated twice from methanol. 447.1 mg of PIB was obtained (conversion = 15.9%, $M_n = 8600$, PDI = 2.3).

Using different IB concentrations (1.0−2.5 mol L^{-1}), an average $k_p^{\pm}/k_c^{\pm} = 0.16 \pm 0.01$ and $k_p = 4.8 \times 10^{-8} \pm 0.4 \times 10^{-8}$ L mol^{-1} s^{-1} were calculated.

UV−Vis Spectroscopy. For the UV−vis spectroscopic measurements a quartz immersion probe 661.300-QX (Hellma, optical path: 0.02 cm) connected to a fiber-optic visible (Tungsten light source, Ocean Optics) and UV (AIS model UV-2, Analytical Instrument Systems, Inc.) light source and a Zeiss MMs 256 photodiode array detector was used. The latter was connected to a personal computer via a TEC5 interface, and the spectra were recorded using “Aspect Plus” software (Zeiss).

Procedure for UV−Vis Spectrometry of Capping PIB with 2-PhFu. The measurement was carried out in a glovebox using a 100 mL three-neck flask equipped with magnetic stir bar. PIB with $M_n = 1000$ was synthesized in pure MeCl at −40 °C using the following concentrations: $[\text{TMPCl}] = 0.04$ mol L^{-1}, $[\text{DTBP}] = 0.0035$ mol L^{-1}, $[BCl_3] = 0.4$ mol L^{-1}, $[\text{IB}] = 0.77$ mol L^{-1}. After 4 h polymerization, the PIB solution was diluted to 0.002 mol L^{-1}, $[BCl_3]$ was adjusted to 0.4 mol L^{-1}, and DTBP was added to maintain its concentration at 0.0035 mol L^{-1}. The obtained solution was cooled to −80 °C, filtered, and warmed to −40 °C. To 50 mL of PIB solution 0.5 mL of 2-PhFu solution was added under stirring, and the acquisition was started. To measure direct initiation, a separate experiment was carried out under the same conditions but in the absence of PIB.

Characterization. Molecular weights were measured at room temperature using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities were determined using the universal calibration curve and Viscotek TriSEC GPC software. ^1H NMR spectroscopy was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Laboratories, Inc.). Dynamic viscosity was measured in an Ostwald viscometer. MeCl was used as reference solvent.[12]

Results and Discussion

All kinetic data in this article are treated in terms of a living cationic polymerization, where equilibrium exists between dormant and active chain ends. Similarly to our earlier report,[3] only ion pairs are considered as active species since in the presence of proton trap DTBP, ion pair dissociation is suppressed by common anions generated in the reaction of adventitious proton sources with proton trap in the presence of Lewis acid (LA). With some coinitiators, notably $TiCl_4$ and Me_2AlCl, ionization involves two molecules of Lewis acid. For $TiCl_4$ we have shown earlier[3] that ionization actually involves the Ti_2Cl_8 dimer present at low concentration; monomeric $TiCl_4$ is too weak and therefore inactive. We postulate that for Me_2AlCl ionization also involves the dimer $Me_4Al_2Cl_2$.[13] The dimerization and ionization equilibrium for these Lewis acids can be expressed as in eqs 3 and 4, respectively. BCl_3 is monomeric,[14] and therefore for this Lewis acid $n = 1$ in eq 4.

$$\text{nLA} \xrightleftharpoons{K_{D0}} \text{LA}_n \qquad (3)$$

$$\text{P-Cl} + \text{LA}_n \xrightleftharpoons[k_{-i}]{k_i} \text{P}^+\text{LA}_n\text{Cl}^- \circlearrowleft_{\text{IB}} k_p^{\pm} \qquad (4)$$

The rate of polymerization (R_p) can be expressed as

$$R_p = -d[\text{IB}]/dt = k_p^{\pm}[\text{P}^+\text{LA}_n\text{Cl}^-][\text{IB}] = k_p^{\text{app}}[\text{IB}] \qquad (5)$$

where $[\text{P}^+\text{LA}_n\text{Cl}^-]$ is the ion pair concentration, [IB] is the concentration of the isobutylene, and k_p^{app} is the first-order apparent rate constant of propagation obtained from the first-order plot of $\ln[\text{IB}]_0/[\text{IB}]$ vs time. Integration of eq 5 yields eq 6

$$\ln\frac{[\text{IB}]_0}{[\text{IB}]} = k_p^{\text{app}}t = k_p^{\pm}\frac{k_i K_{D0}}{k_{-i}}[\text{LA}]^n[\text{P}-\text{Cl}]t \qquad (6)$$

where k_i is the rate constant of ionization, k_{-i} is the rate constant of deactivation, K_{D0} is the equilibrium constant of Lewis acid association, and [P−Cl] is the concentration of total chain ends.

Effect of Temperature on $k_p^{\pm}$. The effect of temperature on the absolute rate constant of propagation for IB polymerization was studied from −80 to −50 °C using 2-PhFu as capping agent in the competition experiment. In contrast to 1,1-diarylethylenes, capping with 2-PhFu is an irreversible reaction independent of the temperature. The M_n’s of the polymers calculated

Table 1. Effect of Temperature on the Competition Reaction[a]

temp (°C)	[IB] (mol L^{-1})	conv (%)	M_n (GPC)	M_w/M_n	M_n (NMR)	$k_p^{\pm}/k_c^{\pm}$	$\overline{k_p^{\pm}/k_c^{\pm}}$	$k_p^{\pm}$ (L mol^{-1} s^{-1})
−80	1.0	12.1	3600	2.2	6900	0.12	0.12	3.6×10^8
−80	1.5	12.7	5300	2.4		0.12		
−80	2.0	13.3	7200	2.4		0.13		
−80	2.5	13.3	8800	2.4		0.13		
−80	3.0	11.3	11900	1.9		0.12		
−80	4.0	11.6	15700	1.9		0.12		
−80	5.0	10.9	17900	1.9		0.11		
−80	6.0	12.9	27200	3.2[b]		0.14		
−70	1.0	11.8	3500	2.3	6800	0.11	0.12	4.4×10^8
−70	1.5	11.5	5000	2.4		0.11		
−70	2.0	12.1	6900	2.3		0.12		
−70	2.5	12.6	8700	2.3		0.12		
−60	1.0	11.1	3100	2.5	6400	0.11	0.11	4.8×10^8
−60	1.5	11.4	5000	2.4		0.11		
−60	2.0	11.3	5800	2.6		0.11		
−60	2.5	11.9	7600	2.6		0.12		
−50	1.0	10.3	3000	2.1	5500	0.099	0.097	4.8×10^8
−50	1.5	9.9	5000	1.8		0.095		
−50	2.0	10.0	5500	2.2		0.096		
−50	2.5	10.4	7100	2.2		0.100		

[a] [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, [2-PhFu] = 0.003 mol L^{-1}, Hex/MeCl 60/40 (v/v), reaction time 1 h at − 80, −70 °C and 3 h at −60, −50 °C. [b] Bimodal molecular weight distribution.

Table 2. Dynamic Viscosity (cP) and $k_c^{\pm}$ (L mol^{-1} s^{-1}) as Functions of Temperature and Solvent Composition

solvent	−80 °C ($k_c^{\pm} \times 10^{-9}$)	−70 °C ($k_c^{\pm} \times 10^{-9}$)	−60 °C ($k_c^{\pm} \times 10^{-9}$)	−50 °C ($k_c^{\pm} \times 10^{-9}$)
MeCl	0.50	0.46	0.42	0.38
Hex	1.73	1.49	1.29	1.10
Hex/MeCl 80/20 (v/v)	1.21 (2.2)	1.01 (2.8)	0.87 (3.4)	0.76 (4.1)
Hex/MeCl 60/40 (v/v)	0.894 (3.0)	0.76 (3.7)	0.68 (4.4)	0.62 (5.0)
Hex/MeCl 50/50 (v/v)	0.778 (3.5)	0.701 (4.0)	0.621 (4.8)	0.556 (5.6)
Hex/MeCl 40/60 (v/v)	0.692 (3.9)	0.607 (4.7)	0.559 (5.1)	0.494 (6.3)

by ^{1}H NMR spectroscopy, assuming one 2-PhFu moiety per chain, agreed well with those determined by GPC (Table 1), suggesting complete capping and the absence of side reactions. This is important, especially for the experiments carried out at −50 °C, where proton elimination from PIB$^+$ may occur.[7] The results indicate, however, that proton elimination is either absent or much slower than the capping reaction. The reactivity ratios were calculated from x_{∞}^{IB} using eq 1 and from the DP$_{n\infty}$ using eq 2. These two methods yielded similar $k_p^{\pm}/k_c^{\pm}$ values (Table 1).

To determine $k_p^{\pm}$, the value of the diffusion-limited second-order rate constant, $k_c^{\pm}$, is necessary, which, however, varies with temperature and other parameters that influence the diffusion coefficient (Smoluchowski equation).[3] Direct rate measurements for the reaction of benzhydryl cations with highly reactive π-nucleophiles yielded a value of (2−4) × 10^9 L mol^{-1} s^{-1} for diffusion control.[15] Therefore, we have arbitrarily set the $k_c^{\pm}$ value to 3 × 10^9 L mol^{-1} s^{-1} in Hex/MeCl 60/40 (v/v) solvent mixtures, at −80 °C. For other temperatures the Stokes−Einstein equation was applied (eq 7)

$$D = \frac{RT}{6\pi\eta r N} \tag{7}$$

where D is the diffusion coefficient, R is the universal gas constant, η is the dynamic viscosity of the system, r is the radius of the molecule, and N is the Avogadro number. Dynamic viscosities of solvent mixtures measured at different temperatures are shown in Table 2, along with $k_c^{\pm}$ values, which were calculated relative to $k_c^{\pm} = 3 \times 10^9$ L mol^{-1} s^{-1} (−80 °C, Hex/MeCl 60/40, v/v).

The absolute rate constants of propagation have been computed using the corrected $k_c^{\pm}$ values. Table 1 shows that the $k_p^{\pm}$ is essentially independent of the temperature. This finding agrees well with the results of Mayr, who has shown that fast bimolecular reactions do not have an enthalpic barrier.[16]

Plesch recently attempted to explain the discrepancies in propagation rate constants between previously accepted values and those obtained by the diffusion clock method by monomer solvation of the propagating carbocation at high monomer concentration (>4 mol L^{-1}).[17] According to the results in Table 1, however, the diffusion clock method yielded virtually identical propagation rate constants in the [IB] = 1−6 mol L^{-1} range.

Effect of Solvent Polarity on $k_p^{\pm}$. To understand the effect of solvent polarity on $k_p^{\pm}$, competition experiments were carried out in different Hex/MeCl solvent mixtures. To keep the solvent polarity constant when different IB concentrations were used, IB was considered as a nonpolar solvent, and its volume was added to the volume of hexanes. Because of polymer precipitation in Hex/MeCl 40/60 (v/v), the concentration of IB could not be raised above 1.0 mol L^{-1} in this solvent mixture.

Table 3 reveals that $k_p^{\pm}$ increases from 1.8 × 10^8 to 8.5 × 10^8 L mol^{-1} s^{-1} with the increase of solvent polarity from Hex/MeCl 80/20 to 40/60 (v/v).

Cationic propagation is considered an ion−dipole reaction, in which the charge is more dispersed in the transition state than in the ground state.[4] Therefore, according to the Hughes−Ingold rule, an increase of solvent polarity should result in a decrease in the propagation rate constant.[18] As indicated above, propagation via ion pairs in the polymerization of IB does not follow this rule, which may be related to the absence of enthalpic barrier for propagation. Reactions without an enthalpic barrier, however, could be further accelerated

Table 3. Absolute Propagation Rate Constants in Solvent Mixtures of Different Apolar/Polar Ratio at −80 °C[a]

(Hex + IB)/MeCl (v/v)	[IB] (mol L^{-1})	$k_p^{\pm}/k_c^{\pm}$ (from x_{∞}^{IB})	$k_p^{\pm}/k_c^{\pm}$ (from $DP_{n\infty}$)	$k_p^{\pm}/k_c^{\pm}$ (average)	$k_p^{\pm}$ (L mol^{-1} s^{-1})
80/20	1.0	0.11	0.063		
80/20	1.5	0.10	0.059	0.083	1.8×10^8
80/20	2.0	0.09	0.062		
80/20	2.5	0.11	0.077		
60/40	1.0	0.17	0.14		
60/40	1.5	0.18	0.16	0.16	4.8×10^8
60/40	2.0	0.16	0.15		
60/40	2.5	0.17	0.15		
50/50	1.0	0.22	0.18		
50/50	1.5	0.22	0.19	0.21	7.2×10^8
50/50	2.0	0.22	0.21		
50/50	2.5	0.22	0.21		
40/60	0.4	0.24	0.20		
40/60	0.6	0.24	0.20	0.22	8.5×10^8
40/60	0.8	0.25	0.21		
40/60	1.0	0.25	0.20		

[a] [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE] = 0.003 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, reaction time 1 h except for 80/20 (v/v) ratio where it was 2 h.

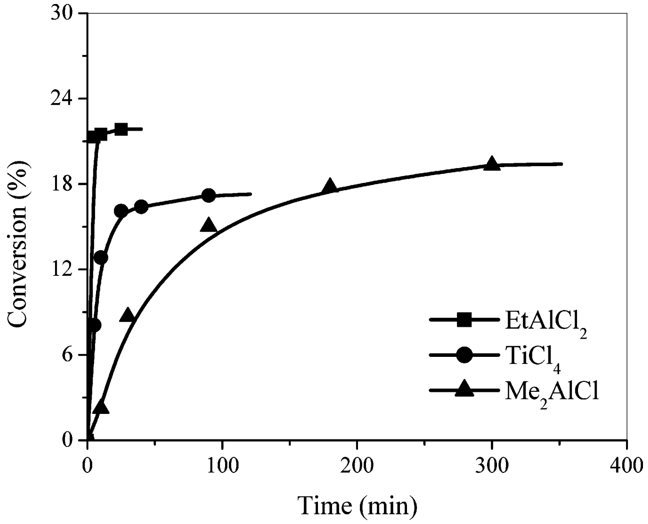

Figure 1. Time vs conversion plot in the competition experiment with [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE] = 0.003 mol L^{-1}, [IB] = 2.0 mol L^{-1}, Hex/MeCl 60/40 (v/v) at −80 °C, and with different Lewis acids [$TiCl_4$] = 0.036 mol L^{-1}, [Me_2AlCl] = 0.2 mol L^{-1}, [$EtAlCl_2$] = 0.007 mol L^{-1}.

by the decrease of the entropic barrier in which solvation may play an important role. However, a similar solvent effect has been reported for the reaction of 2-methyl-1-pentene with the bis(*p*-methoxyphenyl)carbenium ion (where the rate is governed by the enthalpy of activation), where the addition is 4.8 times faster in nitromethane ($\epsilon = 28$) than in chloroform ($\epsilon = 9$).[19]

Effect of Lewis Acid on $k_p^{\pm}$. In addition to $TiCl_4$, competition experiments were also carried out with $EtAlCl_2$ and Me_2AlCl as coinitiators at −80 °C in Hex/MeCl 60/40 (v/v) solvent system. First, the time necessary to reach limiting conversion (x_{∞}^{IB}) was determined. Figure 1 shows the conversion vs time plots for DTE as capping agent. Because the strength of the Lewis acid greatly affects the concentration of the active species, the time to reach limiting conversion depends on the nature of Lewis acid. While with $EtAlCl_2$, the strongest Lewis acid, limiting conversion was reached in 5 min, 25 min and 5 h were necessary to reach limiting conversions with $TiCl_4$ and Me_2AlCl, respectively. Figure 2 shows the conversion vs time plots for $TiCl_4$ with 2-PhFu and DTE as capping agents. Although the capping reaction is diffusion-limited with both DTE and 2-PhFu,[3] the diffusion coefficients may be somewhat different. According to Figure 2, higher limiting conversions were obtained with DTE, suggesting that the diffusion coefficient of DTE is lower than that of 2-PhFu. This is reasonable since DTE is larger than 2-PhFu.

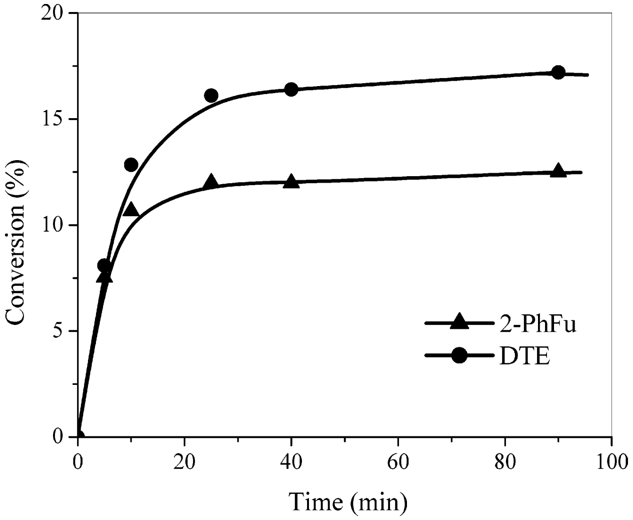

Figure 2. Time vs conversion plot with different *π*-nucleophile; [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE] = [2-PhFu] = 0.003 mol L^{-1}, [IB] = 2.0 mol L^{-1}, [$TiCl_4$] = 0.036 mol L^{-1}, Hex/MeCl 60/40 (v/v) at − 80 °C.

^1H NMR spectroscopy confirmed the absence of uncapped $-C\boldsymbol{H}_2-C(C\boldsymbol{H}_3)_2-Cl$ ends (absence of $C\boldsymbol{H}_2$ signal at 1.92 ppm and $C\boldsymbol{H}_3$ signal at 1.66 ppm). Furthermore, the molecular weights determined by ^1H NMR spectroscopy assuming complete capping were similar to the molecular weights determined by GPC; i.e., all chain ends were capped by the corresponding *π*-nucleophile. The molecular weight distributions of the polymers were close to the expected most probable distribution ($M_w/M_n \sim 2$).

Complete capping in the competition experiment does not mean that the polymerization is living. Competition can also be used to determine $k_p^{\pm}$ when termination or chain transfer occurs (nonliving polymerization), provided that the rate of capping is much higher than the rate of termination or transfer. Living polymerization of IB has been reported with $TiCl_4$[11,20] and Me_2AlCl.[13] With $EtAlCl_2$ termination by alkylation and/or hydridation may be operational and indeed incremental monomer addition has shown that the lifetime of the active chain end in this system is less than 2 min.[21] Nevertheless, the molecular weights calculated by ^1H NMR spectroscopy from the integral values of CH_3 signal in PIB at 1.10 ppm and the aromatic signals of the *π*-nucleophile moiety at the chain end (6.54 ppm, doublet for 2-PhFu, and 7.16 ppm, quartet for DTE) and that measured by GPC (Table 4) are similar, indicating that the chain ends are completely capped with the *π*-nucleophiles.

The calculated $k_p^{\pm}/k_c^{\pm}$ rate constant ratios for $TiCl_4$, Me_2AlCl, and $EtAlCl_2$ as coinitiators in Hex/MeCl 60/40 (v/v) at −80 °C based on x_{∞}^{IB} and $DP_{n\infty}$ are shown in Table 5. Because of the different diffusion coefficient of DTE and 2-PhFu, the rate constant ratios and the calculated $k_p^{\pm}$ values are somewhat different for a given

Table 4. Limiting Molecular Weights of PIB Determined by GPC and ^{1}H NMR Spectroscopy with $TiCl_4$, Me_2AlCl, and $EtAlCl_2$[a]

Lewis acid	π-nucleophile	time	M_n (GPC)	M_n (NMR)	M_w/M_n
$TiCl_4$	2-PhFu	25 min	7 800	7 600	2.3
	DTE	25 min	10 200	10 500	2.2
Me_2AlCl	2-PhFu	5 h	8 500	7 800	2.0
	DTE	5 h	10 700	10 700	2.0
$EtAlCl_2$	2-PhFu	25 min	9 700	10 600	2.0
	DTE	25 min	13 200	15 000	2.0

[a] $[TiCl_4] = 0.036$ mol L^{-1}, $[Me_2AlCl] = 0.2$ mol L^{-1}, $[EtAlCl_2] = 0.007$ mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE] = [2-PhFu] = 0.003 mol L^{-1}, [IB] = 2.0 mol L^{-1}, Hex/MeCl 60/40 (v/v), −80 °C.

Table 5. Absolute Propagation Rate Constants in the Competition Reactions with $TiCl_4$, $EtAlCl_2$, and Me_2AlCl Coinitiators in Hex/MeCl (60/40) v/v at −80 °C[a]

Lewis acid	π-nucleophile	$k_p^\pm/k_c^\pm$ (from x_∞^{IB})	$k_p^\pm/k_c^\pm$ (from $DP_{n\infty}$)	$k_p^\pm/k_c^\pm$ (average)	$k_p^\pm \times 10^{-8}$ (L mol^{-1} s^{-1})
$TiCl_4$	2-PhFu	0.12	0.14	0.13	3.9
	DTE	0.17	0.15	0.16	4.8
Me_2AlCl	2-PhFu	0.12	0.13	0.12	3.6
	DTE	0.18	0.19	0.18	5.4
$EtAlCl_2$	2-PhFu	0.15	0.17	0.16	4.8
	DTE	0.21	0.18	0.19	5.7

[a] $[TiCl_4] = 0.036$ mol L^{-1}, $[Me_2AlCl] = 0.2$ mol L^{-1}, $[EtAlCl_2] = 0.007$ mol L^{-1}, [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE] = [2-PhFu] = 0.003 mol L^{-1}, [IB] = 1.0, 1.5, 2.0, 2.5 mol L^{-1}.

Lewis acid. This uncertainty, however, is not critical considering the experimental error and the fact that the value of 3×10^9 L mol^{-1} s^{-1} was arbitrarily assigned as a diffusion limit in Hex/MeCl 60/40 (v/v) solvent mixtures, at −80 °C. The value of $k_p^\pm$ can be determined more accurately only when the exact value of $k_c^\pm$ is known. Although the overall rates of the polymerizations are vastly different, the $k_p^\pm$ values are practically identical for all three Lewis acids.

The absolute propagation rate constant was also determined with BCl_3 at −40 °C in pure MeCl, given that in Hex/MeCl 60/40 (v/v) solvent mixture the polymerization of IB is virtually absent. Since with BCl_3 direct initiation (polymerization in the absence of added initiator by haloboration-initiation) is significant,[22] competition experiments with 2-PhFu as capping agent were carried out in the presence and absence of initiator. Figure 3 shows the time−conversion plots obtained in the presence and absence of initiator and the difference of the two plots, which is attributed to polymer formation from TMPCl initiator. (This is strictly valid only when monomer conversion is low in the presence of initiator.) This plot reaches a limiting conversion at 16.8% after 5 h. From this limiting conversion $k_p^\pm/k_c^\pm = 0.167$ and from the calculated value of $k_c^\pm = 7.9 \times 10^9$ L mol^{-1} s^{-1} for MeCl at −40 °C, $k_p^\pm = 1.3 \times 10^9$ L mol^{-1} s^{-1} was calculated. This value is virtually identical to that predicted for pure MeCl from the $k_p^\pm$ vs MeCl content plot (Figure 4) for $TiCl_4$. Although in Figure 4 $k_p^\pm$ values obtained at −80 °C are plotted, we have already shown above that $k_p^\pm$ is independent of temperature, and therefore it should be similar for −40 °C.

The propagation rate constant of IB for BCl_3 was also determined from on-line UV−vis monitoring of the diffusion-limited addition of 2-PhFu to living PIB ($M_n = 1000$) in MeCl at −40 °C. The UV−vis spectrum of the reaction mixture (Figure 5) shows one peak at 278 nm, corresponding to the phenyl group, and a second peak at 332 nm, which corresponds to the ion

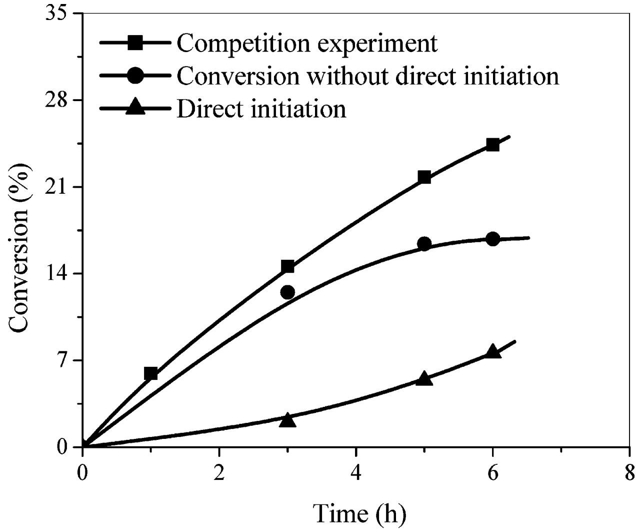

Figure 3. Time vs conversion curve in the competition experiment with BCl_3 coinitiator. Reaction conditions: [TMPCl] = 0.008 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [IB] = 1.0 mol L^{-1}, [2-PhFu] = 0.012 mol L^{-1}, $[BCl_3] = 0.4$ mol L^{-1} in MeCl solvent at −40 °C.

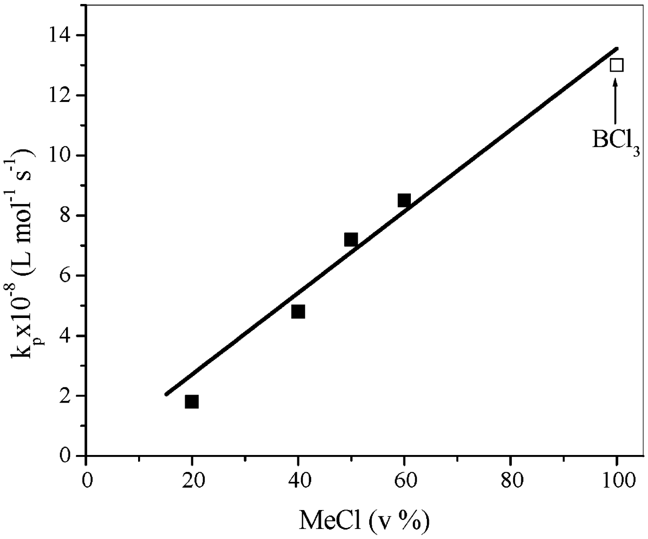

Figure 4. Correlation between the MeCl content and the absolute propagation rate constant.

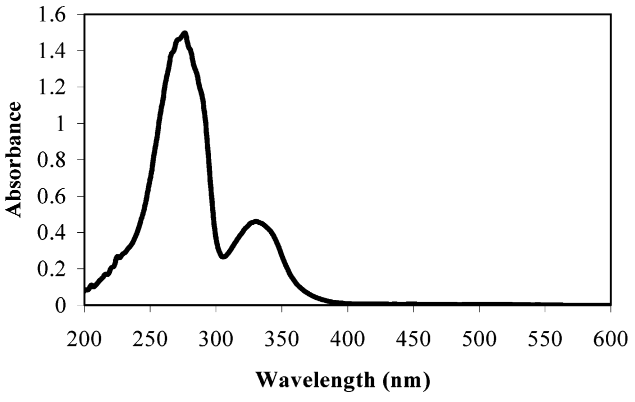

Figure 5. UV−vis spectrum of the PIB−2-PhFu reaction mixture in BCl_3 (0.4 mol L^{-1}) system.

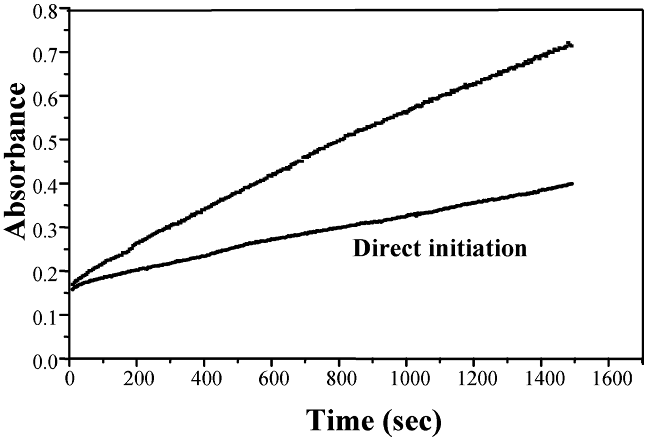

Figure 6. Time vs absorbance curve of the PIB−2-PhFu capping reaction. [PIB] = 0.002 mol L^{-1}, $[BCl_3]$ = 0.4 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, solvent MeCl, [2-PhFu] = 0.003 mol L^{-1}, temperature −40 °C, λ = 340 nm.

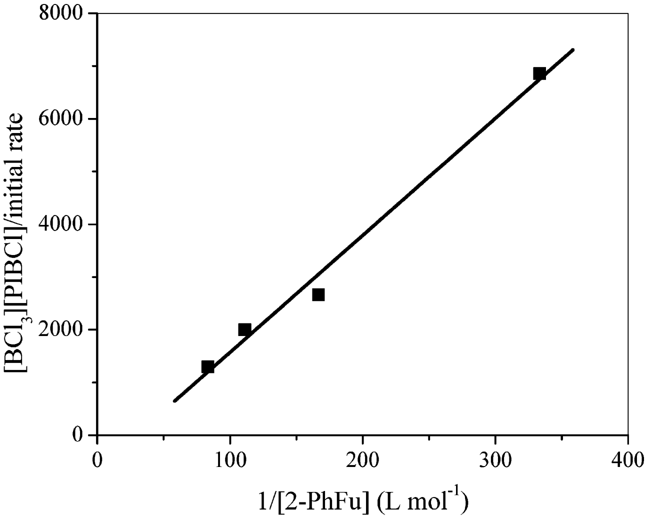

Figure 7. Reciprocal initial rate of capping vs 1/[2-PhFu]; [PIBCl] = 0.002 mol L^{-1}, $[BCl_3]$ = 0.4 mol L^{-1}.

pair of capped PIB. Because of the high BCl_3 concentration (0.4 mol L^{-1}), direct initiation of 2-PhFu was also significant (Figure 6). Therefore, the absorbance values compensated by direct initiation were used to determine the initial rate of capping.

The composite rate constant of capping, k_cK_i, was determined using eq 8.

$$\frac{[\text{PIBCl}][\text{BCl}_3]}{\frac{d}{dt}([\text{PIB}-2\text{-PhFu}^+\text{BCl}_4^-] + [\text{PIB}-2\text{-PhFu}^+])} = \frac{1}{k_cK_i[2\text{-PhFu}]} + \frac{1}{k_i} \quad (8)$$

The denominator on the left side of eq 8 contains the sum of the concentrations of capped ion pairs and free ions. The plot of the left side of eq 8 vs 1/[2-PhFu] should yield a straight line, with the slope and intercept of $1/k_cK_i$ and $1/k_i$, respectively. The plot is shown in Figure 7.

For the calculation of the composite rate constant of the capping reaction, the concentration of PIB−2-$PhFu^+$ carbenium ion was derived from the measured absorbance at the absorption maximum λ_{max} = 340 nm and the corresponding molar absorbance coefficient ϵ_{max} = 30 000. From the slope, using $k_c = 7.9 \times 10^9$ L mol^{-1} s^{-1}, $K_i = 5.7 \times 10^{-12}$ L mol^{-1} was calculated. Because the experiments were conducted in a 2-PhFu concentration range where $k_{-i} \gg k_c$[2-PhFu], the intercept (inaccurately negative in Figure 7) could not be used to determine k_i. From K_i the active center concentration $[PIB^+BCl_4^-]$ can be calculated, and from $k_p^{app} = k_p^{\pm}[PIB^+BCl_4^-] = 3.1 \times 10^{-5}$ s^{-1} (for $[BCl_3]$ = 0.24 mol L^{-1}, [TMPCl] = 0.0116 mol L^{-1}, [IB] = 0.48 mol L^{-1})[14a] $k_p^{\pm} = 2.0 \times 10^9$ L mol^{-1} s^{-1} was obtained.

Calculation of k_i, k_{-i}, K_i, and Thermodynamic Parameters from the Polydispersity−Conversion Curves. Although the absolute rate constant of propagation can be determined conveniently from the competition experiment, information is not provided on the rate constant of ionization and deactivation. The rate constant of deactivation (k_{-i}), however, can be determined from the polydispersity vs conversion (x) plot by curve fitting to eq 9 derived by Muller et al.[23]

$$\bar{M}_w/\bar{M}_n = 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \quad (9)$$

In this equation $\beta = k_{-i}/([I]_0k_p^{\pm})$, where $[I]_0$ is the initiator (polymer) concentration. A similar equation could be derived from the mathematical treatment of the molecular weight distribution as a function of chain length in the living polymerization of IB by Puskas et al.[24] Equation 9 is valid when the fraction of active chain end $[P^+LA_nCl^-]/[I]_0$ is $\leq 10^{-2}$ and $\beta \geq 10$. From the absolute $k_p^{\pm}$ and the apparent propagation rate constant K_i can be calculated, and from K_i and k_{-i} the value of k_i can be obtained.

Thus, the polydispersity vs conversion plots obtained in Hex/MeCl 60/40, 50/50, and 40/60 (v/v) at −80, −60, and −40 °C were fitted to eq 9 and the β values determined. Figure 8 shows the conversion vs polydispersity plots obtained with the TMPCl/$TiCl_4$ initiator system in Hex/MeCl 60/40 (v/v) solvent mixture at different temperatures.

The correlation between the fitted line and the experimental points is excellent at −80 and −60 °C; however, it is significantly worse at −40 °C. This is attributed to slow β-proton elimination at −40 °C,[7] which results in an increase of polydispersity. Therefore, only the low conversion part was fitted at −40 °C. For Hex/MeCl 60/40 (v/v) at − 80 °C a β value of 23.8 was obtained, from which a $k_p^{\pm}/k_{-i}$ ratio of 21 was calculated. This number indicates that the propagation is 21 times faster than deactivation. This value is in excellent agreement with that determined by UV−vis measurements ($k_p^{\pm}/k_{-i} = 20$) reported by us[3] and independently confirmed by Storey et al. recently.[25] The β value increases with the increase of temperature, suggesting that the rate constant of deactivation increases with increasing temperature, since $k_p^{\pm}$ remains constant. Therefore, while on average 21 monomer units are added during an active cycle at −80 °C, only 9 and 2 monomer units are incorporated during an active cycle at −60 and −40 °C, respectively. Thus, lower polydispersity can be obtained at higher temperature.

Table 6 summarizes k_i^{app}, k_{-i}, and K_i^{app} values calculated from the polydispersity vs conversion plots obtained with the TMPCl/$TiCl_4$ initiator system at different temperatures and solvent polarities with the postulate that $k_p^{\pm}$ is also independent of temperature in Hex/MeCl 50/50 and 40/60 (v/v) solvent mixtures. The k_i^{app} value determined here and that obtained by us

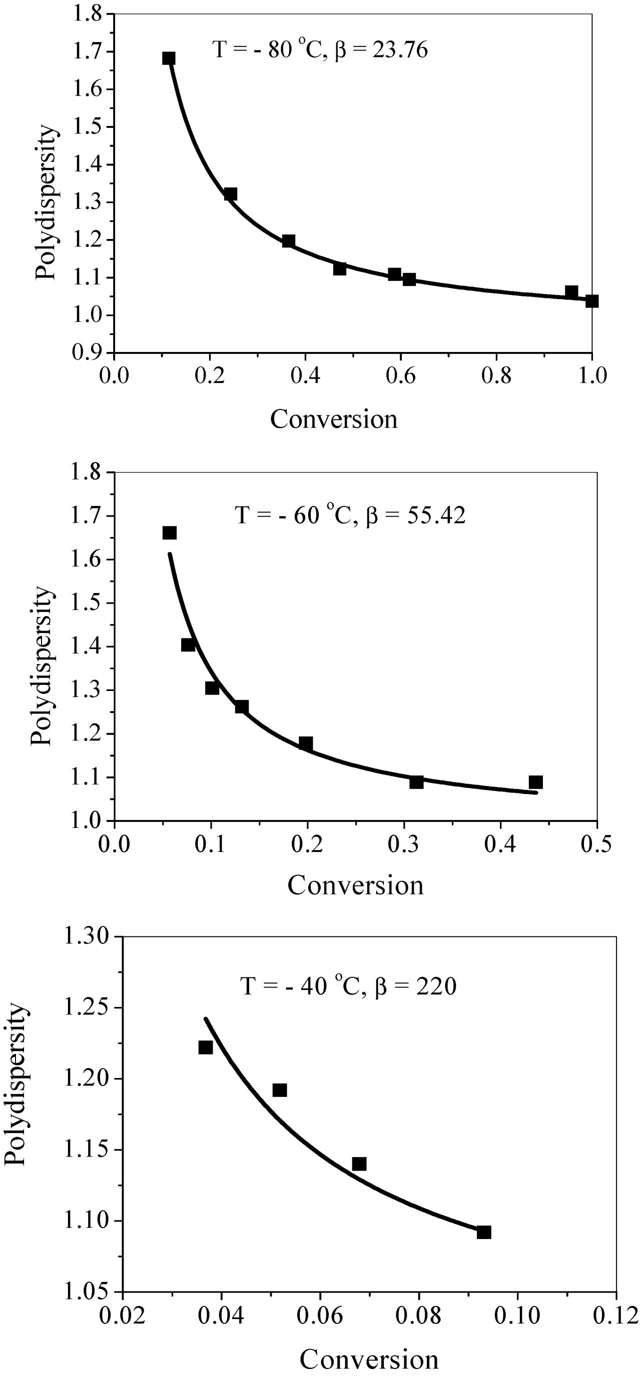

Figure 8. Polydispersity vs conversion plots at different temperatures in Hex/MeCl 60/40 (v/v), [TMPCl] = 0.002 mol L^{-1}, [DTBP] = 0.006 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, [IB] = 2.0 mol L^{-1}.

earlier using visible spectroscopy, with TiCl$_4$ in Hex/MeCl 60/40 (v/v) at −80 °C (k_i^{app} = 15 L mol^{-1} s^{-1}),[26] are virtually identical. The apparent propagation rate constants (k_p^{app}) are also tabulated in Table 6. The k_p^{app} values show a generally observed trend, that the polymerization of IB is faster at lower temperature and higher solvent polarity. At constant solvent polarity the change in temperature only affects the concentration of active centers via change in the K_i^{app} value, which decreases with increasing temperature. For instance at Hex/MeCl 60/40 (v/v) the polymerization is about 40 times faster at −80 °C compared to −40 °C due to a 40 times larger K_i^{app} value at the lower temperature. The higher K_i^{app} value at lower temperature is the result of higher k_i^{app} (likely due to higher [Ti$_2$Cl$_8$]) and lower k_{-i} at lower temperature. The increasing k_{-i} value with increasing temperature, however, mainly determines K_i^{app} and the active center concentration, since the effect of temperature on k_i^{app} is smaller even at Hex/MeCl 60/40 (v/v) and decreases with increasing solvent polarity. For the most polar Hex/MeCl 40/60 (v/v) solvent k_i^{app} remains approximately constant in the −80 to −40 °C range.

The increase of solvent polarity at constant temperature also increases the overall polymerization rate. First, there is a moderate increase of $k_p^{\pm}$ with increasing solvent polarity. More importantly, the active center concentration also increases due to increasing K_i^{app} with increasing solvent polarity. At −80 °C this increase is mainly due to a decreasing k_{-i} value with increasing polarity, as k_i^{app} increases only slightly. At −60 and −40 °C k_{-i} is approximately constant and k_i^{app} increases with increasing solvent polarity, which results in higher K_i^{app}.

The k_i, k_{-i}, and K_i values were also determined for BCl$_3$ and the k_i^{app}, k_{-i}, and K_i^{app} values for Me$_2$AlCl coinitiators (Tables 7 and 8). For BCl$_3$, which has been shown to be monomeric,[14] k_i and K_i represent the absolute values. Me$_2$AlCl is likely dimeric; therefore, for this Lewis acid k_i and K_i are apparent values. These Lewis acids are relatively weak; therefore, K_i is much smaller than that for TiCl$_4$. Since the k_{-i} values are similar to those obtained with TiCl$_4$, the small equilibrium constants are almost entirely due to the smaller k_i values. Direct and quantitative comparison between Lewis acids, however, cannot be made since the rate constant of activation is only an apparent value for TiCl$_4$ and Me$_2$AlCl.

From the temperature dependence of the ionization process thermodynamic parameters ($\Delta H°$, $\Delta S°$, ΔH^{o+}, and ΔS^{o+}) can be calculated according to the following equations:

$$\frac{\Delta H^{o}}{RT} - \frac{\Delta S^{o}}{R} = -\ln K_i \tag{10}$$

$$\ln k = \ln s - \frac{\Delta H^{o+}}{RT} \tag{11}$$

$$s = \frac{kT}{h} e^{\Delta S^{o+}}/R \tag{12}$$

where k is the Boltzmann constant, h Planck's constant, and s the frequency factor (number of successful collisions).

Table 9 shows that the ionization (activation) is exothermic and exoentropic. A detailed discussion, however, is not possible since both the rate and equilibrium constant of ionization are apparent values, and their temperature dependence yields the apparent standard enthalpy ($\Delta H_i^{o,app} = \Delta H_i° + \Delta H_{D0}°$) and entropy ($\Delta S_i^{o,app} = \Delta S_i° + \Delta S_{D0}°$) of ionization. Interestingly, the activation energy for ionization is negative and strongly depends on solvent polarity. This may be attributed to the composite nature of the apparent ionization rate constant ($k_i^{app} = k_i K_{D0}$), since dimerization of TiCl$_4$ is exothermic;[27] therefore, a higher K_{D0} can be expected at lower temperature. While the rate constant of ionization is an apparent value, the rate constant of deactivation is not. Table 9 shows that the entropy of activation for deactivation is very small, consistent with expectations since the translational

Table 6. k_{-i}, K_i^{app}, and k_i^{app} Values from the Conversion−Polydispersity Curves[a]

Hex/MeCl (v/v)	T (°C)	[IB] (mol L^{-1})	k_p (L mol^{-1} s^{-1})	β	k_{app} (s^{-1})	k_{-i} (s^{-1})	K_i^{app} (L^2 mol^{-2})	k_i^{app} (L^2 mol^{-2} s^{-1})
60/40	−80	2.0	4.7×10^8	24	8.8×10^{-4}	2.3×10^7	7.2×10^{-7}	16
60/40	−60	2.0	4.7×10^8	55	1.6×10^{-4}	5.2×10^7	1.3×10^{-7}	6.8
60/40	−40	2.0	4.7×10^8	220	2.4×10^{-5}	2.1×10^8	1.9×10^{-8}	4.0
50/50	−80	1.0	7.2×10^8	11	2.5×10^{-3}	1.7×10^7	1.3×10^{-6}	22
50/50	−60	1.0	7.2×10^8	40	4.6×10^{-4}	5.7×10^7	2.5×10^{-7}	14
50/50	−40	1.0	7.2×10^8	167	7.8×10^{-5}	2.4×10^8	4.2×10^{-8}	10
40/60	−80	0.4	8.6×10^8	5.2	5.6×10^{-3}	9.1×10^6	2.5×10^{-6}	23
40/60	−60	0.4	8.6×10^8	26	1.2×10^{-3}	4.4×10^7	5.4×10^{-7}	24
40/60	−40	1.0	8.6×10^8	119	2.3×10^{-4}	2.1×10^8	1.0×10^{-7}	21

[a] [TMPCl] = 0.002 M, [DTBP] = 0.006 M, [$TiCl_4$] = 0.036 M.

Table 7. k_{-i}, K_i, and k_i Values from the Conversion−Polydispersity Curves Obtained with BCl_3 Coinitiator in MeCl at −40 °C

coinitiator	k_p (L mol^{-1} s^{-1})	β	k_{app} (s^{-1})	k_{-i} (s^{-1})	K_i (L mol^{-1})	k_i (L mol^{-1} s^{-1})
BCl_3	1.7×10^{9} [a]	20	3.1×10^{-5}	2.7×10^8	5.8×10^{-12}	1.6×10^{-3}

[a] Average value for the competition and UV−vis experiment.

Table 8. Comparison of k_{-i}, K_i^{app}, and k_i^{app} Values for Me_2AlCl and $TiCl_4$ Coinitiators in Hex/MeCl 60/40 (v/v) at −80 °C

coinitiator	k_p (L mol^{-1} s^{-1})	β	k_{app} (s^{-1})	k_{-i} (s^{-1})	K_i^{app} (L^2 mol^{-2})	k_i^{app} (L^2 mol^{-2} s^{-1})
Me_2AlCl	4.5×10^{8} [a]	161	1.1×10^{-4}	7.2×10^8	3.5×10^{-9}	2.5
$TiCl_4$	4.7×10^8	24	8.8×10^{-4}	2.3×10^7	7.2×10^{-7}	16

[a] Average value for the competition experiments with 2-PhFu and DTE.

Table 9. Thermodynamic Parameters of the Ionization Process in Different Hex/MeCl Solvent Mixtures

solvent	K_i^{app}		k_{-i}		k_i^{app}	
Hex/MeCl (v/v)	ΔH^{o} (kJ/mol)	ΔS^{o} (kJ/(mol K))	ΔH^{o+} (kJ/mol)	ΔS^{o+} (kJ/(mol K))	ΔH^{o+} (kJ/mol)	ΔS^{o+} (kJ/(mol K))
60/40	−34	−0.29	22	0.0059	−13	−0.29
50/50	−32	−0.28	25	0.026	−7.3	−0.25
40/60	−30	−0.26	29	0.043	−0.59	−0.22

component is zero. The enthalpy of activation for deactivation, however, is relatively large and increases with increasing solvent polarity. Since the enthalpy of activation includes not only differences in chemical bonding in the transition state and reactants but also differences in solvation, the increase of k_{-i} with increasing solvent polarity suggests that the transition state of deactivation is more polar than the ion pair ground state.

Conclusion

The effect of solvent polarity, temperature, and the nature of Lewis acid on the rate constants of propagation, ionization (activation), and reversible termination (deactivation) in the carbocationic polymerization of IB was studied. In agreement with Mayr's finding that fast reactions do not have an enthalpic barrier, the rate constant of propagation for ion pairs is independent of temperature. The propagation rate constant is also independent of the nature of Lewis acid and increases slightly with increasing solvent polarity. Identical propagation rate constants were observed in living and nonliving polymerization, indicating that propagation proceeds on identical active centers; i.e., living polymerization does not involve special kinds of (stabilized, polarized, etc.) active centers. Solvent polarity, temperature, and the nature of Lewis acid, however, have a large effect on overall polymerization rates that can be attributed mainly to the changes in the active center concentration, which decreases with decreasing solvent polarity, increasing temperature, and decreasing Lewis acid strength.

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