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Temperature Effects on the Living Cationic Polymerization of Isobutylene: Determination of Spontaneous Chain-Transfer Constants in the Presence of Terminative Chain Transfer

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ABSTRACT: The living cationic polymerization of isobutylene (IB) was studied using the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$/2,6-di-*tert*-butylpyridine (DTBP) system in hexane (Hex)/methyl chloride (MeCl) (60/40 and 40/60, v/v) solvent mixtures at various temperatures ranging from −25 to −80 °C. From the Arrhenius plots of the apparent rate constants for propagation, negative apparent activation energies were observed and calculated to be −8.5 and −6.9 kcal/mol using Hex/MeCl, 60/40, v/v and 40/60, v/v solvent mixtures, respectively. At temperatures ≤ -60 °C, linear first-order plots and linear M_n versus conversion plots were obtained, suggesting the absence of termination and chain transfer. Irreversible termination was conspicuously observed from the curved $\ln([M]_0/[M])$ versus time plots when the polymerizations were carried out at temperatures ≥ -40 °C in both solvent mixtures. M_n versus conversion plots, however, exhibited linear growth of M_n, on the theoretical line, with increased conversion indicating the absence of chain transfer to monomer. Structural analysis of products obtained at −40 °C using ^1H NMR spectroscopy revealed the presence of olefinic end groups, increasing in content with increased conversion. On the basis of these results, it is concluded that termination at higher temperature involves terminative chain transfer, that is, β-proton elimination from the living chain ends with the eliminated proton being instantaneously entrapped by a proton trap, DTBP. By a kinetic treatment of the terminative chain transfer, the spontaneous chain-transfer constants (k_{tr}/k_p's), zero order in monomer, were determined for the first time. In Hex/MeCl (40/60, v/v), k_{tr}/k_p was calculated to be 1.1×10^{-2} and 7.2×10^{-4} mol/L at −25 and −40 °C, respectively. In Hex/MeCl (60/40, v/v), k_{tr}/k_p was calculated to be 3.3×10^{-3} mol/L at −40 °C.

Introduction

Polyisobutylene (PIB), available only by the cationic polymerization of isobutylene (IB), is a polymer which exhibits a combination of attractive properties such as low T_g, thermal, oxidative, and hydrolytic stability, high barrier properties, and so forth.[1,2] Thus, it is not surprising that the cationic polymerization of IB has a significant academic as well as industrial importance. At selected conditions, IB undergoes living cationic polymerization to yield PIBs with molecular weights up to in excess of 10^5 g/mol and narrow molecular weight distributions ($M_w/M_n < 1.1$). "Selected conditions" to obtain PIBs with high molecular weights invariably entail an organic halide, ester, or ether initiator in conjunction with $TiCl_4$ as coinitiator in solvents (or solvent mixtures) of low to medium polarity at low temperatures (−80 °C) in the presence of a proton trap or a nucleophilic additive.[3,4]

The above conditions under which well-defined PIBs can be obtained, however, are not necessarily applicable for different monomers with different reactivities. In view of our continuing efforts in the synthesis of block copolymers by sequential monomer addition, we have been interested in the living polymerization of IB at relatively higher temperatures (> −60 °C). If, for instance, the living polymerization of IB to high molecular weight is possible at these temperatures, difficulties encountered in the synthesis of block copolymers at −80 °C, such as limited solubility of block segments containing styrenic monomers and high viscosity due to aggregation, could be circumvented. During the studies of block copolymerizations by sequential monomer addition with styrenic monomers at relatively higher temperatures (> −60 °C), however, our preliminary results indicated that irreversible termination is operational.

While a variety of proton traps have been studied in the living cationic polymerization of IB at −80 °C,[3−9] only limited information is available about the effects of temperature on the living polymerization of IB.[6−8] Contrary to our preliminary results, however, results reported by Storey et al. implied that the living polymerization of IB might be possible even at −30 °C.[8] Therefore we have undertaken a more detailed study to investigate temperature effects on the cationic polymerization of IB, the mechanism of irreversible termination at elevated temperatures, and the kinetics of this termination. In this paper, we will discuss the cationic polymerization of IB using the 2-chloro-2,4,4-trimethylpentane (TMPCl) or 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (tBDCCl)/$TiCl_4$/di-*tert*-butylpyridine (DTBP) system in hexane (Hex)/methyl chloride (MeCl) solvent mixtures (60/40 or 40/60, v/v) at various temperatures ranging from −25 to −80 °C. Furthermore, the mechanism of irreversible termination and its kinetics will be discussed.

Experimental Section

Polymerizations were carried out in 75 mL test tubes under a dry nitrogen atmosphere ($[H_2O] < 1$ ppm) in an MBraun 150M stainless steel glovebox (Innovative Technology Inc.). Kinetic studies of IB polymerization were carried out using

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the TMPCl/$TiCl_4$/DTBP system in Hex/MeCl (60/40 or 40/60, v/v) solvent mixtures. For comparison, a difunctional initiator (tBDCCl) was also used otherwise under the same conditions. The total reaction volume was 25 mL, and the addition sequence of the reactants was as follows: solvent mixture (Hex/MeCl), initiator (TMPCl or tBDCCl), proton trap (DTBP), IB, and $TiCl_4$. The all-monomer-in (AMI) technique was used, and parallel runs were quenched with prechilled methanol as a function of time. Control experiments, carried out in the absence of initiator but in the presence of DTBP in Hex/MeCl (60/40, v/v) at otherwise identical conditions, produced both negligible amounts of products (1−3 wt % in 1 h) and very low polymer concentration ($3-8 \times 10^{-5}$ M), indicating that uncontrolled initiation is virtually absent. Although the conversions and polymer concentrations were slightly higher in the Hex/MeCl (40/60, v/v) solvent mixture, uncontrolled initiation is not significant even in this system. The purification procedure of the resulting PIB has been reported.[3] Conversions were measured gravimetrically.

Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer, a model 441 absorbance detector, an on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), a model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent at the flow rate 1 mL/min. The detector signals were simultaneously recorded on a Macintosh computer for the absolute molecular weight and molecular weight distribution determination by MALLS using ASTRA software (Wyatt Technology Inc.). ^1H NMR spectroscopy for structural analysis was carried out on a Bruker 250 MHz spectrometer.

Results and Discussion

Polymerization in the Hex/MeCl (60/40, v/v) Solvent Mixture. In a previous report,[3] we described the living cationic polymerization of IB by the $TiCl_4$/DTBP/−80 °C system using difunctional dicumyl derivatives as initiators in the Hex/MeCl (60/40, v/v) solvent mixture. Chain transfer and termination were not detected at −80 °C, and PIB with close to a Poisson molecular weight distribution was obtained in the presence of DTBP in concentrations only slightly higher than the concentration of protic impurities in the system. In this study, the polymerization of IB was investigated, using TMPCl as initiator in the presence of DTBP, in the temperature range −25 to −60 °C in the Hex/MeCl (60/40, v/v) solvent mixture. The semilogarithmic kinetic plots ($\ln([M]_0/[M])$ versus time) for various temperatures are shown in Figure 1.

At −25 °C, the polymerization rate was extremely low for practical purposes (less than 5% conversion in 1 h) and therefore no further study was carried out. At −40 °C, the first-order kinetic plot may be fitted with a line that exhibits a positive *y*-intercept. However, it is most likely due to experimental error, since conversions are very low within the experimental time scale. When, in a separate experiment, the polymerization at −40 °C was studied at the extended time scale, the deviation of the first-order kinetic plot from linearity was conspicuously observed, as shown in Figure 2. This confirms the presence of irreversible termination in the polymerization of IB at ≥40 °C.

The first-order plot at −60 °C is linear, and it appears that the concentration of the active species remains constant within the experimental time scale. The slope of this plot represents the apparent rate constant for propagation k_{app}, and Figure 1 exhibits a strong increase in k_{app} with decreasing temperature. This indicates a negative apparent activation energy for the rate of IB polymerization in this system. Negative apparent activation energies reported for cationic polymerization of monomers such as isobutylene, α-methylstyrene, and indene were recently compiled by Sigwalt.[10] Very recently we also reported the negative apparent activation energy −3.5 kcal/mol for the living polymerization of α-methylstyrene in conjunction with BCl_3.[11] The generally (although not universally) accepted view is that higher ionization of the chain ends at lower temperature may explain the negative apparent activation energy. The apparent first-order rate constant for propagation at each temperature was plotted versus reciprocal temperature, as shown in Figure 3.

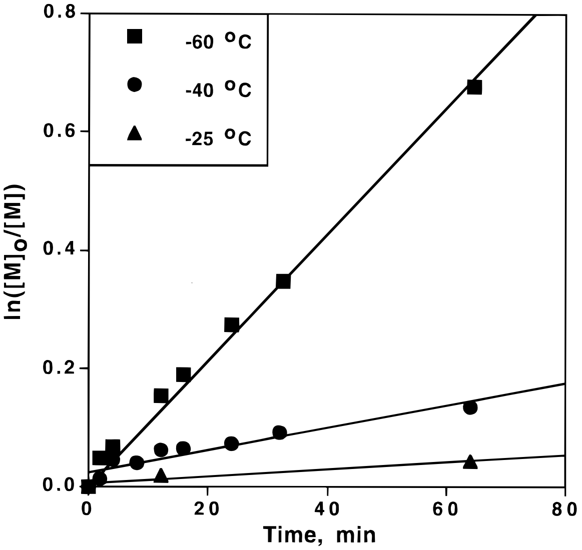


Figure 1. Plot of $\ln([M]_0/[M])$ versus time in the polymerization of IB using the Hex/MeCl (60/40, v/v) solvent mixture. Other polymerization conditions: $[TMPCl]_0 = 0.002$ M, $[TiCl_4] = 0.036$ M, [DTBP] = 0.003 M, and $[IB]_0 = 1.54$ M.

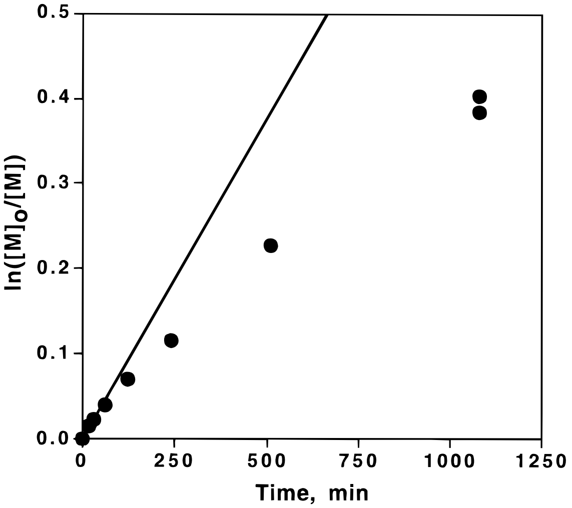


Figure 2. Plot of $\ln([M]_0/[M])$ versus time in the polymerization of IB using the Hex/MeCl (60/40, v/v) solvent mixture at −40 °C. Other polymerization conditions: same as in Figure 1.

The rate constant at −40 °C was calculated using the initial slope of the first-order plot (data points with low conversion where termination is negligible), and the rate constant at −80 °C was taken from our previous report.[3] From the slope, the apparent activation energy was calculated to be −8.5 kcal/mol. This value is the same as that obtained by Storey et al. using the tBDCCl or

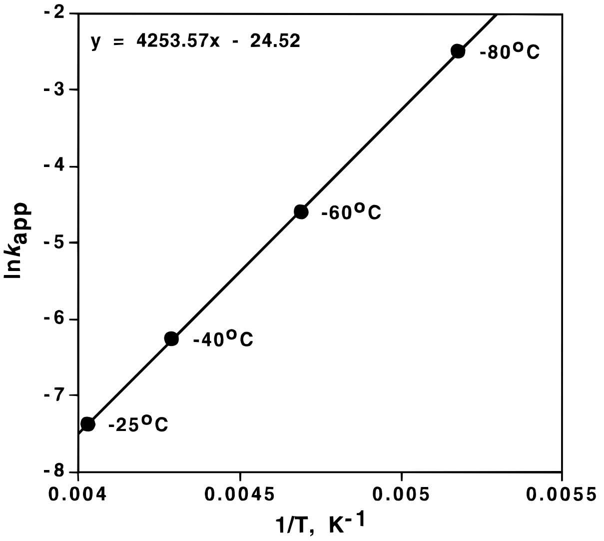


Figure 3. Arrhenius plot of the apparent first-order rate constants in the polymerization of IB using the Hex/MeCl (60/40, v/v) solvent mixture.

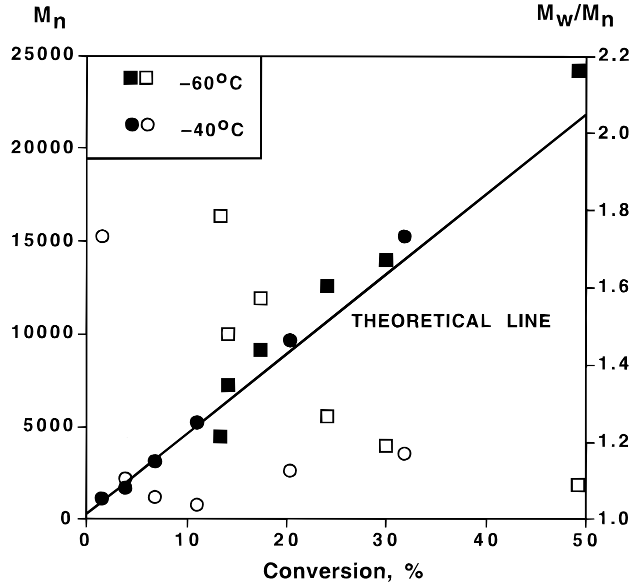


Figure 4. M_n and M_w/M_n versus conversion plots in the polymerization of IB using the Hex/MeCl (60/40, v/v) solvent mixture: filled symbols, M_n; open symbols, M_w/M_n.

dicumyl chloride/TiCl$_4$/IB system in the Hex/MeCl (60/40, v/v) solvent mixture in the presence of 2,4-dimethylpyridine[7] or pyridine.[10] The identical apparent activation energies indicate that the nature of the active species is the same, independently of the type of proton trap. This in turn strongly suggests that the polymerizations take place on identical active centers, that is, there is no interaction of active species with nucleophilic additives.[3,5]

The number-average molecular weight (M_n) versus conversion plots are shown in Figure 4 along with the polydispersity index (M_w/M_n) for the corresponding M_n as the right ordinate. At −60 °C, the M_n values are close to the theoretical line (solid line in Figure 4) and the corresponding M_w/M_n values decrease with increased conversion, as generally encountered in living cationic polymerization. It should be noted, however, that, at −40 °C, although the M_n values exhibit a linear increase on the theoretical line, their corresponding M_w/M_n values increase with increased conversion at conversions higher than ~10%. These results confirm the absence of chain transfer to monomer but clearly point to irreversible termination at higher temperature. This is also in good agreement with the theoretical calculation by Penczek et al.[12] in the absence of chain transfer but in the presence of termination. On the basis of M_w/M_n versus conversion plots, in addition to the two general diagnostic plots (ln[M]$_0$/[M] versus time and M_n versus conversion) for living polymerization, it appears that the temperature should be lowered below −40 °C to achieve the living cationic polymerization of IB in the Hex/MeCl (60/40, v/v) solvent mixture.

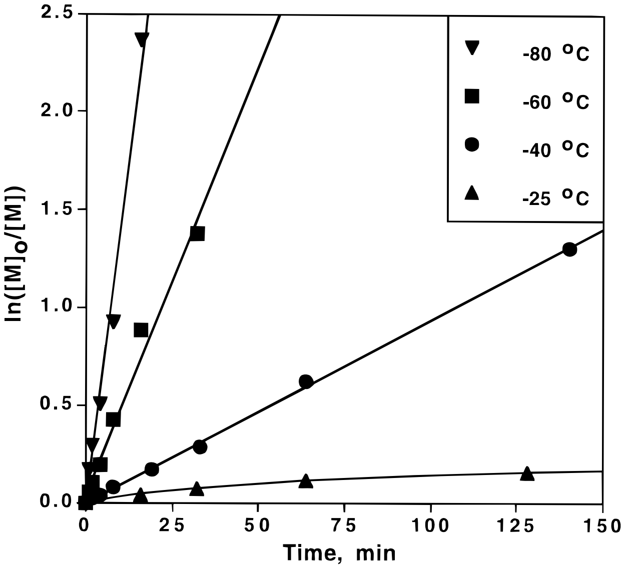


Figure 5. Plot of ln([M]$_0$/[M]) versus time in the polymerization of IB using the Hex/MeCl (40/60, v/v) solvent mixture. Other polymerization conditions: [TMPCl]$_0$ = 0.002 M, [TiCl$_4$] = 0.036 M, [DTBP] = 0.003 M, and [IB]$_0$ = 2.85 M.

Polymerization in the Hex/MeCl (40/60, v/v) Solvent Mixture. Since the polymerization rates were extremely low at higher temperature using the Hex/MeCl (60/40, v/v) solvent mixture, the solvent polarity was increased employing the Hex/MeCl (40/60, v/v) solvent mixture. The effect of temperature on the polymerization rate in this more polar solvent mixture was studied by constructing ln([M]$_0$/[M]) versus time plots at temperatures ranging from −25 to −80 °C. Figure 5 shows ln([M]$_0$/[M]) versus time plots using the Hex/MeCl (40/60, v/v) solvent mixture.

Straight lines, starting from the origin, were obtained except for the polymerization at −25 °C. The M_n values and the corresponding M_w/M_n values are shown as a function of conversion in Figure 6. Linear growth of M_n values, on the theoretical line, with increased conversion indicates the absence of chain transfer to monomer. At −25 °C a monotonic increase of M_w/M_n values with increasing conversion is observed, confirming the presence of irreversible termination. While the ln([M]$_0$/[M]) versus time plot at −40 °C exhibits linearity up to 75% conversion, monotonic deviation from linearity was observed when the polymerization was carried out for a prolonged time using a mono- or difunctional initiator (TMPCl or tBDCCl), as shown in Figure 7. M_n and M_w/M_n versus conversion plots are shown in Figure 8. Similar to what has been observed in Hex/MeCl (60/40, v/v) at −40 °C, the M_n values increase linearly with conversion, indicating the absence of chain transfer to monomer, while the increase of M_w/M_n values with

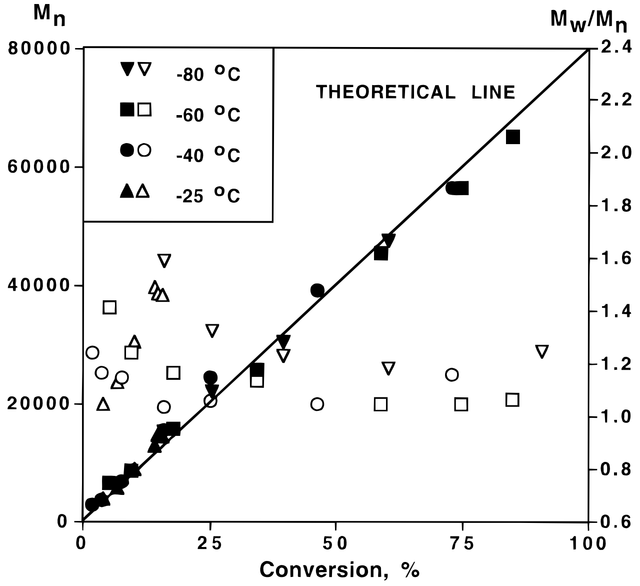


Figure 6. M_n and M_w/M_n versus conversion plots in the polymerization of IB using the Hex/MeCl (40/60, v/v) solvent mixture: filled symbols, M_n; open symbols, M_w/M_n.

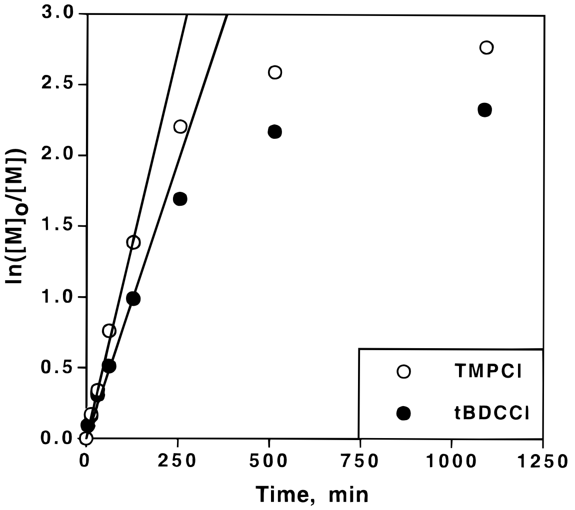


Figure 7. Plot of ln([M]$_0$/[M]) versus time in the polymerization of IB at −40 °C using the Hex/MeCl (40/60, v/v) solvent mixture. Other polymerization conditions: [TMPCl]$_0$ (=2-[tBDCCl]$_0$) = 0.002 M, [TiCl$_4$] = 0.037 M, [DTBP] = 0.004 M, and [IB]$_0$ = 2.7 M (for TMPCl) or 1.4 M (for tBDCCl).

conversion corroborates the presence of irreversible termination.

Apparent rate constants in the Hex/MeCl (40/60, v/v) solvent mixture followed the Arrhenius relationship, and the negative apparent activation energy was calculated to be −6.9 kcal/mol. The polymerization was also studied using tBDCCl, in the Hex/MeCl (40/60, v/v) solvent mixture under otherwise equivalent conditions. As compared in Table 1, slightly different but the same orders of rate constants and similar values of the apparent activation energy were obtained, indicating that there is no significant kinetic difference using TMPCl or tBDCCl as initiator.

Apparent rate constants and the apparent activation energies obtained using Hex/MeCl (60/40 and 40/60, v/v) solvent mixtures are also compared in Table 1. At higher temperatures, the effect of solvent polarity on the polymerization rate is more significant than that at −80 °C. For example, at −40 and −60 °C, the apparent rate constants are 4−5 times greater when the more polar solvent mixture, Hex/MeCl (40/60, v/v), is employed. However, at −80 °C, only a ~1.7-fold increase in the polymerization rate is observed with the Hex/MeCl (40/60, v/v) solvent mixture. While these tendencies can be attributed to the temperature- and/or solvent polarity-dependent equilibrium between dormant and active species, only qualitative comparison is possible due to the limited data obtained in this study.

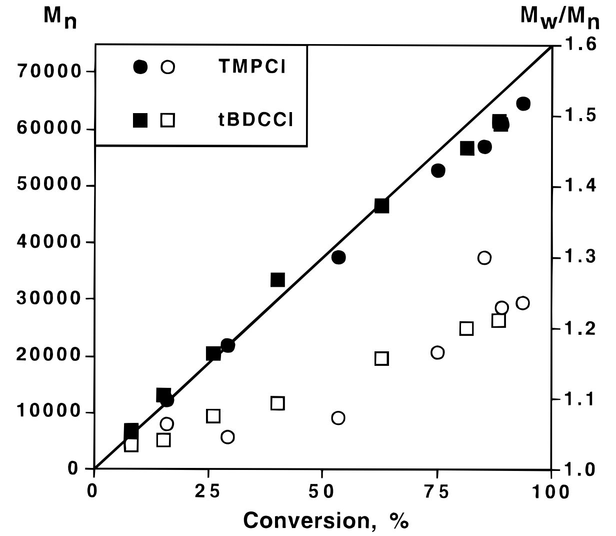


Figure 8. M_n and M_w/M_n versus conversion plots in the polymerization of IB at −40 °C using the Hex/MeCl (40/60, v/v) solvent mixture: filled symbols, M_n; open symbols, M_w/M_n.

It is also notable that, in the more polar solvent, the magnitude of the negative apparent activation energy is smaller than that in the less polar solvent. The apparent rate constant is a complex parameter, as it is a product of the absolute rate constant and the concentration of active species which is, in turn, determined by the equilibrium constant between dormant and active species. Therefore, the negative apparent activation energy is the sum of the enthalpy of the ionization equilibrium between dormant and active species (ΔH_i°) and the activation enthalpy of the propagation ($\Delta H_p^\ddagger$). The effect of solvent polarity on the negative apparent activation energy can be explained by the magnitude of changes in ΔH_i° and $\Delta H_p^\ddagger$. In a more polar solvent, the equilibrium between dormant and active species shifts toward the active species; that is, ΔH_i° is expected to decrease in more polar solvent. On the contrary, the rate constant of propagation of the active species is well-known to decrease with increasing solvent polarity, thereby increasing $\Delta H_p^\ddagger$.[13] Therefore, slightly higher apparent activation energy in more polar solvent suggests that the magnitude of change in $\Delta H_p^\ddagger$ is larger than that in ΔH_i° with increased solvent polarity.

Mechanism of Irreversible Termination. In the foregoing sections, it was concluded that the temperature should be lowered below −40 °C in order to achieve the living polymerization of IB in Hex/MeCl (60/40 and 40/60, v/v) solvent mixtures using TiCl$_4$ as coinitiator. The observed deviation of the ln([M]$_0$/[M]) versus time plot from linearity was attributed to the presence of irreversible termination at higher temperature, and the absence of chain transfer to monomer was proved by

Table 1. Apparent First-Order Rate Constants (k_{App}) and Apparent Activation Energies (E_{App}) in the Polymerization of IB[a]

solvent mixture		$10^3 k_{app}$, min^{-1} at different temp				
(Hex/MeCl, v/v)	initiator	−25 °C	−40 °C	−60 °C	−80 °C	E_{app}, kcal/mol
60/40	TMPCl	0.6	1.9[b] (1.0)[c]	10	83[d]	−8.5
40/60	TMPCl		9.4	44	144	−6.9
40/60	tBDCCl		6.3	30	120	−6.4

[a] Polymerization conditions: $[TMPCl]_0 = 2[tBDCCl]_0 = 0.002$ M, $[TiCl_4] = 0.036$ M, and [DTBP] = 0.003 M. [b] From Figure 1. [c] From Figure 2. [d] From ref 3.

Table 2. Structural Analysis of PIBs Prepared at −40 °C by ^{1}H NMR Spectroscopy[a]

no.	$[IB]_0$, M	polymerization time, h	M_n[b]	PIB-olefin, %	PIBCl, %
1	1.0	2	2400	6.0	94.0
2	1.0	4	4200	14.4	85.6
3	1.54	2	2700	6.6	93.4
4	1.54	4	4800	17.4	82.6

[a] Polymerization conditions: same as in Figure 2. [b] Calculated by ^{1}H NMR spectroscopy.

the linear increase of M_n with conversion on the theoretical line. These observations might be accounted for in terms of *terminative chain transfer*.[14] Kinetically, chain transfer can be first order or zero order in monomer. Chain transfer is first order in monomer when the active site transfers directly to a monomer or when the monomer is involved in the rate-determining step. Transfer of zero order in monomer usually involves proton transfer to a counteranion (or some transfer agent) which is rate determining, followed by protonation of monomer. It was reported that a zero-order chain-transfer reaction in monomer concentration is more important in the cationic polymerization of IB and that a first-order chain-transfer reaction is negligible. The zero-order chain-transfer reaction was also proposed to occur via β-proton elimination by the counteranion, and therefore it is also called *spontaneous chain transfer*. In the presence of a proton trap, direct chain transfer to monomer is unaffected; however, spontaneous chain transfer is aborted, since the eliminated proton is trapped by the proton trap ([DTBP] > [chain end]). This spontaneous chain transfer in the presence of a proton trap kinetically leads to irreversible termination, and from the mechanistic aspects, this is also called terminative chain transfer.

Whereas the hypothesis of terminative chain transfer smoothly explains our observations, that is, the deviation of the $\ln([M]_0/[M])$ versus time plot from linearity and the linear increase of M_n with conversion on the theoretical line, no direct proof has been given for this mechanism, as one of reviewers pointed out. Therefore, we carried out structural analysis of PIBs obtained at −40 °C by ^{1}H NMR spectroscopy to determine the presence of terminal unsaturation. Using the same conditions as in Figure 1, IB was polymerized with two monomer concentrations ($[IB]_0 = 1.0$ and 1.54 M) and the reaction was quenched at low conversions. Under these conditions, the contents of PIB-olefins were below 20%, and the coupling reaction between PIB-olefin and living PIB was not observed from GPC.[5] A summary of results is shown in Table 2, and representative ^{1}H NMR spectra are shown in Figure 9.

From peak assignments, it can be seen that terminal groups of PIB comprise three different structures, as shown in Chart 1. Relative amounts of PIB-olefin were determined by comparison of the integration area (A) of each end group, that is, using the equation $(A_f + 2A_h)/(A_c + A_e + 2A_h)$. Since only PIB with a chloro end (PIBCl) is obtained at −80 °C, PIB-olefins (whether *exo* or *endo*) obtained at −40 °C prove the kinetically observed termination is due to β-proton elimination at the living chain-ends, and the absence of chain transfer to monomer also corroborates the mechanism of terminative chain transfer. The hypothesis of β-proton elimination by the counteranion is also supported by the formation of close to statistical amounts of the *endo*-olefin, since only the *exo*-olefin is observed when β-proton elimination is caused by a free base in the polymerization system.[5]

Kinetic Model for Determination of Spontaneous Chain-Transfer Constants. First-order chain transfer, which can be diagnosed by the nonlinearity of the M_n versus conversion plot, is apparently absent (or below our detection limit) in our system. Therefore, we can determine the spontaneous chain-transfer constant in the presence of terminative chain transfer, that is, in the presence of a proton trap, since the rate of terminative chain transfer is essentially that of spontaneous chain transfer in the absence of a proton trap. The rate of spontaneous chain transfer can be expressed by eq 1.

$$\frac{d([PIB^+Ti_2Cl_9^-] + [PIBCl])}{dt} = -k_{tr}[PIB^+Ti_2Cl_9^-] \quad (1)$$

$[PIB^+Ti_2Cl_9^-]$ and [PIBCl] denote the concentrations of active and dormant species, respectively, and k_{tr} denotes the rate constant of spontaneous (or monomolecular) chain transfer. The concentration of active species can be expressed using the equilibrium constant K_i as in eq 2.

$$[PIB^+Ti_2Cl_9^-] = K_i[PIBCl][TiCl_4]^2 \quad (2)$$

As $1 \gg K_i[TiCl_4]^2$ (i.e., $[PIBCl] \gg [PIB^+Ti_2Cl_9^-]$), eq 1 can be rewritten as eq 3.

$$\frac{d[PIBCl]}{dt} = -k_{tr}K_i[PIBCl][TiCl_4]^2 \quad (3)$$

Using the integrated form of eq 3, the rate of polymerization, in the presence of terminative chain transfer, is expressed by eq 4.

$$-\frac{d[M]}{dt} = k_pK_i[TiCl_4]^2[PIBCl]_0 \exp(-k_{tr}K_i[TiCl_4]^2t)[M] \quad (4)$$

In eq 4, [M] refers to the monomer concentration at a given time and k_p refers to the absolute rate constant for propagation. In the absence of spontaneous or terminative chain transfer ($k_{tr} = 0$), eq 4 is converted

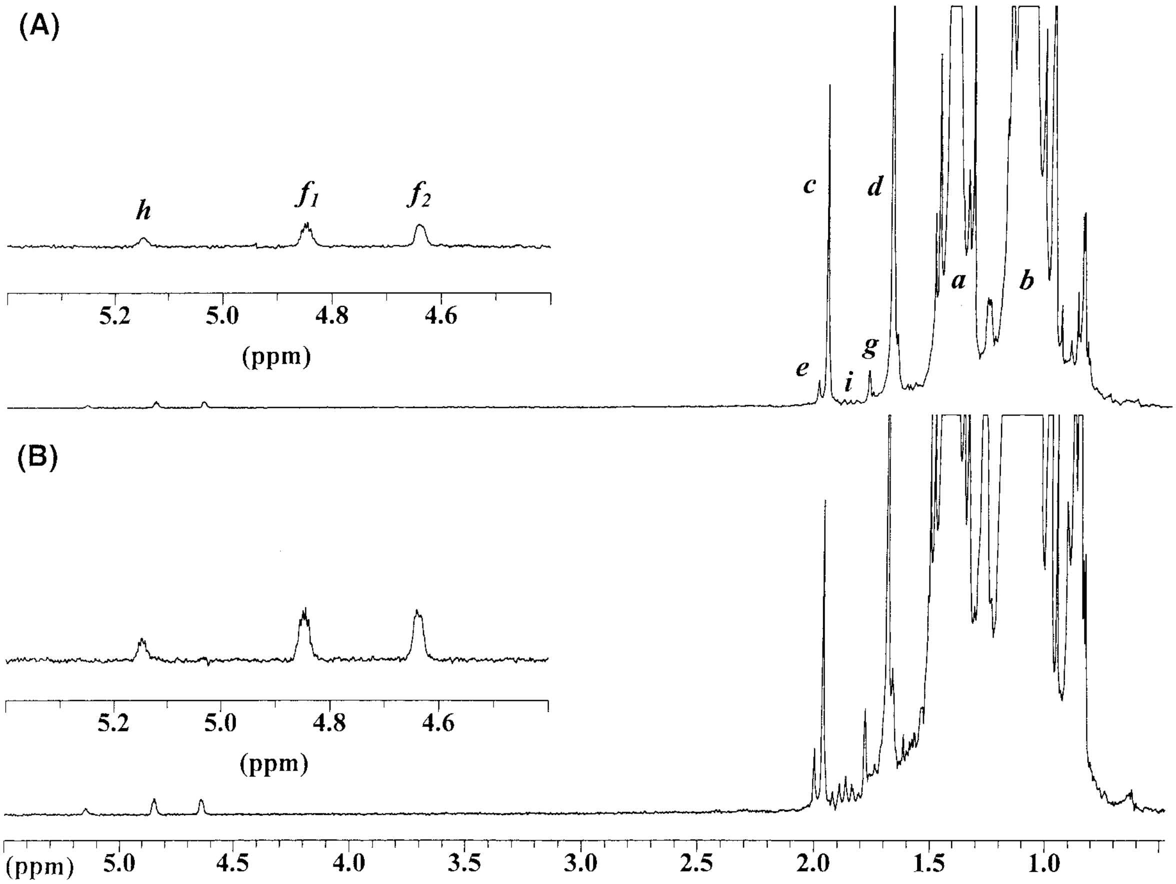
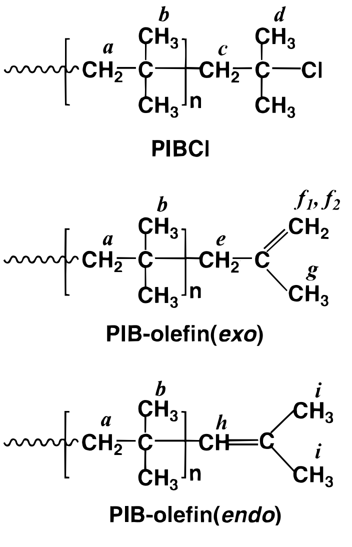


Figure 9. 250 MHz ^{1}H NMR spectra of PIBs prepared at −40 °C and quenched after 2 h (A) and 4 h (B). Other polymerization conditions: same as in Figure 1.

Chart 1



PIBCl

PIB-olefin(*exo*)

PIB-olefin(*endo*)

to eq 5, which is a first-order kinetic equation valid at low temperature, as in Figures 1 and 5.

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{PIB}^+\mathrm{Ti}_2\mathrm{Cl}_9^-][\mathrm{M}] \qquad (5)$$

Integration of eq 4 yields a semilogarithmic kinetic equation such as eq 6.

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = \frac{k_\mathrm{p}}{k_\mathrm{tr}}[\mathrm{PIBCl}]_0[1 - \exp(-k_\mathrm{tr}K_\mathrm{i}[\mathrm{TiCl}_4]^2t)] \qquad (6)$$

Using eq 6, it is possible to calculate numerically k_{tr}/k_p and $k_{tr}K_i$ assuming $[\mathrm{PIBCl}]_0 \cong [\mathrm{TMPCl}]_0$ (or $2[\mathrm{tBDCCl}]_0$). One can also calculate the maximum monomer conversion for a given system at an infinite time using this equation.

As shown in Figure 10, spontaneous chain-transfer constants (k_{tr}/k_p's) at −25 and −40 °C were obtained by fitting the experimental results with eq 6, and a summary of results is shown in Table 3. One can also determine k_{app}'s using two constants (k_p/k_{tr} and $k_{tr}K_i$) obtained as a pre-exponential term and an exponential decay term from eq 6, respectively, as given in Table 3. Although a 2−4-fold discrepancy between the k_{app}'s in Table 1 and in Table 3 is observed, they are in good agreement considering the experimental errors in Table 1, associated with curved $\ln([\mathrm{M}]_0/[\mathrm{M}])$ versus time plots.

There have been few attempts in the literature to simultaneously determine the chain-transfer constants of zero order in monomer (k_{tr}/k_p) and first order in monomer ($k_{tr,M}/k_p$). k_{tr}/k_p and $k_{tr,M}/k_p$ can be differentiated by plotting $1/\mathrm{DP}_n$ versus $1/[\mathrm{M}]_0$ at low conversions (Mayo plot) or by using the corresponding differential equation. $k_{tr,M}/k_p$ can be obtained from the intercept; however, the slopes of Mayo plots generally give $(k_{tr} + k_t)/k_p$, that is, the zero-order chain-transfer constant together with the rate constant of termination. Thus, if termination is operational, k_{tr}/k_p cannot be calculated separately. k_{tr}/k_p and $k_{tr,M}/k_p$ values were obtained by Sigwalt et al. in cationic grafting of various monomers from PIB bearing chloromethylbenzene groups as initiating sites and $\mathrm{AlEt_2Cl}$ as coinitiator in $\mathrm{CH_2Cl_2}$/methylcyclohexane (50/50, v/v).[15] At −50 °C only first-

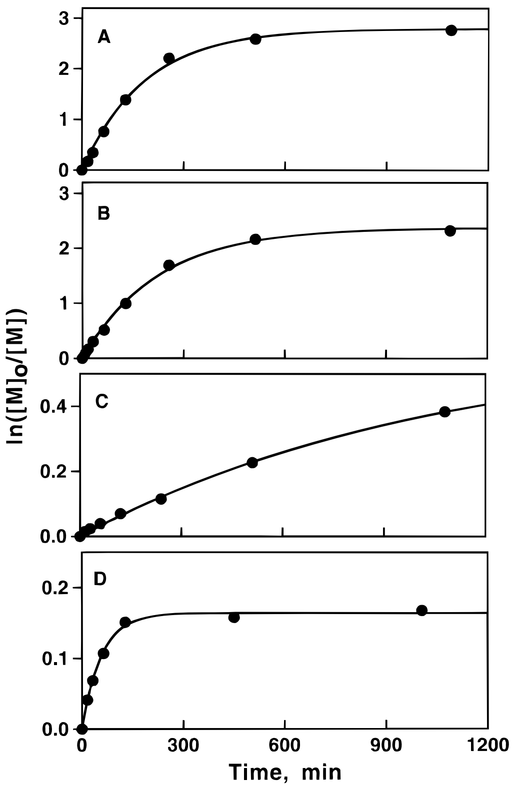


Figure 10. Comparison of calculated and experimental ln([M]$_0$/[M]) versus time plots for the polymerization of IB at −40 (A, B, and C) and −25 °C (D). A and B are from Figure 7, C is from Figure 2, and D is from Figure 5.

Table 3. Ratios of k_{tr}/k_p in the Polymerization of IB Using Hex/MeCl Solvent Mixtures

temp, °C	solvent mixture (Hex/MeCl, v/v)	initiator	k_{tr}/k_p, mol/L	k_{app},[a] min^{-1}
−25	40/60	TMPCl	1.1×10^{-2}	2.8×10^{-3}
−40	40/60	TMPCl	7.2×10^{-4}	1.5×10^{-2}
−40	40/60	tBDCCl	8.4×10^{-4}	1.0×10^{-2}
−40	60/40	TMPCl	3.3×10^{-3}	5.6×10^{-4}

[a] Calculated from the curve fitting using eq 6, assuming $[\mathrm{PIBCl}]_0 \cong [\mathrm{TMPCl}]_0$ and $[\mathrm{TiCl_4}] \cong [\mathrm{TiCl_4}]_0$.

order transfer was detected for styrene ($k_{tr,M}/k_p = 2.4 \times 10^{-3}$) and indene ($k_{tr,M}/k_p = 7.5 \times 10^{-4}$). Both first-order and zero-order transfer ($k_{tr,M}/k_p = 10^{-4}$ and $k_{tr}/k_p = 4 \times 10^{-4}$ mol/L) were observed in the polymerization of α-methylstyrene under the same conditions.[16] For the polymerization of IB, only first-order transfer constants are reported. In conjunction with $TiCl_4$ in CH_2Cl_2, $k_{tr,M}/k_p$ was found to be 5×10^{-4} at −14 °C, which decreased to 3×10^{-5} at −48 °C.[17] With the cumyl acetate/BCl_3 initiating system in CH_2Cl_2 at −10 °C, only zero-order transfer was detected; however, the chain-transfer constant could not be determined.[18]

Thus, the zero-order chain-transfer constants reported in Table 3 are the first such values in the cationic polymerization of IB. As expected, k_{tr}/k_p is higher at the higher temperature, and this can be readily explained in terms of the lower activation energy of propagation compared to transfer. Due to the high activation energy difference ($\Delta E \sim -20$ kcal/mol), k_{tr}/k_p rapidly decreases with decreasing temperature. From the Arrhenius relationship k_{tr}/k_p is estimated to be $\sim 10^{-5}$ at −60 °C and $\sim 10^{-7}$, or practically zero, at −80 °C. Interestingly, at −40 °C, a higher k_{tr}/k_p was obtained in the less polar solvent mixture. Since a higher k_p is expected in the less polar solvent, the higher k_{tr}/k_p ratio results from a relatively larger increase in k_{tr} in the less polar solvent under these conditions. This is in line with the transition state being less polar than the ground state.[19] It is important to note that these values can be used as a practical guide in the synthesis of block copolymers and functional polymers at elevated temperatures, that is, in the presence of irreversible termination. For example, using eq 6 and $k_{tr}/k_p \sim 10^{-5}$ at −60 °C in the Hex/MeCl (40/60, v/v) solvent mixture, one can predict that, with $[\mathrm{PIBCl}]_0 = 2 \times 10^3$ M, the IB conversion should be limited below ~90% in order to retain ~99% of the living chain ends. If a higher initiator concentration is used, one can also increase the IB conversion, retaining ~99% of the living chain ends.

Conclusion

On the basis of two diagnostic plots (ln[M]$_0$/[M] versus time and M_n versus conversion), it is concluded that temperature should be lowered below −40 °C in order to achieve the living polymerization of IB in Hex/MeCl (60/40 and 40/60, v/v) solvent mixtures using $TiCl_4$ as coinitiator. It was proven that irreversible termination at higher temperatures involves terminative chain transfer, that is, β-proton elimination from the living chain ends with the eliminated proton being instantaneously entrapped by a proton trap, DTBP. It is also notable that the negative apparent activation energy (−8.5 kcal/mol), obtained using DTBP as a proton trap in the Hex/MeCl (60/40, v/v) solvent mixture, is the same as the value reported by Storey et al. using 2,4-dimethylpyridine[8] or pyridine[10] as a proton trap under similar conditions. This strongly suggests that the polymerizations take place on identical active centers, that is, there is no interaction of active species with nucleophilic additives.

For the first time, k_{tr}/k_p's were determined for IB polymerization by kinetic treatment of the terminative chain transfer at −25 and −40 °C. From the temperature dependence of k_{tr}/k_p, ~ −20 kcal/mol of apparent activation energy difference ($E_{tr} - E_p$) was calculated, indicating that the proton elimination has a very high activation energy. More importantly, no evidence was observed that the mechanism of propagation in the "living" condition (≤ -60 °C) is different from that for the "non-living" condition (> -60 °C). It appears that the relative magnitude of k_{tr}/k_p is the only factor which distinguishes the living systems from the classical cationic systems. Therefore, we conclude that the living polymerization of IB under "selected conditions" is not due to the presence of special active species, different from a classical ion pair or free ion, but due to the reversible termination and the suppression of chain transfer.

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