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Determination of Propagation Rate Constants in Carbocationic Polymerization of Olefins. 1. Isobutylene

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ABSTRACT: The propagation rate constant for ion pairs ($k_p^{\pm}$) in the polymerization of isobutylene in conjunction with $TiCl_4$ in hexanes/methyl chloride 60/40 (v/v) at −80 °C has been determined using two different diffusion clock methods. The rate constant $k_p^{\pm}$ was in the range of $(0.3-1.0) \times 10^9$ L mol^{-1} s^{-1}, 4 orders of magnitude higher than presently accepted values. The first method involved on-line UV−vis monitoring of the addition of the π-nucleophiles 1,1-bis(4-methylphenyl)ethylene, 1,1-bis(4-*tert*-butylphenyl)ethylene, and 2-phenylfuran to hydrochlorinated isobutylene *n*-mers ($n = 2, 3, 36$). The apparent rate constants of capping, k_cK_i, and the rate constant of ionization, k_i, have been determined. For a given n the k_cK_i values were identical independent of the nature and nucleophilicity of the π-nucleophile, which was attributed to diffusion-limited addition. Using the diffusion-limited second-order rate constant of $k_c \sim 3 \times 10^9$ L mol^{-1} s^{-1}, K_i and k_{-i} have been calculated. From the concentration of active chain ends (determined from K_i) and the apparent rate constant of propagation for isobutylene ($k_p^{\pm}$[active chain ends], determined separately), the absolute propagation rate constant of $k_p^{\pm} = 1 \times 10^9$ L mol^{-1} s^{-1} was calculated. The second simple 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 conversions and number-average degrees of polymerization, $k_p^{\pm} = (3-6) \times 10^8$ L mol^{-1} s^{-1} have been obtained.

Introduction

The aim of contemporary polymer synthesis is to control all elementary reactions involved in the polymerization. To accomplish this goal, knowledge of the polymerization mechanism and of the rate constants of the elementary reactions, such as propagation, chain transfer, and termination, is necessary. These kinetic parameters are readily available for radical and anionic polymerizations. Numerous kinetic studies of carbocationic polymerization generally failed, however, to yield reliable rate constants for propagation (k_p). The difficulties involving the determination of k_p have been analyzed by Kennedy and Marechal[1] and more recently by Plesch.[2] One of the main problems is the fragmentary knowledge of the mechanism due to the multiplicity of possible chain carriers (free ions, ion pairs, and different solvated species) and the complexity of carbocationic reaction paths.[1] Interestingly, the advent of living carbocationic polymerization, where only initiation and propagation need to be considered, has not contributed to establishing reliable rate constants. When one works in a common range of polymerization conditions where only free ions (P^+) and ion pairs (P^+A^-) need to be considered, the polymerization rate is adequately described by eq 1.

$$R_p = (k_p^{+}[P^+] + k_p^{\pm}[P^+A^-])[M] \qquad (1)$$

When only the total concentration of the active centers is known, an average k_p is often used

$$R_p = k_p([P^+] + [P^+A^-])[M] \qquad (2)$$

where

$$k_p = \frac{k_p^{\pm}[P^+A^-] + k_p^{+}[P^+]}{[P^+A^-] + [P^+]} \qquad (3)$$

Then the task reduces to the determination of the rate of monomer consumption and the concentration of active species. While the determination of the former is relatively straightforward, that of the latter usually requires assumptions to be made, as none of the three principal methods (initial group determination, cation trapping, and rapid spectroscopy) are without ambiguity. Sources of uncertainty and errors have been discussed by Plesch[2] and more recently by Matyjaszewski and Pugh.[3] Due to these uncertainties, published rate constants of propagation vary considerably; e.g., for isobutylene (IB) k_p's from 10^3 to 10^8 L mol^{-1} s^{-1} have been reported. Despite similarly large variation with some other monomers, it is generally accepted that the rate constants of propagation in the carbocationic polymerization of alkenes are similar for most systems with $k_p \sim 10^{5\pm1}$ L mol^{-1} s^{-1}.[4]

Very recently, a novel method for the determination of the rate constant of propagation was reported and applied in the carbocationic oligomerization of IB.[5] The reaction of IB was carried out with the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ or $AlCl_3$ initiating system in CH_2Cl_2 at −78 °C in the presence of trim-

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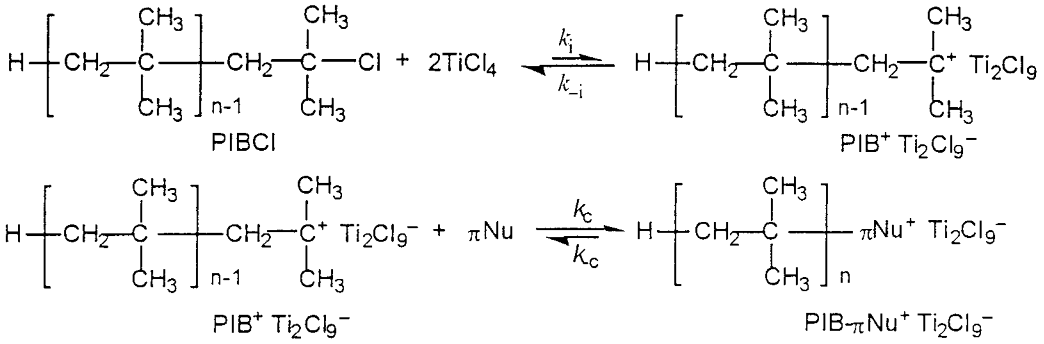
Scheme 1. Ionization Equilibrium of PIBCl ($K_i = k_i/k_{-i}$) and Capping/Decapping Equilibrium ($K_c = k_c/k_{-c}$)



ethylallylsilane, which acts as a terminator. From the ratio of the telomerization products and the rate of termination, established by using the diffusion clock method, $k_p \sim (6 \pm 2) \times 10^8$ L mol^{-1} s^{-1} was obtained. It was stressed that this k_p is more than 4 orders of magnitude higher than those Plesch considered reliable. Since preliminary studies with styrene also indicated considerably larger k_p's compared to accepted values, the authors concluded that either low molecular weight model compounds are not relevant for macromolecules or revision of generally accepted propagation rate constants may be necessary.

We have previously reported on the addition reactions of non-(homo)polymerizable monomers 1,1-diphenylethylene (DPE) and 1,1-bis(4-methylphenyl)ethylene (DTE) to hydrochlorinated isobutylene (IB) *n*-mers, H-[IB]$_n$-Cl (n = 2, 3, 4, 36) (cf. Scheme 1), in the presence of $TiCl_4$ in hexanes (Hex)/methyl chloride (MeCl) 60/40 (v/v) at −80 °C using on-line visible spectroscopy.[6] The apparent rate constants of capping, k_cK_i, increased with increasing n for the capping with both DPE and DTE: for n = 3, 4, and 36, it was approximately 3, 4, and 5 times higher, respectively, than for n = 2. Although the overall reactivities increased from oligomeric to polymeric H-[IB]$_n$-Cl, this could be accounted for by a similar increase in the rate constant of ionization k_i, due to an increase of back-strain (i.e., release of steric strain upon ionization) with increasing n. Consequently, absolute reactivities of H-[IB]$_n^+$ cations should be similar for all n. The capping reaction of IB n-mers was approximately 15 times faster with DTE than with DPE, which was ascribed to a higher nucleophilicity of DTE compared to that of DPE. We have now extended our studies to other non-(homo)polymerizable π-nucleophiles (πNu) with increased nucleophilicity, 1,1-bis(4-*tert*-butylphenyl)ethylene (DBE) and 2-phenylfuran (2-PhFu), and established that capping is diffusion-controlled ($k_c \sim 3 \times 10^9$ L mol^{-1} s^{-1}). From the measured k_cK_i values the equilibrium constant of ionization K_i can be calculated, which then allows the determination of k_p. In this report we apply this technique and a simple diffusion clock method to determine the rate constant of propagation in the carbocationic polymerization of IB.

Experimental Section

Materials. The synthesis and purification of chemicals and solvents have been described previously,[7] except for the following: DBE was prepared according to literature[8] from 4-*tert*-butylphenylmagnesium bromide (Aldrich) and 4-*tert*-butylacetophenone (Aldrich), and the crude product was recrystallized from ethanol to yield shiny, opalescent crystals. ^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.40 (s, 18H, $-C(CH_3)_3$), 5.45 (s, 2H, CH_2=), 7.3−7.5 (dd, 8H, aromatic). 2-PhFu was synthesized according to the procedure reported elsewhere[9] and obtained as a clear, colorless liquid (bp 89−91 °C, 7 mmHg). ^{1}H NMR (250 MHz, $CDCl_3$, δ): 6.55 (dd, 1H, 4-H furanyl), 6.73 (d, 1H, 3-H furanyl), 7.3−7.6 (m, 4H, *o*, *m* aromatic), 7.7−7.8 (m, 2H, 5-H furanyl and *p* aromatic).

General Reaction Procedure. All reactions were carried out at −80 °C under a dry nitrogen atmosphere using [H-[IB]$_n$-Cl] = 2.0×10^{-3} mol L^{-1}, [$TiCl_4$] = 1.64×10^{-2} mol L^{-1}, and [2,6-di-*tert*-butylpyridine, DTBP] = 3.0×10^{-3} mol L^{-1} (unless otherwise noted). The solution of H-[IB]$_n$-Cl, $TiCl_4$, and DTBP in Hex/MeCl 60/40 (v/v) was kept for ~1 h to allow complex inorganic salts to precipitate. Then, the solution was filtered in a vacuum, and the reference spectrum was taken. Finally, the π-nucleophile was added, and the accumulation of the UV−vis spectra started.

UV−vis Spectroscopy. For the UV−vis spectroscopic measurements a quartz immersion probe 661.000-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 the "Aspect Plus" software (Zeiss).

Determination of the Rate and Equilibrium Constants via UV−vis Spectroscopy. For the calculation of the rate and the equilibrium constants of the capping/decapping reaction, the concentration of diarylcarbenium ions was derived from the measured absorbance at the absorption maximum λ_{max} and the corresponding molar absorption coefficient ϵ_{max} (Figure 1). A more detailed description of the procedure has been previously given.[7]

Competition Experiments. Competition experiments were carried out in Hex/MeCl 60/40/ (v/v) at −80 °C using the following concentrations: [TMPCl]$_0$ = 2.0×10^{-3} mol L^{-1}, [DTBP] = 3.5×10^{-3} mol L^{-1}, [$TiCl_4$] = 3.6×10^{-2} mol L^{-1}, [π-nucleophile]$_0$ = 3.0×10^{-3} mol L^{-1}, and [IB] = 1−2.5 mol L^{-1}. To keep the polarity of the polymerization mixture constant, the volume of IB was deducted from that of hexanes—this compensation is especially important at high concentrations of IB. Monomer conversions were determined by gravimetric analyses.

Characterization. Molecular weights and molecular weight distributions were measured at room temperature, using a Waters HPLC system equipped with a model 510 pump, a model 486 tunable UV/vis detector, a model 250 dual refractometer/viscometer detector (Viscotek), 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. The flow rate of THF, which was used as an eluent, was 1.0 mL/min. ^{1}H NMR spectra were recorded on Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent (Cambridge Isotope Laboratories, Inc.).

Results and Discussion

Kinetics of the Capping/Decapping Reaction. Scheme 1 describes the capping of PIBCl with non-

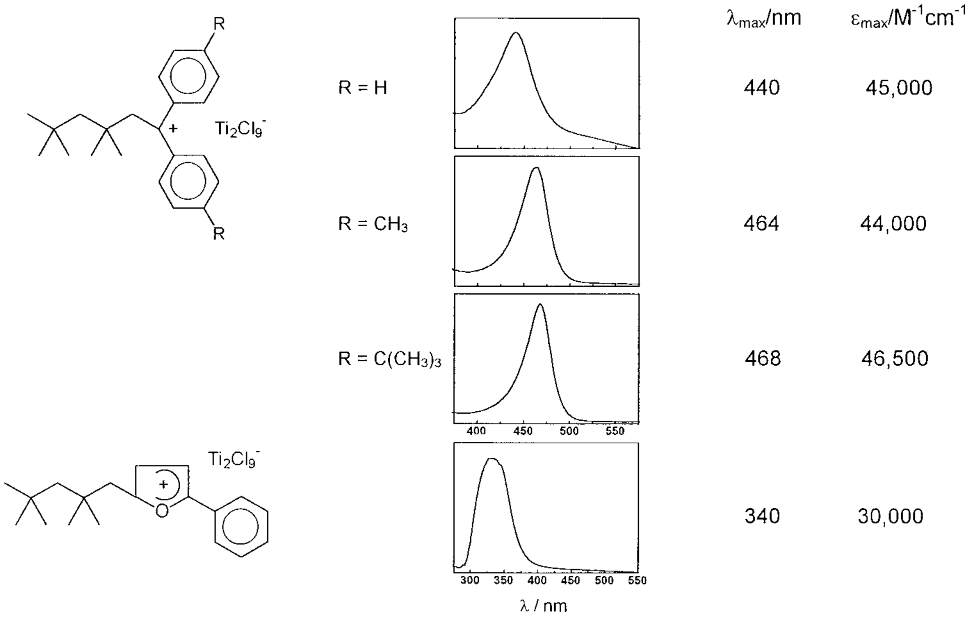


Figure 1. UV−vis characteristics of PIB−πNu$^+$Ti$_2$Cl$_9^-$.

(homo)polymerizable π-nucleophiles. This scheme applies to all π-nucleophiles used in this study (diarylethylenes and 2-PhFu) with the only difference that capping is reversible with diarylethylenes, while it is irreversible with 2-PhFu ($k_{-c} \sim 0$).[10] Capping is a two-step process that involves the ionization of the chain end and subsequent addition of the π-nucleophile.

According to Scheme 1, the equilibrium constant of ionization of PIBCl is expressed as in eq 4.

$$K_i = \frac{k_i}{k_{-i}} = \frac{[\mathrm{PIB^+Ti_2Cl_9^-}]}{[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2} \tag{4}$$

Considering that the concentration of free PIB$^+$ ions is negligible compared to that of ion pairs in Hex/MeCl 60/40 (v/v),[11] the initial evolution (i.e., when decapping is negligible) of capped species with time is described by eq 5.

$$\frac{d}{dt}([\mathrm{PIB{-}\pi Nu^+Ti_2Cl_9^-}] + [\mathrm{PIB{-}\pi Nu^+}]) = k_c[\mathrm{PIB^+Ti_2Cl_9^-}][\pi\mathrm{Nu}] \tag{5}$$

The left side of eq 5 contains the sum of the concentrations of capped ion pairs and free ions, which should exhibit the same λ_{max} and ϵ_{max},[12] and therefore the extent of dissociation is not relevant.

Assuming steady state for PIB$^+$Ti$_2$Cl$_9^-$, i.e.,

$$\frac{d}{dt}[\mathrm{PIB^+Ti_2Cl_9^-}] = k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2 - k_{-i}[\mathrm{PIB^+Ti_2Cl_9^-}] - k_c[\mathrm{PIB^+Ti_2Cl_9^-}][\pi\mathrm{Nu}] = 0 \tag{6}$$

the concentration of PIB$^+$Ti$_2$Cl$_9^-$ is given according to eq 7.

$$[\mathrm{PIB^+Ti_2Cl_9^-}] = \frac{k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2}{k_{-i} + k_c[\pi\mathrm{Nu}]} \tag{7}$$

Using this expression, eq 5 yields eq 8.

$$\frac{d}{dt}([\mathrm{PIB{-}\pi Nu^+Ti_2Cl_9^-}] + [\mathrm{PIB{-}\pi Nu^+}]) = \frac{k_c k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2[\pi\mathrm{Nu}]}{k_{-i} + k_c[\pi\mathrm{Nu}]} \tag{8}$$

If $k_{-i} \gg k_c[\pi\mathrm{Nu}]$, the second term in the denominator of eq 8 can be neglected, and eq 8 can be written as eq 9a.

$$\frac{d}{dt}([\mathrm{PIB{-}\pi Nu^+Ti_2Cl_9^-}] + [\mathrm{PIB{-}\pi Nu^+}]) = k_c K_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2[\pi\mathrm{Nu}] \tag{9a}$$

If $k_{-i} \ll k_c[\pi\mathrm{Nu}]$ instead, k_{-i} in the denominator of eq 8 can be neglected to generate eq 9b.

$$\frac{d}{dt}([\mathrm{PIB{-}\pi Nu^+Ti_2Cl_9^-}] + [\mathrm{PIB{-}\pi Nu^+}]) = k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2 \tag{9b}$$

Addition of π-Nucleophile to H-[IB]$_n$-Cl. According to Scheme 1, ionization of PIBCl requires two molecules of TiCl$_4$. It is based on our earlier finding,[13] that the polymerization of IB is second order in TiCl$_4$ and proceeds via Ti$_2$Cl$_9^-$ counteranions. We do not imply, however, that ionization is a termolecular reaction. This reaction may be envisioned as a reaction of PIBCl with the dimer Ti$_2$Cl$_8$, or it may be a stepwise reaction, ionization by monomeric TiCl$_4$ to form PIB$^+$TiCl$_5^-$ which subsequently reacts with another molecule of TiCl$_4$. In either case k_i is an apparent (composite) rate constant. That the polymerization of IB is second order in TiCl$_4$ has been confirmed by others,[11,14] most recently by Storey and Donalley[15] for low [TiCl$_4$]/[chain ends] ratio, for which Kaszas and Puskas[16] and later Puskas and Lanzendorfer[17] claimed first-order dependency. This would have been difficult to explain, since due to the very low extent of chain end ionization there should be no "shortage" of TiCl$_4$ to form dimeric anions even at low [TiCl$_4$]/[chain ends] ratio.

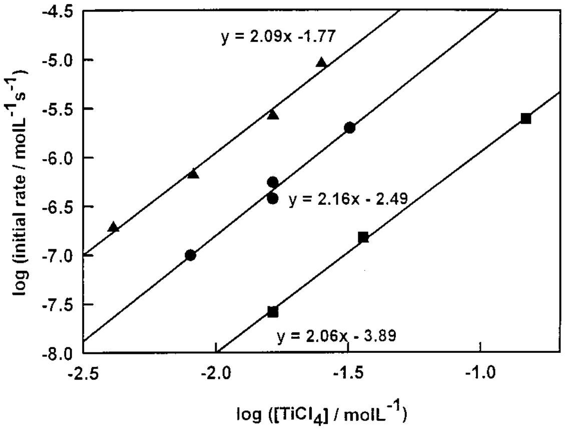


Figure 2. Bilogarithmic plot of the initial rate of capping versus the concentration of $TiCl_4$ for determining the order in $TiCl_4$ in the capping reaction of TMPCl (0.002 mol L^{-1}) with DPE = 0.002 mol L^{-1}(■), DTE = 0.002 mol L^{-1}(●), and 2-PhFu = 0.050 mol L^{-1}(▲) in Hex/MeCl 60/40 (v/v) at −80 °C.

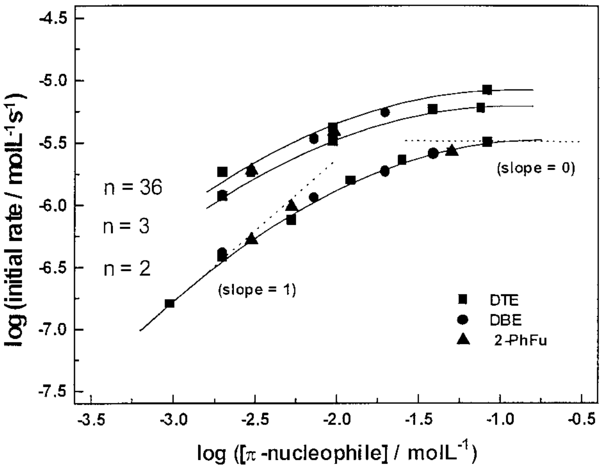


Figure 3. The log initial rate of capping versus log [π-nucleophile] for the capping reaction of hydrochlorinated IB *n*-mers in Hex/MeCl 60/40 (v/v) at −80 °C.

Thus, both eqs 9a and 9b predict that the initial capping rate is proportional to $[TiCl_4]^2$. This prediction has now been tested experimentally in the capping reaction of TMPCl with DPE, DTE, and 2-PhFu at different $TiCl_4$ concentrations. Figure 2 shows the corresponding bilogarithmic plots of the initial capping rates as a function of $[TiCl_4]$, which indeed confirms second-order dependence on $[TiCl_4]$. The close to second-order dependency even at [2-PhFu] > $[TiCl_4]$ suggests that ionization is mainly by Ti_2Cl_8 (see later).

According to eq 9a, the capping reaction should be first-order with respect to [πNu] when $k_{-i} \gg k_c[\pi\text{Nu}]$, which has been observed at [DPE] < 2×10^{-2} M and [DTE] < 3×10^{-3} M.[6] According to eq 9b, the capping rate should be independent of [πNu] when $k_{-i} \ll k_c[\pi\text{Nu}]$, e.g., at high πNu concentrations. Equation 9b was found to be valid ($k_{-i} \ll k_c[\pi\text{Nu}]$) at [DTE] > ~$8 \times 10^{-2}$ M.[6] Thus, the reactivity of DTE was optimal in accessing both the first-order region (from which k_cK_i was calculated) and the zeroth-order region (which allowed the determination of k_i).

To verify the universal nature of the method, we studied the capping reaction of hydrochlorinated IB *n*-mers, H-[IB]$_n$-Cl ($n = 2, 3, 36$) with DBE and 2-PhFu, which should be more nucleophilic than DTE. The log(initial rate of capping) versus log [πNu] plots for the capping reaction of H-[IB]$_n$-Cl ($n = 2$, 3, and 36) are shown in Figure 3. For a given *n* the same plateau is reached independent of the nature of the π-nucleophile, and therefore the same k_i value should be obtained independent of the π-nucleophile as predicted by eq 9b. The different capping agents not only give the same plateau but also give identical graphs, suggesting diffusion-limited addition with all three π-nucleophiles (see later).

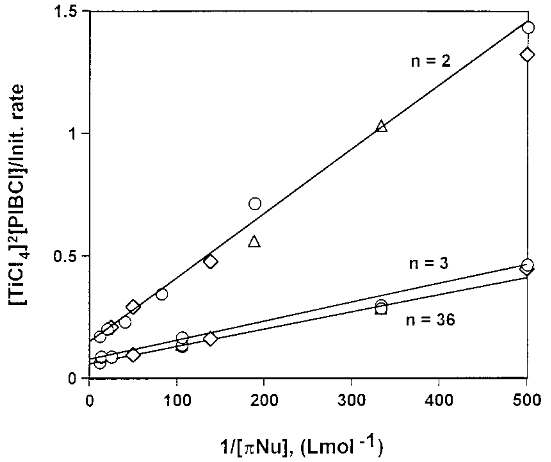


Figure 4. Reciprocal initial rate of capping versus 1/[π-Nu] (○, DTE; ◇, DBE; △, 2-PhFu) for the capping reaction of hydrochlorinated IB *n*-mers in Hex/MeCl 60/40 (v/v) at −80 °C.

While the log(initial rate of capping) versus log [πNu] plots show the change in the rate-determining step from addition of the π-nucleophile (slope of unity) to ionization of H-[IB]$_n$-Cl (slope of zero), for the accurate determination of k_cK_i and k_i it is more advantageous to plot the reciprocal initial rate of capping as a function of 1/[πNu]. Equation 8 can be transformed to eq 10.

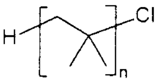
$$\frac{[\text{PIBCl}][\text{TiCl}_4]^2}{\frac{d}{dt}([\text{PIB}-\pi\text{Nu}^+\text{Ti}_2\text{Cl}_9^-] + [\text{PIB}-\pi\text{Nu}^+])} = \frac{1}{k_cK_i[\pi\text{Nu}]} + \frac{1}{k_i} \quad (10)$$

The plot of the left side of eq 10 vs 1/[πNu] should yield a straight line, with the slope and intercept of $1/k_cK_i$ and $1/k_i$, respectively.

The reciprocal initial rates of capping of H-[IB]$_n$-Cl with DBE (for $n = 2$ and 3) and 2-PhFu (for $n = 2$ and 36) are shown in Figure 4. For comparison, the corresponding data points for DTE (for $n = 2$, 3, and 36) from ref 6 are also shown.

The k_cK_i and k_i values determined from Figure 4 are shown in Table 1. Comparing the corresponding k_cK_i and k_i values calculated using DTE alone, which are also included in Table 1, we find the agreement quite reasonable. The k_cK_i values indicate that the overall reactivity of H-[IB]$_n$-Cl increases with increasing *n;* for $n = 3$ and 36 it is approximately 3 and 4 times higher, respectively, than for $n = 2$. The k_i values increase in the same order; for $n = 3$ and 36, k_i is approximately 2 and 3 times higher, respectively, than for $n = 2$. Therefore, the increased reactivity is mainly attributable to a similar increase in k_i and K_i due to an increase in back-strain with increasing *n*.

Table 1. Kinetic and Thermodynamic Parameters for the Capping Reaction of H-[IB]$_n$-Cl ($n = 2, 3, 36$) with DTE, DBE, and 2-PhFu[a]

	k_cK_i/ $L^3\ mol^{-3}\ s^{-1}$	k_i/ $L^2\ mol^{-2}\ s^{-1}$	K_i/ $10^{-7}\ L^2\ mol^{-2}$	k_{-i}/ $10^7\ s^{-1}$
$n = 2$	400 (350)	6.5 (6)	1.3	5.0
$n = 3$	1310 (1060)	13.7 (11)	4.4	3.1
$n = 36$	1430 (1730)	16.4 (15)	4.8	3.4

[a] k_cK_i and k_i determined from Figure 4. K_i and k_{-i} calculated using $k_c \sim 3 \times 10^9$ L mol^{-1} s^{-1}. k_cK_i and k_i values in parentheses are from ref 6.

The identical plateaus in Figure 3 and intercepts in Figure 4 obtained with DTE, DBE, and 2-PhFu were predicted by our kinetic considerations (eqs 9b and 10). However, the plots in Figures 3 and 4 are the same for a given n independent of the nature and nucleophilicity of the π-nucleophile in the entire concentration range. Therefore, for a given n the respective k_cK_i values are identical, suggesting a diffusion-limited addition with all three nucleophiles. The relative nucleophilicities of the π-nucleophiles could be determined from their nucleophilicity parameter N. However, those for diarylethylenes are not known, and only that of 2-PhFu has very recently been determined ($N = 3.6$).[18] Since the electrophilicity parameter of PIB$^+$ $E = 7.5$ has already been reported,[19] the linear free energy relationship[20] (eq 11, slope parameter, $s \cong 1$)

$$\log k = s(N + E) \tag{11}$$

can be used to predict $k_c \sim 10^{11}$ L mol^{-1} s^{-1}; i.e., the addition of 2-PhFu to PIB$^+$ is diffusion-limited.

Using the known value of diffusion-controlled second-order rate constant $k_c \sim 3 \times 10^9$ L mol^{-1} s^{-1}, which was also used in ref 5, K_i and k_{-i} were calculated for the first time (see Table 1). K_i is very small and varies very little from 1.3×10^{-7} L^2 mol^{-2} ($n = 2$) to 4.8×10^{-7} L^2 mol^{-2} ($n = 36$). Consequently, k_{-i} is quite large and remains virtually constant at $(3-5) \times 10^7$ L^2 mol^{-2} s^{-1}. The equilibrium constant of ionization allows us to calculate the concentration of PIB$^+$Ti$_2$Cl$_9^-$. For instance, at [chain end] $= 2.0 \times 10^{-3}$ mol L^{-1} and [TiCl$_4$] $= 3.6 \times 10^{-2}$ mol L^{-1} (which are commonly used concentrations for IB polymerization), [PIB$^+$Ti$_2$Cl$_9^-$] $= 1.3 \times 10^{-12}$ mol L^{-1}. This concentration is well below the detection limit of any currently available analytical technique.

From the concentration of active chain ends and the apparent rate constant of propagation for IB ($k_p^{app} = k_p^{\pm}$ [PIB$^+$Ti$_2$Cl$_9^-$], assuming only ion pairs), the absolute rate constant of propagation, $k_p^{\pm}$, can be calculated. At [chain end] $= 2.0 \times 10^{-3}$ mol L^{-1}, [TiCl$_4$] $= 3.6 \times 10^{-2}$ mol L^{-1}, and [DTBP] $= 3.0 \times 10^{-3}$ mol L^{-1} (proton trap) in Hex/MeCl 60/40 (v/v) at -80 °C, $k_p^{app} = 1.38 \times 10^{-3}$ s^{-1}.[13a] Under otherwise identical conditions, similar values were calculated for [chain end] $= 2.0 \times 10^{-3}$ mol L^{-1} and [TiCl$_4$] $= 3.6 \times 10^{-2}$ mol L^{-1} concentrations from published studies on the polymerization of IB in the presence of pyridine[14] ($k_p^{app} = 1.1 \times 10^{-3}$ s^{-1}) and 2,4-dimethylpyridine[11] ($k_p^{app} = 1.0 \times 10^{-3}$ s^{-1}). From $k_p^{app} = 1.38 \times 10^{-3}$ s^{-1} the absolute rate constant of propagation $k_p^{\pm} = 1.0 \times 10^9$ L mol^{-1} s^{-1} was calculated. This value agrees well with that reported by Mayr[5] but is much higher than that presently accepted.

Competition Experiment. When the rate constant k_c of the addition of a π-nucleophile to a polymer cation is known, no decapping takes place ($k_{-c} \sim 0$), and the capped cationic ends do not initiate polymerization of the monomer; a simple competition experiment can also be used to determine k_p. Thus, polymerization in the presence of a π-nucleophile at well-chosen concentrations will stop short of completion when all chain ends are capped. From the limiting conversion (x_∞^{IB}) or the limiting number-average degree of polymerization (DP$_{n,\infty}$), k_p can be calculated according to eqs 18 and 20, which are derived as follows. The rate of IB consumption is given by eq 12a.

$$-\frac{d[IB]}{dt} = k_p^{\pm}[PIB^+Ti_2Cl_9^-][IB] \tag{12a}$$

Integration of eq 12a yields the pseudo-first-order expression in eq 12b.

$$\ln\left(\frac{[IB]_0}{[IB]_t}\right) = k_p^{\pm}\int[PIB^+Ti_2Cl_9^-]\,dt \tag{12b}$$

Similar equations can be developed for the consumption of the π-nucleophile.

$$-\frac{d[\pi Nu]}{dt} = k_c^{\pm}[PIB^+Ti_2Cl_9^-][\pi Nu] \tag{13a}$$

$$\ln\left(\frac{[\pi Nu]_0}{[\pi Nu]_t}\right) = k_c^{\pm}\int[PIB^+Ti_2Cl_9^-]\,dt \tag{13b}$$

By combining eqs 12b and 13b and rearranging the resulting equation, one obtains eq 14 for the ratio $k_p^{\pm}/k_c^{\pm}$ of the propagation and the capping rate constant

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln([IB]_0/[IB]_t)}{\ln([\pi Nu]_0/[\pi Nu]_t)} \tag{14}$$

With

$$x_\infty^{IB} = 1 - [IB]_\infty/[IB]_0 \tag{15}$$

as the final IB conversion at $t = \infty$, eq 14 yields eq 16.

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{16}$$

Provided that the initial concentration of the π-nucleophile is larger than the concentration of chain ends (i.e., $[\pi Nu]_0 > [PIBCl]_0$) and thus

$$[\pi Nu]_\infty = [\pi Nu]_0 - [PIBCl]_0 \tag{17}$$

we can transform eq 16 into eq 18.

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - x_\infty^{IB})}{\ln(1 - [PIBCl]_0/[\pi Nu]_0)} \tag{18}$$

Alternatively, the degree of polymerization reached at $t = \infty$, DP$_{n,\infty}$ can be used to determine $k_p^{\pm}/k_c^{\pm}$. With

$$DP_{n,\infty} = x_\infty^{IB}([IB]_0/[PIBCl]_0) \tag{19}$$

Table 2. Competition Experiments of IB/π-Nucleophile in Hex/MeCl 60/40 (v/v) at − 80 °C

[IB]/ mol L^{-1}	π-nucleophile	conv (%)	M_n	M_w/M_n	DP$_n$	DP$_n$/[IB]
1.0	DTE	14.9	4710	2.3	78	78
1.5		14.6	6380	2.3	108	72
2.0		15.5	8990	2.4	155	78
2.5		14.8	12100	2.2	210	84
1.0	DBE	18.7	5520	1.8	91	91
1.5		18.8	7620	1.9	128	85
2.0		19.3	10900	1.7	187	93
2.5		17.7	12000	1.9	206	82
1.0	2-PhFu	12.0	4300	2.1	72	72
1.5		11.7	6180	2.1	105	70
2.0		11.8	8770	2.1	151	76
2.5		12.5	9660	2.4	167	67

[a] [TMPCl]$_0$ = 0.002 mol L^{-1}, [DTBP] = 0.0035 mol L^{-1}, [DTE]$_0$ = [DBE]$_0$ = [2-PhFu]$_0$ = 0.003 mol L^{-1}, [TiCl$_4$] = 0.036 mol L^{-1}, reaction time 25 min.

Equation 18 gives eq 20.

$$\frac{k_p^{\pm}}{k_c^{\pm}} = \frac{\ln(1 - \mathrm{DP}_{n,\infty}[\mathrm{PIBCl}]_0/[\mathrm{IB}]_0)}{\ln(1 - [\mathrm{PIBCl}]_0/[\pi\mathrm{Nu}]_0)} \qquad (20)$$

Although eqs 18 and 20 have been derived for the exclusive presence of ion pairs, identical mathematical formulas could be obtained for k_p^+/k_c^+, i.e., when only free ions are present. When capping is diffusion-limited, differentiation between $k_c^{\pm}$ and k_c^+ is unnecessary since $k_c^{\pm} = k_c^+$.

Competition experiments have been carried out with IB/DTE, IB/DBE, and IB/2-PhFu. The results are shown in Table 2. In all three series of experiments the limiting conversion was reached within 25 min.

As predicted by eq 18, identical limiting conversions were reached at different [IB]. The molecular weight distributions of the products were close to the expected most probable distribution ($\bar{M}_w/\bar{M}_n = 2$). ^{1}H NMR spectroscopy confirmed that all chain ends were capped by the corresponding π-nucleophile. The $k_p^{\pm}$ values were calculated using eq 18 and the average conversions as well as eq 20 and average DP$_{n,\infty}$[IB] ratios (which should be constant). The two methods yielded similar $k_p^{\pm}$ values for the experiments with DTE (4.4×10^8 and 4.6×10^8 L mol^{-1} s^{-1}), DBE (5.5×10^8 and 5.2×10^8 L mol^{-1} s^{-1}), and 2-PhFu (3.5×10^8 and 4.2×10^8 L mol^{-1} s^{-1}). Although the $k_p^{\pm}$ determined from the capping experiments is approximately 2 times higher than the values determined from competition, this is still a reasonable agreement considering the possible errors mainly in the determination of apparent rate constant.

Scope and Limitations. Since the k_p determined in this work is much higher than accepted values, we should examine the scope and limitations of the methods presented in this paper before revising the generally accepted propagation rate constants. In our kinetic treatment of the capping reaction only ion pairs were considered. The contribution of free ions was neglected on the basis of a report[11] that the propagation of IB involves mainly ion pairs under conditions essentially identical to ours. Since our calculations indicate that the concentration of ion pairs is very low ($\sim 10^{-12}$ mol L^{-1}), and the active species are thought to be mainly free ions at this low concentration, it is rational to reexamine this postulate.

Considering the presence of both ion pairs (PIB$^+$Ti$_2$Cl$_9$$^-$) and free ions (PIB$^+$), the initial evolution of ([PIB−πNu$^+$Ti$_2$Cl$_9$$^-$] + ([PIB−$\pi$Nu$^+$]) with time is described by eq 21.

$$\frac{\mathrm{d}}{\mathrm{d}t}([\mathrm{PIB}{-}\pi\mathrm{Nu}^+\mathrm{Ti_2Cl_9}^-]) + ([\mathrm{PIB}{-}\pi\mathrm{Nu}^+]) = k_c^{\pm}[\mathrm{PIB}^+\mathrm{Ti_2Cl_9}^-][\pi\mathrm{Nu}] + k_c^{+}[\mathrm{PIB}^+][\pi\mathrm{Nu}] \qquad (21)$$

Assuming steady state separately for PIB$^+$ as well as for PIB$^+$Ti$_2$Cl$_9$$^-$, the concentration of PIB$^+$ is given as

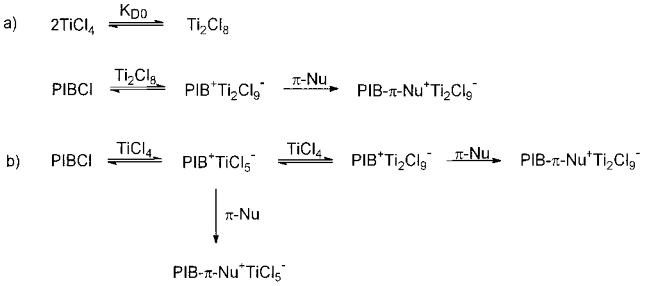
$$[\mathrm{PIB}^+] = \frac{k_d[\mathrm{PIB}^+\mathrm{Ti_2Cl_9}^-]}{k_{-d}[\mathrm{Ti_2Cl_9}^-] + k_c^+[\pi\mathrm{Nu}]} = \frac{[\mathrm{PIB}^+\mathrm{Ti_2Cl_9}^-]}{([\mathrm{Ti_2Cl_9}^-]/K_d) + (k_c^+[\pi\mathrm{Nu}]/k_d)} \qquad (22)$$

where k_d is the rate constant of ion pair dissociation to free ions, k_{-d} is the rate constant of the reverse reaction, and K_d is the equilibrium constant of dissociation ($=k_d/k_{-d}$). Since ion pairs and free ions presumably have similar reactivity[21] ($k_c^{\pm} \cong k_c^+$), the contribution of ion pairs relative to free ions depends on their relative concentrations. This is determined by the denominator on the right side of eq 22. Since K_d and k_{-d} are estimated to be $\sim 10^{-6}$–10^{-7} mol L^{-1} and $\sim 10^9$–10^{10} L mol^{-1} s^{-1} (i.e., diffusion limited), respectively, k_d is about 10^2–10^4 s^{-1}.[21] In the absence of any common ion source ([Ti$_2$Cl$_9$$^-$] = [PIB$^+$]), the first term is negligible compared to the second term in the denominator of eq 22. Thus, at [πNu] $\sim 10^{-3}$ mol L^{-1}, [PIB$^+$] $\ll$ [PIB$^+$Ti$_2$Cl$_9$$^-$] when $k_c^+ > 10^6$–10^8 L mol^{-1} s^{-1}. Therefore, the concentration of free ions will be negligible compared to that of ion pairs even in the absence of common ion source when capping is fast. Although our kinetic treatment of capping is therefore valid, since in the absence of any common ion source propagation takes place mainly by free ions, the rate constant cannot be calculated. Under common conditions, however, ion pair dissociation is suppressed by counteranions formed in the reaction of adventitious proton sources (present at $\sim 10^{-3}$ mol L^{-1}) with proton trap in the presence of Lewis acid. For example, even [Ti$_2$Cl$_9$$^-$] = 10^{-5} mol L^{-1} common anion concentration would reduce the free ion concentration to [PIB$^+$] $\ll$ [PIB$^+$Ti$_2$Cl$_9$$^-$]. Capping with diarylethylenes and 2-alkyl(or aryl)furans also results in the formation of common anions since the capped species are fully ionized, and the equilibrium constant of dissociation $K_d \sim 10^{-4}$ mol/L.[22] Therefore, at [PIBCl] = 2.0×10^{-3} mol L^{-1}, even at 1% capping [PIB$^+$] $\ll$ [PIB$^+$Ti$_2$Cl$_9$$^-$] would hold. Thus, we conclude that neglecting free ions both in the capping reaction and in propagation is justified.

Kinetic evaluation of the competition reaction does not necessitate any assumption about the identity of active species. In the exclusive presence of ion pairs or free ions, competition yields $k_p^{\pm}$ or k_p^+, respectively. When capping results in stable carbenium ions in the competition reaction, the formation of common anion suppresses ion pair dissociation, and as discussed above, the concentration of free ions will be negligible compared to that of the paired ions. Under these conditions competition yields $k_p^{\pm}$. However, ion pairs and free ions should have very similar reactivity and in some cases exhibit identical reactivity.[23] Therefore, differentiation between free ions and ion pairs may be unnecessary.

We will now examine the assumption of $k_c = 3 \times 10^9$ L mol^{-1} s^{-1} for the value of the diffusion-limited second-

Scheme 2. Addition of π-Nucleophile to PIBCl via Direct (a) or Stepwise (b) Ionization of PIBCl



order rate constant. This value was also used by Roth and Mayr[5] for the diffusion-limited addition of 2-methallyltrimethylsilane to oligomeric PIB cations. It was based on direct rate measurements for the reaction of benzhydryl cations with highly reactive π-nucleophiles, such as allylsilanes, alkyl vinyl ethers, silyl enol ethers, and silyl ketene acetals, which yielded a value of (2−4) $\times 10^9$ L mol^{-1} s^{-1} for diffusion control.[24] However, these reactions take place between two small molecules, while capping involves a macromolecule and a small molecule. In addition, the direct rate measurements were carried out at 20 °C, while our experiments have been conducted at −80 °C.

The bimolecular rate constant k_a for the diffusion-controlled reaction of A and B (when reactions occur with every encounter) in the absence of interaction potential was first derived by Smoluchowski[25]

$$k_a = \frac{4\pi r_{AB}(D_A + D_B)/N_0}{1000} \qquad (23)$$

where r_{AB} is the sum of the radii of A and B (i.e., the distance of closest approach), D_A and D_B are the diffusion coefficients, and N_0 is the Avogadro number. For instance for $D_A = D_B = 1 \times 10^{-5}$ cm^2 s^{-1} (typical values), r_{AB} = 4 Å, and $k_a = 6 \times 10^9$ L mol^{-1} s^{-1}, which is a typical upper limit. Although diffusion-limited reactions do not have an enthalpic barrier, their observed activation energy will not be zero, but will be determined by the temperature dependence of ($D_A + D_B$), which is related to the viscosity (η) of the solution by Walden's rule ($D\eta$ = constant). In highly dilute solutions (used in this work) the diffusion coefficient of π-nucleophile should not be affected by the presence of PIB and should be similar to other small molecules. The translational diffusion coefficient of PIB macromolecules (D_{PIB}) however should be smaller. D_{PIB} has been measured in cyclohexane[26] and heptane[26,27] at 25 °C for different molecular weights (MW) and was found to scale approximately with MW$^{-0.6}$. In heptane for MW = 1000 and 1600 $D_{PIB} = 0.74 \times 10^{-5}$ and 0.6×10^{-5} cm^2 s^{-1} was determined, respectively.[27] At MW $\sim 2 \times 10^4 - 2 \times 10^6$ D_{PIB} was found to be much smaller and ranged from 1.6×10^{-6} to 1.3×10^{-7} cm^2 s^{-1}. Thus, at low molecular weights at a viscosity of about 0.4 cP (η for heptane at 25 °C) $D_{PIB} \sim 10^{-5}$ cm^2 s^{-1} is a good approximation for low molecular weights. It is important to point out that even at $D_{PIB} = 0$, there is only a factor of 2 decrease in the diffusion-limited rate constant. In addition, segmental diffusion may actually increase with increasing molecular weight. With decreasing temperature the decrease of the diffusion coefficient is determined by the temperature dependence of the viscosity of the solvent. The reciprocal viscosity varies nearly exponentially with temperature. However, the "activation energy" for the flow to occur is usually small, typically about 2 kcal/mol. Thus, the viscosity of hexane at −80 °C is only about 5 times higher (about 1.6 cP) than that at 20 °C. Since the viscosity of MeCl at −80 °C is 0.46 cP,[28,29] we estimate the viscosity of Hex/MeCl 60/40 (v/v) solvent mixture at −80 °C is approximately ~1 cP, and therefore the diffusion-limited second-order rate constant is approximately 3×10^9 L mol^{-1} s^{-1}.

Elementary Events in the Living Cationic Polymerization of IB. The rate constant of reactions involved in the living cationic polymerization of IB have now been determined for the first time

$$k_i = 16.4 \text{ L}^2\text{mol}^{-2}\text{ s}^{-1}$$

$$k_{-i} = 3.4 \times 10^7 \text{ s}^{-1}$$

$$k_p^{\pm} = 7 \times 10^8 \text{ L mol}^{-1}\text{ s}^{-1}$$

where $k_p^{\pm} = 7 \times 10^8$ L mol^{-1} s^{-1} is the average value of the two $k_p^{\pm}$'s determined by the two different methods. While $k_p^{\pm}$ and k_{-i} are rate constants of elementary reactions (propagation and deactivation) k_i is an apparent rate constant of ionization. To ascertain this composite rate constant, we may compare the mechanism of π-nucleophile addition via a direct reaction of PIBCl with the dimer Ti_2Cl_8 (Scheme 2a) or a stepwise ionization (Scheme 2b). We recall that capping of TMPCl is second-order in [$TiCl_4$] at [2-PhFu] = 0.05 mol L^{-1} (where ionization is the slowest step) even at [2-PhFu] > [$TiCl_4$]. Capping with 2-PhFu is diffusion-limited, and the reaction of $TMP^+TiCl_5^-$ with $TiCl_4$ may be at most also diffusion limited. Thus, at [2-PhFu] > [$TiCl_4$] first-order $TiCl_4$ dependency should have been found if ionization and the formation of $Ti_2Cl_9^-$ is a stepwise reaction. The observed close to second order suggests that ionization takes place by Ti_2Cl_8, and therefore $k_i = k_i^{abs}K_{D0}$, where k_i^{abs} is the absolute rate constant of ionization and K_{D0} is the equilibrium constant of $TiCl_4$ dimerization. A similar conclusion can be reached if one considers that $k_p^{\pm} = 7 \times 10^8$ L mol^{-1} s^{-1} and the propagation of IB is second order in $TiCl_4$ at [IB]/[$TiCl_4$] ~ 50−100. We acknowledge that this finding is in contradiction with the conclusion of Storey and Choate.[11] When K_{D0} is small, [Ti_2Cl_8] ≪ [$TiCl_4$], and therefore Storey and Choate hypothesized that dimeric counterions must form overwhelmingly by the stepwise reaction. We believe that this conclusion was premature as one has to consider the whole first term (containing [$TiCl_4$]) relative to the second term (containing [Ti_2Cl_8]) in eq 8 of ref 11 to determine which pathway is operational. From the results presented here it appears that the second term is much higher than the first one. Very recently, ab initio calculations have been performed on monomeric and dimeric titanium(IV) halides to determine the nature and magnitude of self-interactions.[32] It was found that Ti_2Cl_8 is lower in energy than separated monomers by 4.9 kcal/mol. The free energies of dimerization have also been calculated as a function of temperature. On the basis of the results obtained considering rotational, translational, and vibrational effects, we calculated $K_{D0} \cong 1$ L mol^{-1} at −80 °C. Assuming negligible solvation effects, $k_i^{abs} \cong 16.4$ L mol^{-1} s^{-1}.

From k_i, k_{-i}, and $k_p^{\pm}$ the sequence of events for an average polymer chain can be ascertained. Using typical concentrations of [$TiCl_4$] = 3.6×10^{-2} mol L^{-1} and [IB]

= 1 mol L^{-1}, the following time intervals (τ) between two consecutive events have been calculated.

$$\tau_{\mathrm{i}} = 1/k_{\mathrm{i}}[\mathrm{TiCl_4}]^2 = 49\ \mathrm{s}$$

$$\tau_{-\mathrm{i}} = 1/k_{-\mathrm{i}} = 2.9 \times 10^{-8}\ \mathrm{s} = 29\ \mathrm{ns}$$

$$\tau_{\mathrm{p}} = 1/k_{\mathrm{p}}[\mathrm{IB}] = 1.4 \times 10^{-9}\ \mathrm{s} = 1.4\ \mathrm{ns}$$

Thus, the time interval between two ionization (activation) is relatively long (49 s). The ionized chain ends stay active for a very short time; only 29 ns before reversible termination (deactivation) takes place, and the polymer end goes back to a dormant, inactive state. Propagation is 20 times faster than deactivation, however (monomer incorporates on average every 1.4 ns), and 20 monomer units are added during one active cycle. This results in a relatively broad molecular weight distribution at the beginning of the polymerization. The number of monomer molecules added during one active cycle decreases with conversion as [IB] decreases, and hence the molecular weight distribution progressively narrows. The starting [IB] may be decreased to decrease the number of monomer units incorporated during one active cycle; this yields PIB with a lower polydispersity index. For instance, at [IB] = 0.1 mol L^{-1}, used in this work to obtain the PIB 36-mer, two monomer units are incorporated during one active cycle even at the onset of the polymerization. At [TiCl$_4$] = 3.6 × 10^{-2} mol L^{-1} and [IB] = 1 mol L^{-1}, about 4 and 40 min would be necessary for the formation of a PIB with a DP = 100 and 1000, respectively. The actual time however will be longer, because [IB] decreases with conversion.

Conclusion

The absolute rate constant of propagation for the polymerization of IB in Hex/MeCl 60/40 (v/v) at −80 °C was determined using two different diffusion clock methods. Both methods yielded similar $k_{\mathrm{p}}^{\pm}$ values, ranging from 0.3 to 1 × 10^9 L mol^{-1} s^{-1}, which are more than 4 orders of magnitude higher than currently accepted values. The presented methods are general and can be used to calculate k_{p} for other monomers, e.g. styrene, for which we have recently published preliminary data on capping with DTE.[30] Assuming diffusion-limited addition of DTE to polystyryl cation (predicted by the linear free energy relationship), we calculate $k_{\mathrm{p}}^{\pm}$ = 5 × 10^9 L mol^{-1} s^{-1}, i.e., diffusion-limited propagation in the polymerization of styrene in $\mathrm{CHCl_3/CH_2Cl_2}$ (70:30 v:v) at −75 °C. This value is 6 orders of magnitude higher than that reported by the stopped-flow method.[31] We are currently engaged in a study to confirm that capping of polystyryl cation with DTE (as well as DBE and 2-PhFu) is diffusion-limited. If diffusion-limited propagation of styrene is verified, a comprehensive revision of propagation rate constants in cationic polymerization will be necessary.

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