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Living carbocationic polymerization

XLVI. Living isobutylene polymerization induced by the common ion effect*

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I. Abstract

Conventional cationic polymerization can be converted into living carbocationic polymerization ($LC^{\oplus}Pzn$) by the introduction of common anion into the charge. Thus the conventional polymerization of isobutylene (IB) induced by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ combination yields $LC^{\oplus}Pzn$ of IB upon the addition of tetrabutyl ammonium chloride ($\underline{n}$-Bu_4NCl), most likely due to the $\underline{n}$-$Bu_4NCl + TiCl_4 \rightleftharpoons \underline{n}$-$Bu_4N^{\oplus} + TiCl_5^{\ominus}$ equilibrium. A kinetic model has been developed and tested which corroborates these propositions. By this model we have gained for the first time quantitative insight into the quasiliving equilibrium.

II. Introduction

The Winstein spectrum, Figure 1 (1,2), is an important guide-post for the exploration of $LC^{\oplus}Pzn$. The message conveyed by this spectrum of equilibria is that $LC^{\oplus}Pzn$'s are due to low ionicity species congregating at the far left of the spectrum, whereas the highly ionic species on the right induce conventional (i.e., chain transfer- and termination-dominated) polymerizations (1).

A further heretofore unexplored/unexploited message of the spectrum is that by the introduction of common anions into a conventional cationic polymerization charge the equilibria

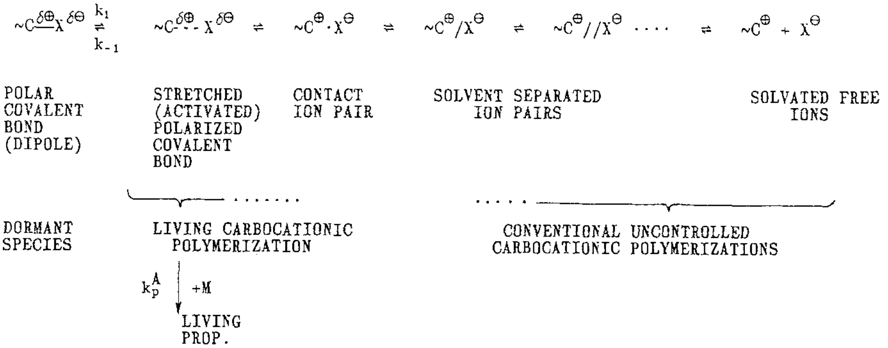

Figure 1. The Winstein spectrum of ionicities of propagating species in carbocationic polymerization

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*For part XLV see J. E. Puskas, G. Kaszas, J. P. Kennedy, W. G. Hager: J. Polym. Sci., Part A, Polym. Chem., in press

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***To whom offprint requests should be sent could be displaced toward the left and thus the concentration of the species that lead to conventional polymerization could be eliminated; in other words the possibility exists to convert conventional cationic polymerization systems into living ones by the addition of common ions to the former. The preparative challenge is to find practical systems to prove this proposition. Japanese authors obtained $LC^{\oplus}Pzn$ of styrene by using the $CH_3SO_3H/SnCl_4$ initiating system in the presence of n-Bu_4NCl (3). The effect of this salt has been attributed to the suppression of highly dissociated species (3,4).

This initial report on common ion effects in $LC^{\oplus}Pzn$'s concerns the first demonstration that a conventional isobutylene polymerization induced by the $TMPCl/TiCl_4$ combination can be readily converted into a $LC^{\oplus}Pzn$ by the addition of the common anion $TiCl_5^{\ominus}$. $TiCl_5^{\ominus}$ is visualized to arise *in situ* by the introduction of n-Bu_4NCl to the charge, i.e., by n-Bu_4NCl + (excess) $TiCl_4 \rightleftarrows n\text{-}Bu_4N^{\oplus} + TiCl_5^{\ominus}$ (cationic olefin polymerization charges usually contain excess Friedel-Crafts acid in respect to the initiator).

III. Experimental

The synthesis of TMPCl (5) and the source and purity of the other chemicals used ($TiCl_4$, CH_2Cl_2, CH_3Cl, IB, hexanes) have been described (5,6,7). n-Bu_4NCl (Tokyo Kasei) was used as received. General procedures and analytical techniques have also been described (3,4,5). Polymerizations were carried out at -80°C under a blanket of N_2 (dry box) using large (75 mL) culture tubes (total volume was 20 mL). The charges were thoroughly mixed prior to and during $TiCl_4$ addition. Both the AMI and diagnostic IMA techniques were employed (8). Polymerizations were quenched by prechilled methanol, the products were washed with methanol and dried to weight constancy at room temperature. Specific conditions, concentrations, etc., are given in the legends of Tables and Figures.

IV. Results and Discussion

IV.1. Living Polymerization in the Presence of n-Bu_4NCl

Table I shows the data obtained in a series of experiments in which IB polymerizations were induced by the $TMPCl/TiCl_4$ combination using methyl chloride/hexanes (60/40) mixed solvent at -80°C in the presence of various amounts of n-Bu_4NCl. Both the AMI and IMA techniques were used (8). Figure 2 shows the corresponding $\overline{M}_n$ versus W_p (g of PIB converted) plot, and the inset the N (number of moles of PIB formed i.e., g of PIB/$\overline{M}_n$) versus W_p plot. Clearly, the $\overline{M}_n$ versus W_p plot is rectilinear and starts at the origin, and the experimental points are close to the theoretical line constructed with I_{eff} = 100%. This plot together with the horizontal N versus W_p plot (which indicates N_0 = [TMPCl]), demonstrate living polymerization.

A control experiment, i.e., the same charge under the same conditions specified in Table I, first series, except in the absence of n-Bu_4NCl, gave ~100% conversion, ~30% I_{eff} within less than a minute, $\overline{M}_n$ = 15,200 and $\overline{M}_w/\overline{M}_n$ = 2.4 with GPC traces strongly skewed toward high molecular weights.

TABLE I. LC$^{\oplus}$Pzn of IB in the presence of n-Bu$_4$NCl

	$\overline{M}_n$ (g/mole)	$\overline{M}_w/\overline{M}_n$	W_p (g)	I_{eff}* (%)	N·10^4
1**	[n-Bu$_4$NCl]=5.6·10^{-4}mole, IMA technique				
1.1	4950	1.70	1.390	109	2.8
1.2	4150	1.90	1.2104	106	2.9
1.3	15000	1.55	3.9270	96	2.6
1.4	16610	1.60	4.3370	95	2.6
2***	[n-Bu$_4$NCl]=1,64·10^{-3}mole, IMA technique				
2.1	2780	1.46	0.7014	92.4	2.5
2.2	6600	1.54	1.2883	79.4	1.9
2.3	8500	1.48	2.1782	93.8	2.5
2.4	10170	1.46	2.9150	104.8	2.8
2.5	11700	1.50	3.2974	103.5	2.8
3****	[n-Bu$_4$NCl]=1.58·10^{-3}mole, AMI technique				
3.1	3600	1.29	0.8756	88.9	2.4
3.2	4300	1.21	1.2582	107.0	2.9
3.3	4700	1.20	1.2386	96.0	2.6
3.4	4800	1.16	1.1672	89.0	2.4

*I_{eff}=(g of PIB/$\overline{M}_n$ of PIB)/mole of TMPCl

**[TMPCl]=2.7·10^{-4} mole, [TiCl$_4$]=3.7·10^{-4} mole,[IB]=0.0234 mole

***[TMPCl]=2.6·10^{-4} mole, [TiCl$_4$]=3.7·10^{-4} mole,[IB]=0.0117 mole, in CH$_3$Cl/Hex. (60/40), 1 ml IB/8 min., five times

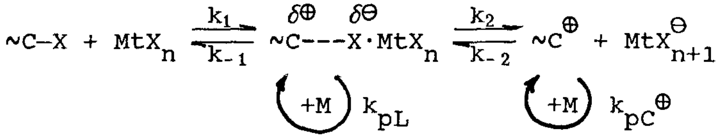
****[TMPCl]=2.7·10^{-4} mole, [TiCl$_4$]=3.7·10^{-4} mole, [IB]=0.0234 mole in CH$_3$Cl/Hex. (60/40), 1,5,8,10 minutes

TABLE II. Influence of n-Bu$_4$NCl concentration on rate of propagation. ([TMPCl]=2.7·10^{-4} mole, [TiCl$_4$]=3.7·10^{-3} mole, [IB]=0.013 mole, CH$_2$Cl$_2$/Hex., 60/40, -80°)

	W_p (g)	Conv. (%)	Time (sec)	n-Bu$_4$NCl·10^3 (mole)	-ln(1-conv)
1	0.1008	14	20	1.85	0.151
2	0.1512	21	40		0.236
3	0.2232	31	60		0.371
4	0.5473	77	240		1.464
5	0.6244	87	420		2.025
6	0.1440	20	20	0.62	0.220
7	0.1872	26	40		0.301
8	0.2736	38	60		0.478
9	0.6986	97	240		3.506
10	0.7217	~100	420		—
11	0.1945	27	20	0.30	0.314
12	0.2304	32	40		0.385
13	0.4105	57	60		0.843
14	0.7198	~100	240		—
15	0.7210	~100	420		—
16	0.2161	30	20	0.15	0.356
17	0.3457	48	40		0.653
18	0.5185	72	60		1.273
19	0.7019	97	240		3.650
20	0.7213	~100	420		—
21	0.2521	35	20	0.062	0.431
22	0.5330	74	40		1.347
23	0.6698	93	60		2.670
24	0.7204	~100	240		—
25	0.7198	~100	420		—

IV.2. The Influence of n-Bu_4NCl Concentration on the Rate of Propagation in Living IB Polymerization: A Kinetic Model and Analysis

As suggested by the Winstein spectrum, carbocationic polymerizations (including living and conventional systems) may be visualized to proceed by a combination of three fundamental species: a covalent dormant species, a living species in which the critical "living" bond is stretched, and a set of more or less dissociated ion pairs, which yield conventional polymerization. Just as the dissociated ionic species are represented as a set of species, (see Figure 1), the undissociated species may also be imagined to consist of a set of contributing species. In the presence of a Friedel-Crafts acid (MtX_n) the simplified Winstein spectrum (in which all propagating ion pairs are symbolized by $\sim C^{\oplus} + MtX_{n+1}^{\ominus}$) becomes:

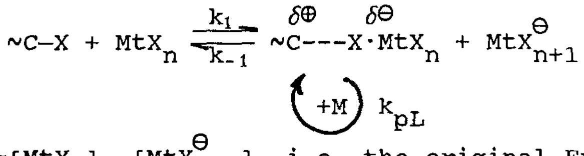


$$\sim C{-}X + MtX_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\circlearrowleft +M\ k_{pL}}{\sim \overset{\delta\oplus}{C}{-}{-}{-}\overset{\delta\ominus}{X}\cdot MtX_n} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\circlearrowleft +M\ k_{pC^{\oplus}}}{\sim C^{\oplus}} + MtX_{n+1}^{\ominus}$$

where the curved arrows symbolize living and conventional propagation characterized by the rate constants k_{pL} and $k_{pC^{\oplus}}$. The equilibria between the three fundamental species are governed by the equilibrium constants $K_1=k_1/k_{-1}$ and $K_2=k_2/k_{-2}$. The first, so-called quasiliving, equilibrium that exist between dormant and living species has been discussed in detail (9). Specifically, for the TMPCl/$TiCl_4$/IB system:

$$\sim CH_2C(CH_3)_2Cl + TiCl_4 \rightleftharpoons \overset{\delta\oplus}{CH_2C(CH_3)_2}{-}{-}{-}\overset{\delta\ominus}{Cl\cdot TiCl_4} \rightleftharpoons \sim CH_2C(CH_3)_2^{\oplus} + TiCl_5^{\ominus}$$

According to this model, the addition of n-Bu_4NCl to the system which contains excess $TiCl_4$ (2) will produce the common ion $TiCl_5^{\ominus}$, which by mass law action, will virtually eliminate the dissociated ion pairs of the equilibrium and push the equilibria toward the left. Thus in the presence of added common ion $TiCl_5^{\ominus}$ (i.e. $MtX_{n+1}^{\ominus}$), the simplified Winstein spectrum will contain only one equilibrium between the dormant and living species, and the concentration of the living species will decrease in proportion with the concentration of the common ion:



$$\sim C{-}X + MtX_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\circlearrowleft +M\ k_{pL}}{\sim \overset{\delta\oplus}{C}{-}{-}{-}\overset{\delta\ominus}{X}\cdot MtX_n} + MtX_{n+1}^{\ominus}$$

where $[MtX_n]=[MtX_n]_o-[MtX_{n+1}^{\ominus}]$, i.e. the original Friedel-Crafts acid concentration will decrease in proportion to the common ion added.

The overall rate of propagation

$$-\frac{d[M]}{dt} = k_{pL}[\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{X}\cdot MtX_n]\cdot[M] = k_p^A[M] \qquad (1)$$

where the apparent rate constant of propagation $k_p^A = k_{pL}[\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{X}\cdot MtX_n]$ can be experimentally determined. Obviously, the amount of the initiator that has entered the Winstein spectrum is equal to that originally introduced into the charge $[I]_0$ minus the unused portion $[I]$:

$$[I]_0-[I] = [\sim C-X] + [\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{X}\cdot MtX] \qquad (2)$$

and

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{X}\cdot MtX_n]\cdot[MtX_{n+1}^{\ominus}]}{[\sim C-X]\cdot[MtX_n]} \qquad (3)$$

Thus

$$[\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{X}\cdot MtX_n] = \frac{[I]_0-[I]}{1+[MtX_{n+1}^{\ominus}]/(K_1[MtX_n])} \qquad (4)$$

and

$$k_p^A = k_{pL}\frac{[I]_0-[I]}{1+[MtX_{n+1}^{\ominus}]/(K_1[MtX_n])} \qquad (5)$$

or

$$\frac{[I]_0-[I]}{k_p^A} = \frac{1}{k_{pL}} + \frac{1}{k_{pL}\cdot K_1}\cdot\frac{[MtX_{n+1}^{\ominus}]}{[MtX_n]} \qquad (6)$$

$$\frac{[I]_0-[I]}{k_p^A} = \frac{1}{k_{pL}} + \frac{1}{k_{pL}\cdot K_1[MtX_n]_0}\cdot\frac{[MtX_{n+1}^{\ominus}]}{1-[MtX_{n+1}^{\ominus}]/[MtX_n]_0} \qquad (7)$$

This equation can be analyzed graphically by determining k_p^A (obtainable from conversion vs. time experiments) as a function of different $[MtX_{n+1}^{\ominus}]$. Thus a series of experiments were carried out to test this model in the TMPCl/TiCl$_4$/IB system and to express quantitatively the common ion effect by the addition of various concentrations of *n*-Bu$_4$NCl to the charge (it is assumed that the *n*-Bu$_4$NCl + excess TiCl$_4$ reaction is quantitative and that the product is completely dissociated, that is: $[\textit{n}\text{-Bu}_4\text{NCl}] = [MtX_{n+1}^{\ominus}]$).

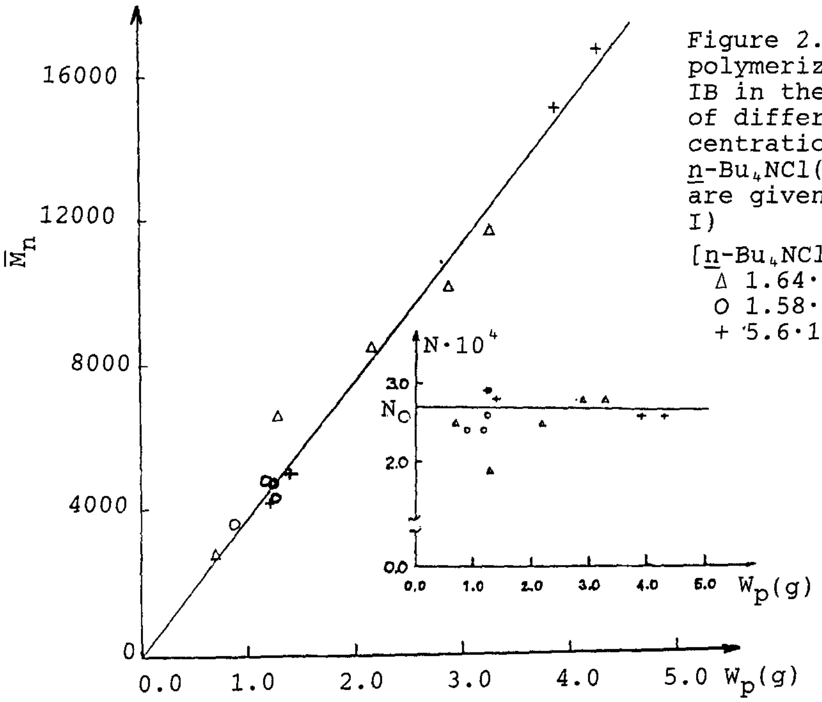


Figure 2. Living polymerization of IB in the presence of different concentrations of n-Bu$_4$NCl(conditions are given in Table I)

[n-Bu$_4$NCl]:
Δ $1.64\cdot10^{-3}$ mole
O $1.58\cdot10^{-3}$ mole
+ $5.6\cdot10^{-4}$ mole

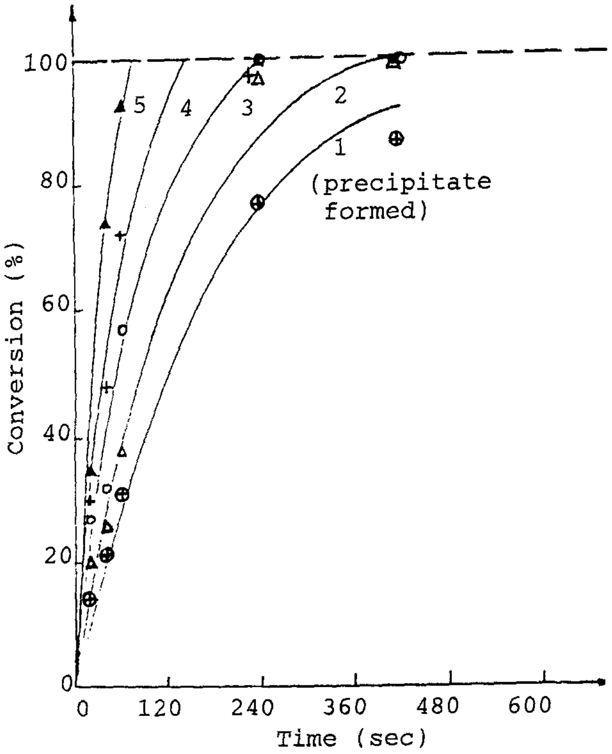


Figure 3. Influence of n-Bu$_4$NCl concentration on rate of propagation (conditions are given in Table II)

[n-Bu$_4$NCl]:
1. $1.85\cdot10^{-3}$ mole
2. $6.2\cdot10^{-4}$ mole
3. 3.10^{-4} mole
4. $1.5\cdot10^{-4}$ mole
5. $6.2\cdot10^{-5}$ mole

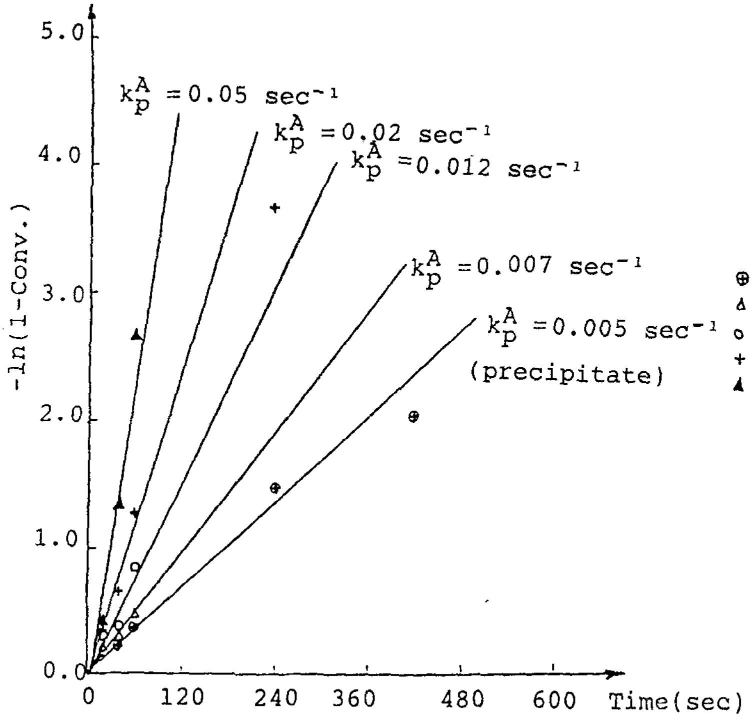
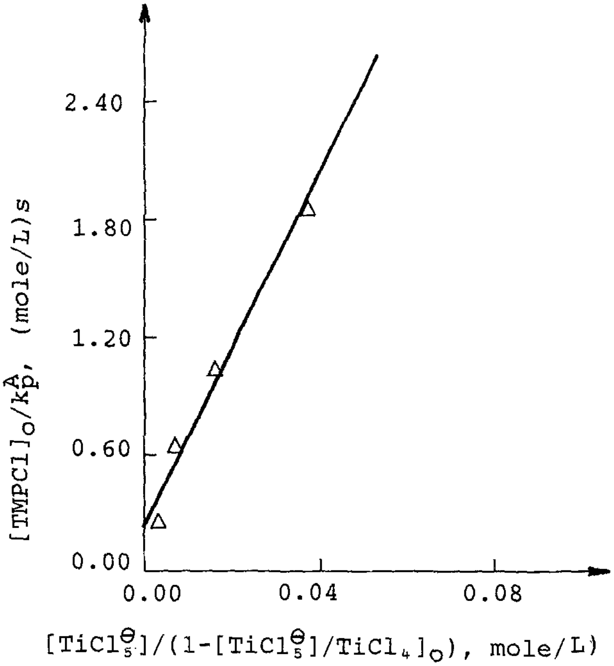


Figure 4. The first order plot of IB polymerizations in the presence of different concentrations of n-Bu_4NCl. [n-Bu_4NCl] =
⊕ $1.85\cdot10^{-3}$,
△ $6.2\cdot10^{-4}$,
○ 3.10^{-4},
\+ $1.5\cdot10^{-4}$,
▲ $6.2\cdot10^{-5}$mole

Figure 5. Apparent rate constants of propagation in IB polymerization



Results are summarized in Table II. Figure 3 shows conversion vs. time plots and Figure 4 the corresponding first order plot together with the k_p^A values. Evidently by increasing the concentration of the common ion (i.e., $[MtX_{n+1}^{\ominus}]$) the rate of polymerization decreases proportionately.

On hand of the k_p^A data we are able to substantiate our model expressed by eq.(7). Figure 5 shows the $[I]_0-[I]/k_p^A$ vs. $[MtX_{n+1}^{\ominus}]/(1-[MtX_{n+1}^{\ominus}]/[MtX_n]_o)$ plot. Gratifyingly the plot is rectilinear yielding $k_{pL} \sim 3$ sec^{-1} (mole/L)$^{-1}$ and $K_1 = 5.5 \cdot 10^{-2}$ from the intercept and slope, respectively. The linearity of this plot is strong evidence for the existence of the quasiliving equilibrium and for the common ion effect in the $LC^{\oplus}Pzn$ of IB. In this manner we have for the first time gained quantitative insight into the dormant ⇌ living, i.e., so-called quasiliving, equilibrium.

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