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Living Carbocationic Polymerization. LVII. Kinetic Treatment of Living Carbocationic Polymerization Mediated by the Common Ion Effect

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LIVING CARBOCATIONIC POLYMERIZATION. LVII. KINETIC TREATMENT OF LIVING CARBOCATIONIC POLYMERIZATION MEDIATED BY THE COMMON ION EFFECT†

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ABSTRACT

The effect of anion concentration on the apparent rate constant of polymerization k_p^A of isobutylene (IB) induced by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system using the CH_2Cl_2/nC_6H_{14} (60/40 v/v) solvent system at −40 and −80°C was studied by the use of nBu_4NCl. Computer simulation has shown that k_p^A decreases several orders of magnitude upon the addition of even a very small amount of common anion $TiCl_5^-$ to the charge. The rate of change is reduced in the concentration range of experimental interest. It was concluded that the decrease of k_p^A with increasing $TiCl_5^-$ concentration is mainly due to the decreasing contribution of propagation by free ions. The contribution (%) of propagation by free ions to the apparent rate of propagation was calculated.

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†For Paper LVI in this series, see J. P. Kennedy, S. Midha, and Y. Tsunogae, *Macromolecules, 26*, 429 (1993).

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INTRODUCTION

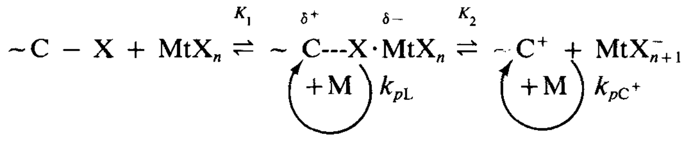
We recently discovered that conventional IB polymerization, e.g., TMPCl/$TiCl_4$/IB/CH_2Cl_2/$n$$C_6H_{14}$/−80°C, can be readily converted to living polymerization by the introduction of a common anion salt, e.g., $n$$Bu_4NCl$ [1]. This common anion salt effect was explained by simple mass law action; specifically, it was assumed that the addition of $n$$Bu_4NCl$ to a conventional polymerization system containing excess $TiCl_4$ rapidly produces the counteranion $TiCl_5^-$ (by $n$$Bu_nNCl$ + $TiCl_4$ → $n$$Bu_4N^+$ + $TiCl_5^-$) which by mass action, pushes the Winstein ionicity spectrum [see Scheme 1, where MtX_n, K_1, K_2, k_{pL}, and k_{pC^+} are, respectively, the Friedel-Crafts acid ($TiCl_4$, etc.), the two equilibrium constants, and the rate constants of the living and free ionic propagation] toward the left, i.e., toward the slower-propagating stretched dipoles that give rise to living carbocationic polymerization on LC^+Pzn [2].

Our earlier kinetic treatment of the common salt effect started with two arguable assumptions [1]. It was assumed 1) that the free ion concentration in the Winstein spectrum becomes negligible upon the addition of even a small amount of $n$$Bu_4NCl$ and 2) that the polymerization rate reduction observed upon increased $n$$Bu_4NCl$ addition is due to a bimolecular reaction between the common anion $TiCl_5^-$ and the growing living species $\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{Cl}\cdot TiCl_4$. While the observations in our earlier publication could be explained on the basis of these two assumptions, it was felt that additional experimentation was needed to clarify and gain further insight into the mechanism.

In contrast to our earlier paper in which we assumed that by the introduction of the common anion salt, $n$$Bu_4NCl$, the concentration of the "free" cations giving rise to conventional polymerization is for all practical purposes reduced to zero, in the present report we assume that the three fundamental species in the simplified Winstein spectrum (see above) are always present but their relative concentrations change depending on the concentration of added common salt.

EXPERIMENTAL

The source and purity of chemicals together with general techniques have been described [1, 3-5]. The polymerization of IB was initiated by the TMPCl/$TiCl_4$ system in CH_2Cl_2/hexanes (60/40 v/v) solvent mixtures at −80 and −40°C in the presence of various amounts of $n$$Bu_4NCl$. The $n$$Bu_4NCl$ was dissolved in CH_2Cl_2 and dried over CaH_2. After 7 days the solution was filtered and the CH_2Cl_2 was removed by a vacuum pump.



$$\sim C - X + MtX_n \overset{K_1}{\rightleftharpoons} \sim \underset{(+M)\ k_{pL}}{\overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n} \overset{K_2}{\rightleftharpoons} \sim \underset{(+M)\ k_{pC^+}}{C^+} + MtX_{n+1}^-$$

SCHEME 1.

RESULTS AND DISCUSSION

Computer Modeling of the Common Ion Effect

The living polymerization of olefins has been discussed in terms of the Winstein spectrum [2], a very much simplified version of which is shown in the Introduction. Conventional polymerizations are postulated to proceed by "free" carbocations $\sim C^+$ shown on the right, whereas living systems arise by the nondissociated polarized species symbolized by $\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n$. These symbols cover subspectra of ionicities whose nature has been discussed [2]. The apparent rate constant of the propagation is

$$k_p^A = \sum_{i=1}^{n} k_{pi}\cdot c_i$$

where k_{pi} is the propagation rate constant of the growing chain end in state i and c_i is determined by the stoichiometry of the equilibria in the Winstein spectrum. For the simplified Winstein spectrum:

$$k_p^A = k_{pL}\left[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n\right] + k_{pC^+}[\sim C^+] \tag{1}$$

where $[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n]$ and $[\sim C^+]$ are the concentrations of the living and free carbenium ion centers, respectively [2].

The equilibrium constants are

$$K_1 = \frac{\left[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n\right]}{[\sim C - X][MtX_n]} \tag{2}$$

and by Szwarc and Shultz [6] for $[MtX_{n+1}^-] \neq [\sim C^+]$:

$$K_2 = \frac{[\sim C^+][MtX_{n+1}^-]}{\left[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n\right]} \tag{3}$$

Assuming 100% initiator efficiency, the initial initiator concentration:

$$[I]_0 = [\sim C - X] + \left[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n\right] + [\sim C^+] \tag{4}$$

From Eqs. (2)-(4):

$$[I]_0 = [\sim C^+] + [\sim C^+]\frac{[MtX_{n+1}^-]}{K_2} + [\sim C^+]\frac{[MtX_{n+1}^-]}{K_1\cdot K_2[MtX_n]} \tag{5}$$

or

$$[\sim C^+] = \frac{[I]_0}{1 + \dfrac{[MtX_{n+1}^-]}{K_2} + \dfrac{[MtX_{n+1}^-]}{K_1\cdot K_2[MtX_n]}} \tag{6}$$

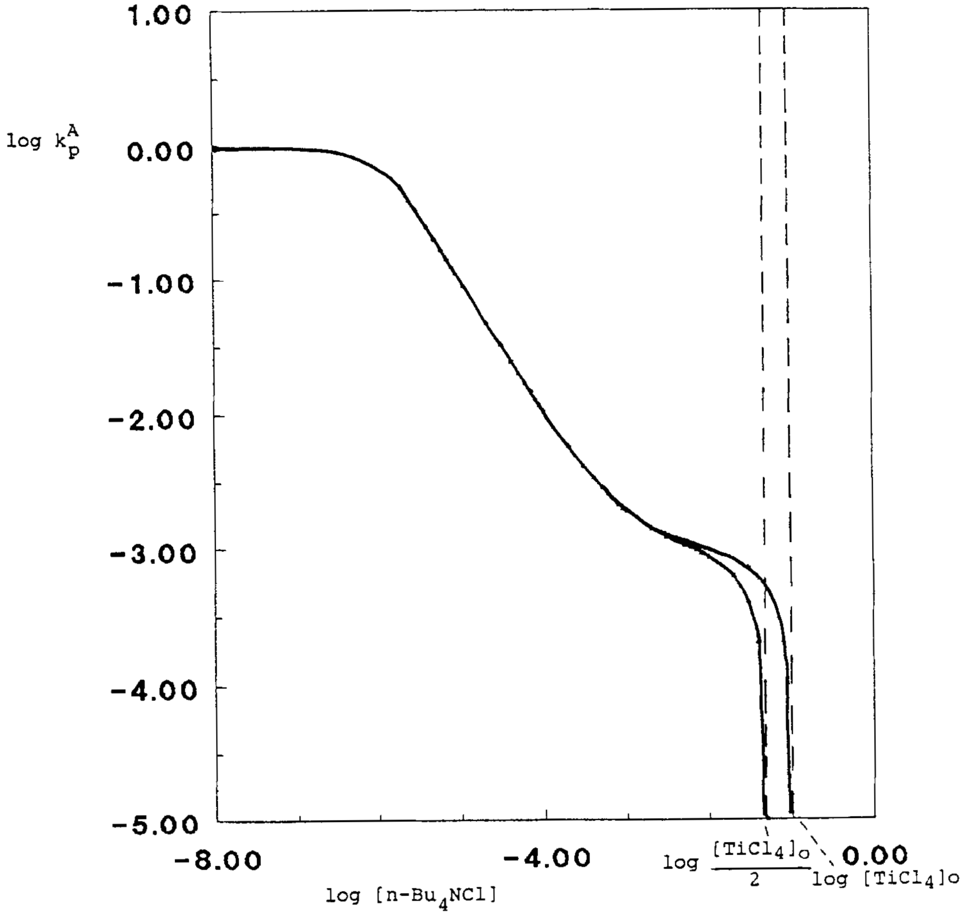


FIG. 1. Influence of common ion concentration on the apparent rate constant of polymerization (computer model) using Eqs. (7)–(9). $[TMPCl]_0 = 0.01$ mol/L, $[TiCl_4] = 0.1$ mol/L, $K_1 = 10^{-2}$ L/mol, $k_{pL} = 10^2\ L\cdot mol^{-1}\cdot s^{-1}$, $k_{pC^+} = 10^6\ L\cdot mol^{-1}\cdot s^{-1}$, $K_2 = 10^{-7}\ mol\cdot L^{-1}$.

Thus

$$k_p^A = \left(k_{pC^+} + k_{pL}\frac{[MtX_{n+1}^-]}{K_2}\right)\frac{[I]_0}{1 + \dfrac{[MtX_{n+1}^-]}{K_2} + \dfrac{[MtX_{n+1}^-]}{K_1 \cdot K_2[MtX_n]}} \qquad (7)$$

When nBu$_4$NCl is added to the system, it immediately reacts with the Friedel–Crafts acid. Assuming complete conversion and $\sim 10^{-5}$–10^{-7} mol/L free cation [7, 8]:

$$[MtX_{n+1}^-] = [\sim C^+] + [nBu_4NCl] \approx [nBu_4NCl] \qquad (8)$$

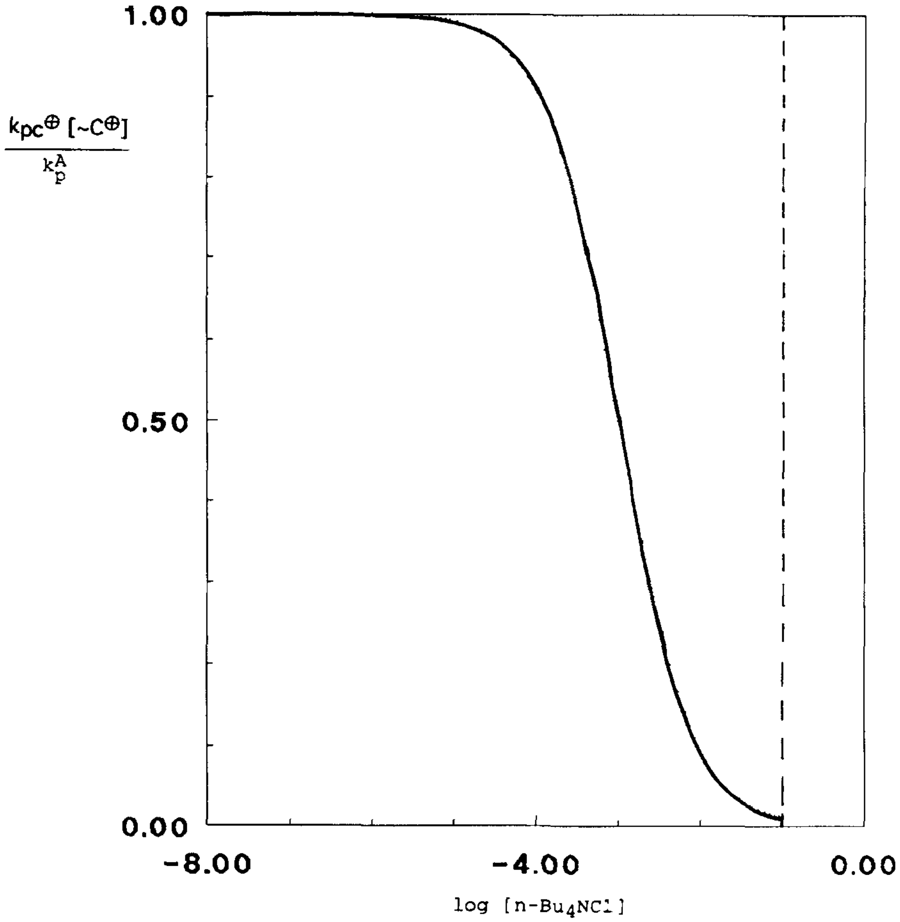


FIG. 2. Contribution of the ionic propagation to the apparent rate constant of polymerization. Conditions as in Fig. 1.

and

$$[MtX_n] = [MtX_n]_0 - \left[\sim \overset{\delta+}{C}\text{---}\overset{\delta-}{X}\cdot MtX_n\right] - [\sim C^+] - [nBu_4NCl] \approx [MtX_n]_0 - [nBu_4NCl] \qquad (9)$$

Equation (7), in combination with Eqs. (8) and (9), was used (without any assumptions or simplifications) for computer modeling the influence of common ion concentration on k_p^A. Figures 1 and 2 show the results, and the legend of Fig. 1 gives the arbitrary constants used. These values have been estimated by considering the usual bimodal GPC traces of conventional PIBs and $[\sim C^+] \approx 10^{-5}$-$10^{-7}$ mol/L [7, 8]. The bimodal GPC traces suggest that the polymerizations proceed by both

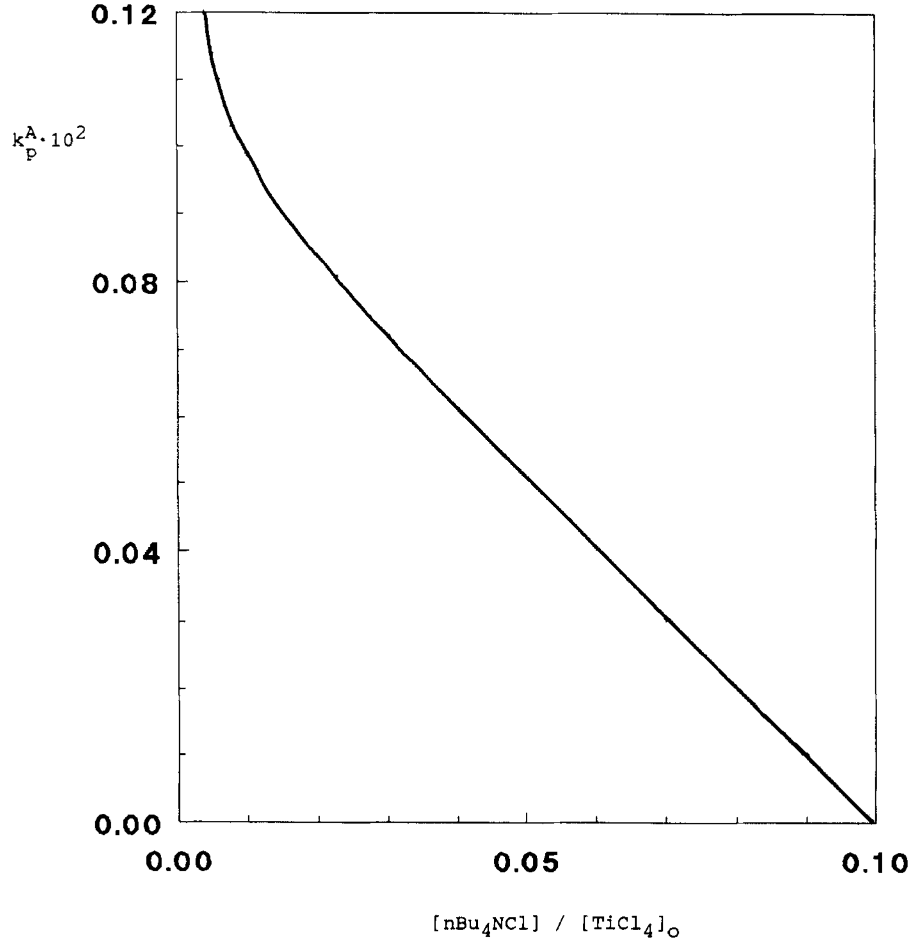


FIG. 3. Apparent rate constants of the polymerization versus [nBu$_4$NCl]/[TiCl$_4$]$_0$ ratio. Conditions as in Fig. 1.

living ($\sim\overset{\delta+}{C}\text{---}\overset{\delta-}{Cl}\cdot TiCl_4$) and free ($\sim C^+$) species, the former providing the relatively slowly growing low molecular weight species while the latter provide the rapidly growing higher molecular weight fraction [7]. Evidently k_p^A decreases rapidly with increasing [nBu$_4$NCl] and becomes nearly constant or its rate of change is reduced in the range of the initiator concentrations, usually $\sim 10^{-3}$-10^{-2} mol/L. When [nBu$_4$NCl] $\approx$ [TiCl$_4$], k_p^A decreases rapidly again. According to Fig. 2, the decrease is mainly due to a decrease in the proportion of free cationic propagation.

Figures 3 and 4 show these calculated changes in the concentration range of our experiments. k_p^A decreases several orders of magnitude upon the addition of even a very small amount of common ion salt (see Fig. 1, compare log k_p^A at log [nBu$_4$NCl] = from -6 to -4), and the observable changes of that are usually within one order of magnitude in our experiments.

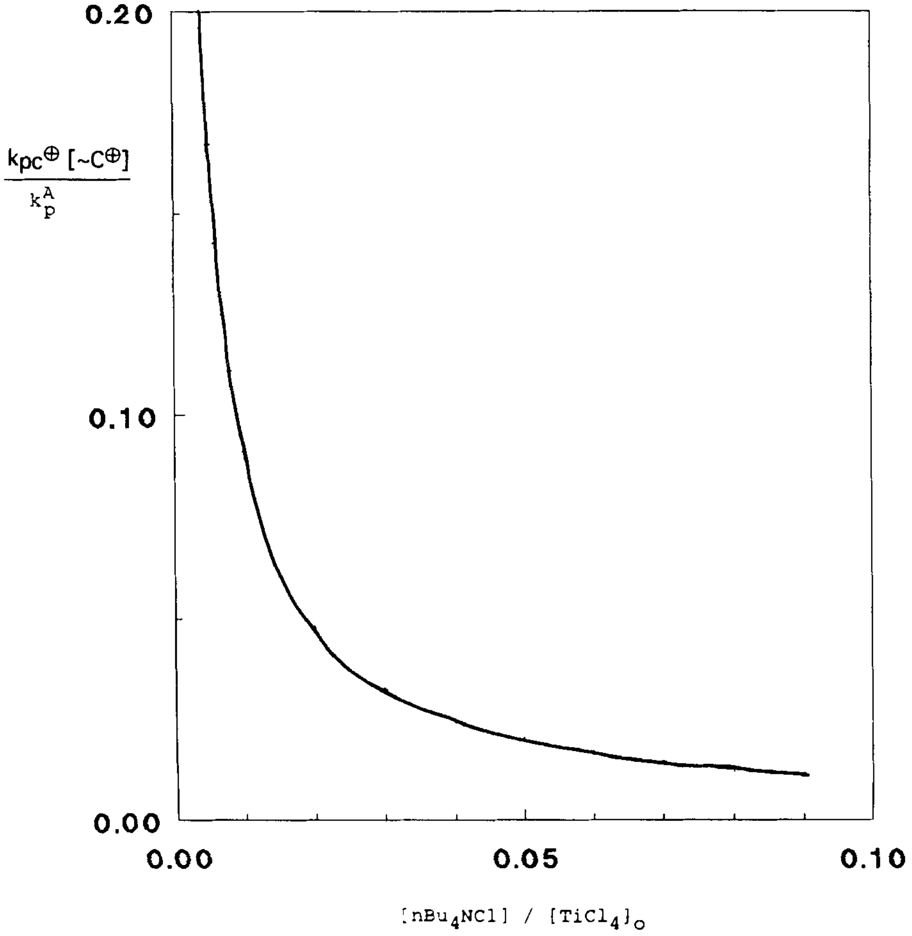


FIG. 4. Contribution of the conventional free ionic propagation to the apparent rate of propagation vs [*n*Bu$_4$NCl]/[TiCl$_4$]$_0$ ratio. For conditions, see Fig. 1.

The effect of *n*Bu$_4$NCl Concentration on the k_p^A of IB Polymerization

The addition of *n*Bu$_4$NCl to a conventional IB polymerization system converts the system into a living one, and it has been postulated that this effect is due to a decreasing concentration of the free ionic species in the Winstein spectrum [1, 2]. Additional experiments were carried out to study the influence of very small amounts of added salt on k_p^A and on the livingness of IB polymerization. Figure 5 shows the GPC traces of the products obtained under various conditions specified in the legend. Unfortunately, we were unable to determine the rates at −80°C because conversions reached ~100% in less than 20 seconds in each experiment. In the presence of [*n*Bu$_4$NCl] = 1.34×10^{-4} mol/L, a multimodal distribution is obtained. By increasing the salt concentration, the distribution becomes unimodal and narrower. Evidently the addition of the common ion salt decreases but does

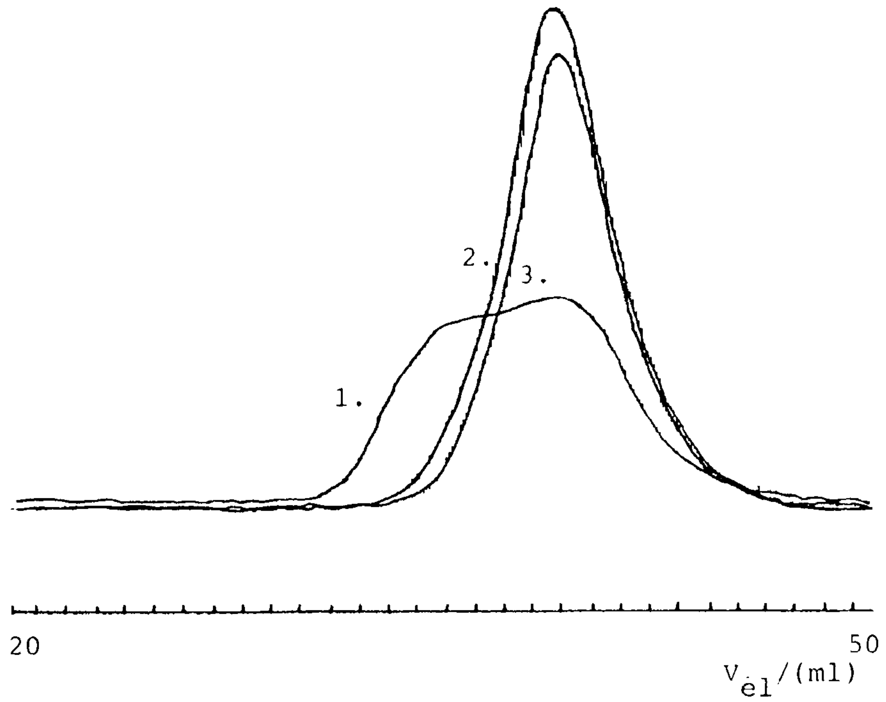


FIG. 5. GPC traces of PIBs obtained in the presence of $n\text{Bu}_4\text{NCl}$. [TMPCl] = 1.35 × 10^{-2} mol/L, [TiCl_4] = 0.18 mol/L, [IB] = 0.62 mol/L, CH_2Cl_2/hexane (60/40), V_{total} = 20 mL, −80°C. 1: [$n\text{Bu}_4\text{NCl}$] = 1.34 × 10^{-4} mol/L, $\overline{M}_n$ = 3800, $\overline{M}_w/\overline{M}_n$ = multimodal. 2: [$n\text{Bu}_4\text{NCl}$] = 6.5 × 10^{-4} mol/L, $\overline{M}_n$ = 3100, $\overline{M}_w/\overline{M}_n$ = 1.84. 3: [$n\text{Bu}_4\text{NCl}$] = 1.3 × 10^{-3} mol/L, $\overline{M}_n$ = 3100, $\overline{M}_w/\overline{M}_n$ = 1.63.

not completely eliminate the concentration of the free ionic species even at −80°C. At −40°C, and with higher $n\text{Bu}_4\text{NCl}$ concentrations, polymers with unimodal distribution are obtained (see Table 1 for conditions).

The conversion and the rate data obtained at −40°C are collected in Table 1, and Figure 6 shows the corresponding first-order plots together with k_p^{A} values.

By using Eq. (7), we can analyze the common ion induced rate reduction. Assuming $[\text{TiCl}_4] \approx [\text{TiCl}_4]_0 - [n\text{Bu}_4\text{NCl}] \approx [\text{TiCl}_4]_0$ (a similar approximation has already been used in Eq. 9, i.e., $[\text{TiCl}_4] \gg [n\text{Bu}_4\text{NCl}]$) and by introducing

$$a = k_{p\text{C}^+}[\text{I}]_0$$

$$b = k_{p\text{L}}\,[\text{I}]_0/K_2$$

$$c = 1/K_2 + 1/(K_1 \cdot K_2 \cdot [\text{TiCl}_4]_0)$$

and with the approximations in Eqs. (8) and (9), Eq. (7) can be written as

$$k_p^{\text{A}} = (a + b[n\text{Bu}_4\text{NCl}])\frac{1}{1 + c[n\text{Bu}_4\text{NCl}]} \qquad (10)$$

TABLE 1. The Influence of $n\text{Bu}_4\text{NCl}$ Concentration on the Rate of Propagation at −40°C ([TMPCl] = 1.35×10^{-2} mol/L, $[\text{TiCl}_4]$ = 0.19 mol/L, [IB] = 0.6 mol/L, CH_2Cl_2/hexane (60/40 v/v), V = 20 mL)

	W_p, g	Conversion, %	Time, s	$[n\text{Bu}_4\text{NCl}] \times 10^3$ mol/L	−ln (1 − conversion)
1.	0.4018	60	60	6.75	0.92
2.	0.5492	82	120		1.72
3.	0.6430	95	180		2.96
4.	0.6702	100	300		—
5.	0.6596	98	600		—
6.	0.2712	40	60	13.5	0.52
7.	0.3891	58	120		0.87
8.	0.5030	75	180		1.39
9.	0.5901	88	300		2.13
10.	0.6672	100	600		—
11.	0.1634	24	60	27.0	0.28
12.	0.2867	43	120		0.56
13.	0.3918	59	180		0.88
14.	0.5073	75	300		1.38
15.	0.5994	88	600		2.14
16.	0.0870	13	60		0.14
17.	0.2210	33	120	40.5	0.40
18.	0.2947	44	180		0.58
19.	0.4554	68	300		1.13
20.	0.5961	89	600		2.22

Since $c\,[n\text{Bu}_4\text{NCl}] \gg 1$

$$k_p^{\text{A}} = a/c \cdot 1/[n\text{Bu}_4\text{NCl}] + b/c \tag{11}$$

i.e., k_p^{A} is a linear function of $1/[n\text{Bu}_4\text{NCl}]$. Using the KT-transformation [9] for data in this concentration range, we obtain

$$\frac{k_p^{\text{a}}}{\alpha + z} = \left(\frac{a}{c} - \frac{b}{c} \cdot \frac{1}{\alpha}\right)\frac{z}{\alpha + z} + \frac{b}{c}\cdot\frac{1}{\alpha} \tag{12}$$

where $z = 1/[n\text{Bu}_4\text{NCl}]$ and $\alpha = \sqrt{z_{\min} \cdot z_{\max}}$. By using the apparent rate constants published in Ref. 1 and those shown in Fig. 6, the above dependence has been analyzed graphically as shown in Fig. 7 (for data, see Table 2). The plots are linear for both sets of data, yielding $b/c = 2.29 \times 10^{-3}$ (s^{-1}) and $a/c = 1.47 \times 10^{-4}$

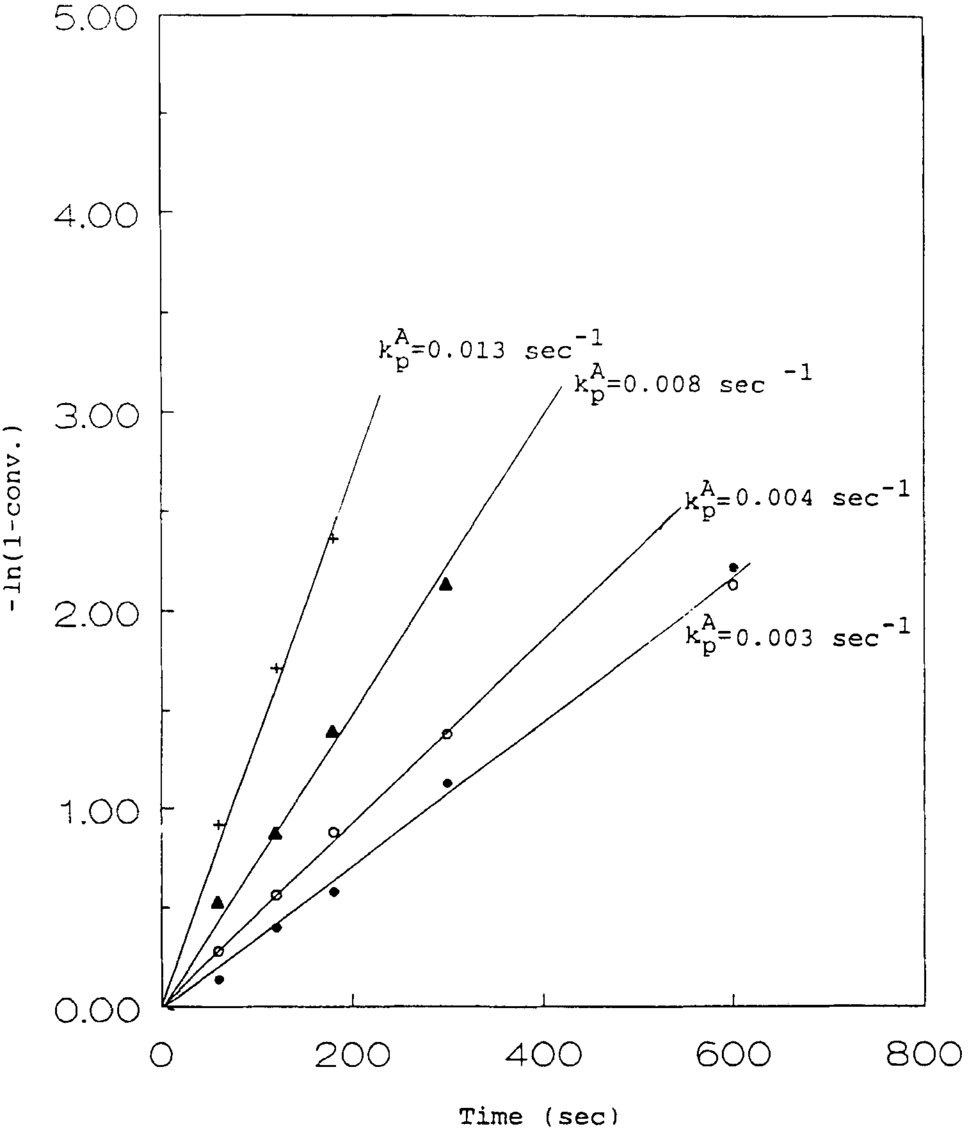


FIG. 6. First-order plot of IB polymerization in the presence of different concentrations ($\times 10^3$ mol/L) of nBu$_4$NCl: 6.75 (+), 13.5 (▲), 27.0 (○), 40.5 (●).

(mol·s^{-1}·L^{-1}) at −80°C and $b/c = 7.45 \times 10^{-4}$ (s^{-1}) and $a/c = 8.16 \times 10^{-5}$ (mol·s^{-1}·L^{-1}) at −40°C from the intercepts and slopes, respectively.

We can now calculate the contribution of free ionic propagation to the apparent rate of polymerization by using the following equation:

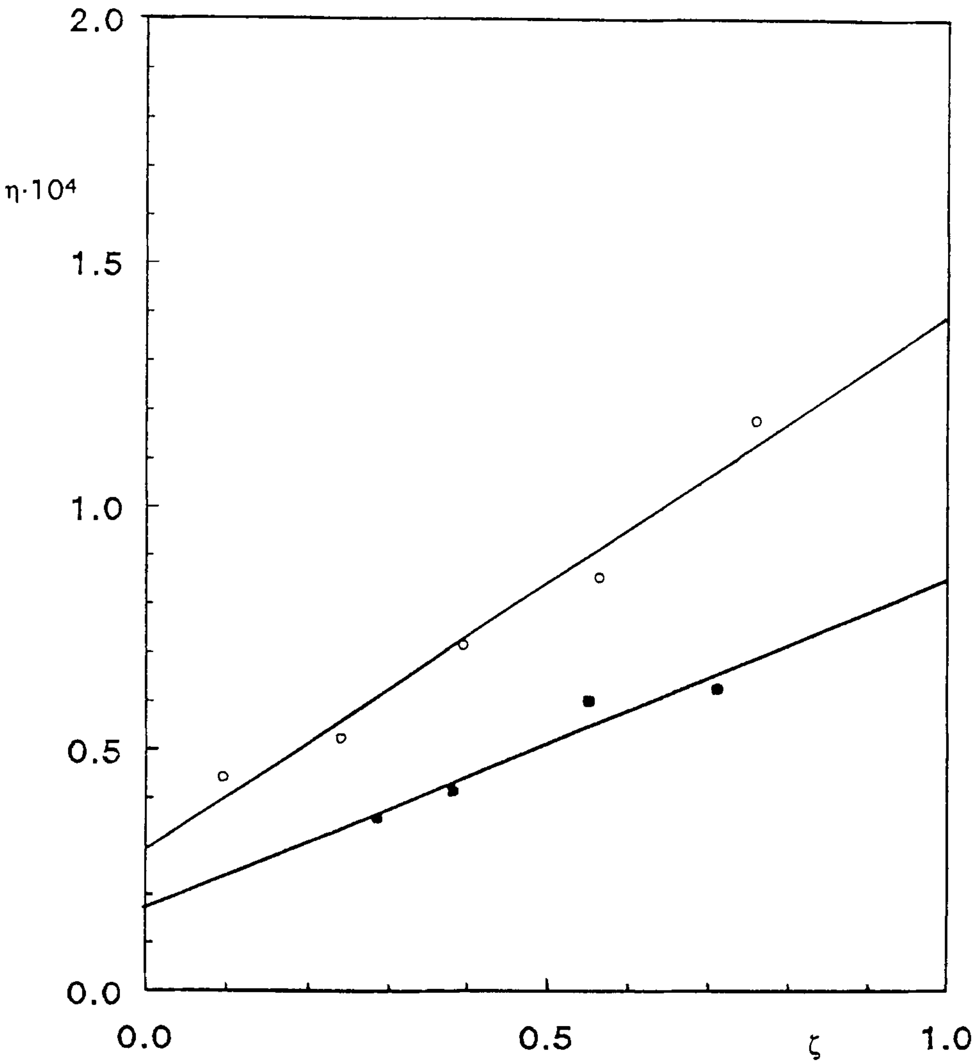


FIG. 7. KT representation of k_p^A vs $1/[n\text{Bu}_4\text{NCl}]$ data in LC$^+$Pzn of IB in the presence of added salt at (○) −80°C and (●) 40°C. Data in Table 2.

$$\frac{a}{a + b\cdot[n\text{Bu}_4\text{NCl}]} = \frac{a/c}{a/c + (b/c)[n\text{Bu}_4\text{NCl}]}$$

According to the data in Table 3, the contribution of free ionic propagation is decreasing even in the concentration range in which the calculated k_p^A curves are flat (see Figs. 1–4).

TABLE 2. KT-Transformation of the k_p^A vs $1/[n\text{Bu}_4\text{NCl}]$ Dependence (Eq. 11) obtained in Studies of the Influence of Common Ion Concentration on the Apparent Rate Constant

	$[n\text{Bu}_4\text{NCl}] \times 10^3$ mol/L	$z = \dfrac{1}{[n\text{Bu}_4\text{NCl}]}$ L/mol	$\zeta = \dfrac{z}{\alpha + z}$	$\eta = \dfrac{k_p^A}{\alpha + z}$
$T = -80°\text{C}$; $[\text{TiCl}_4]_0 = 0.175$ mol/L (data from Ref. 1)				
1	3.1	322	0.760	1.18×10^{-4}
2	7.55	132	0.565	8.56×10^{-5}
3	15.1	66	0.395	7.15×10^{-5}
4	31.2	32	0.240	5.24×10^{-5}
	$\alpha = \sqrt{32 \cdot 322} = 101.5$			
$T = -40°\text{C}$; $[\text{TiCl}_4] = 0.19$ mol/L (this work)				
5	6.75	148	0.713	6.25×10^{-5}
6	13.5	74	0.554	5.98×10^{-5}
7	27.0	37	0.383	4.14×10^{-5}
8	40.5	24	0.287	3.58×10^{-5}
	$\alpha = \sqrt{24 \cdot 148} = 59.6$			

TABLE 3. Contribution of Ionic Polymerization to the Reduced Apparent Rate Constants in the Presence of Different Salt Concentrations

	$[n\text{Bu}_4\text{NCl}] \times 10^3$ mol/L	$\dfrac{a/c}{a/c + (b/c)[n\text{Bu}_4\text{NCl}]} \times 100$, %
$T = -80°\text{C}$		
1	3.1	95.4
2	7.55	89.5
3	15.1	81.1
4	31.2	67.4
$T = -40°\text{C}$		
5	6.75	94.2
6	13.5	89.0
7	27.0	80.2
8	40.5	73.0

NOTE ADDED AS A RESULT OF REFEREE'S COMMENTS

According to recently published experimental results [10], the propagation order is ~2 with respect to $TiCl_4$ in the 5-*tert*-butyl-1,3-dicumylmethylether and 5-*tert*-butyl-1,3-dicumylchloride/$TiCl_4$ initiated IB polymerization system because "$TiCl_4$ forms bimolecular associates (or bimolecular complex gegenions)." These findings are indeed consistent with Ref. 11.

In the *n*-$Bu_4NCl/TiCl_4$ reaction the formation of the $Ti_2Cl_9^-$ common ion would reduce the $TiCl_4$ concentration twice as much as that of the $TiCl_5^-$ common ion. In our system the salt concentrations employed were far below even half of the total amount of added $TiCl_4$. Thus, the effect of the presence of $Ti_2Cl_9^-$ on the apparent rate constant (k_p^A) is insignificant in the range of our interest (see Fig. 1).

Current investigations to elucidate the influence of conditions (such as solvent, temperature, etc.,) on the extent of dimeric association of $TiCl_4$ are in progress in our laboratories and will be the subject of future communications.

CONCLUSION

According to our computation, the large decrease (several orders of magnitude) of the apparent rate constant of polymerization k_p^A in the range of low *n*Bu_4NCl concentrations is mainly due to the decreasing contribution of propagation by free carbocations. In the concentration range close to that of the $TiCl_4$, the reduction of the $TiCl_4$ concentration due to the reaction between *n*Bu_4NCl and $TiCl_4$ becomes important and leads to a fast decrease of k_p^A. The calculated k_p^A values are within one order of magnitude in the concentration range of our experimental interest (see Fig. 1) which is in good agreement with the observations.

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