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Articles

Initiation via Haloboration in Living Cationic Polymerization. 2. Kinetic and Mechanistic Studies of Isobutylene Polymerization[‖]

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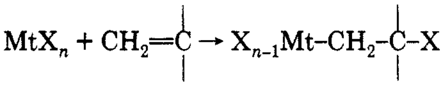
ABSTRACT: We have discovered that in the presence of a proton trap to trap protic impurities, BCl_3 alone can initiate the polymerization of isobutylene, leading to low molecular weight asymmetric telechelic polyisobutylenes carrying a BCl_2 head group and a tertiary chloro end group. Two polymerization schemes are proposed to explain the results, one based on initiation by self-dissociation of BCl_3 and another involving haloboration–initiation. Kinetic and mechanistic studies support the proposed new initiation mechanism via haloboration and explain the apparent livingness of the polymerization.

Introduction

The mechanism of initiation in cationic polymerization using Lewis acids appeared to be clarified by the discovery of cocatalysis, i.e., that most Lewis acids, particularly the halides of boron, titanium, and tin, require an additional cation source to initiate polymerization. There have been reports, however, that in many systems Lewis acids alone, in the absence of a separately added initiator, are able to initiate cationic polymerization. The polymerization of isobutylene for instance was claimed in the absence of a separately added initiator by $AlBr_3$ or $AlCl_3$,[1], $TiCl_4$,[2] $AlEtCl_2$,[3] and BCl_3.[4]

Three fundamentally different theories have been presented to explain the still controversial existence of direct initiation. According to the Sigwalt–Olah theory, initiation is by halometalation as follows:



$$\mathrm{MtX}_n + \mathrm{CH_2{=}}\overset{|}{\underset{|}{\mathrm{C}}} \rightarrow \mathrm{X}_{n-1}\mathrm{Mt{-}CH_2{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}X}$$

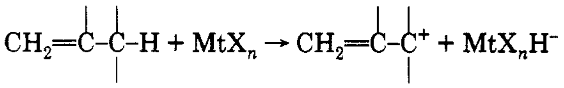
In the presence of excess Lewis acid the metalloorganic compound may ionize or may eliminate HCl, a conventional cationogen.

Self-ionization was proposed by Korshak, Plesch, and Marek to explain direct initiation:

$$2\mathrm{TiCl_4} \rightleftarrows \mathrm{TiCl_3^+TiCl_5^-} \rightleftarrows \mathrm{TiCl_3^+} + \mathrm{TiCl_5^-}$$

A similar mechanism was proposed for the polymerization of isobutylene by $AlCl_3$,[1], i.e., self-ionization of the $AlCl_3$ yielding $AlCl_2^+$ cations that immediately add to the double bond of the monomer.

According to Kennedy, allylic self-initiation may explain results with olefins possessing an allylic hydrogen. The following scheme was suggested:



$$\mathrm{CH_2{=}}\overset{|}{\mathrm{C}}\mathrm{{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}H} + \mathrm{MtX}_n \rightarrow \mathrm{CH_2{=}}\overset{|}{\mathrm{C}}\mathrm{{-}}\overset{|}{\underset{|}{\mathrm{C}}}{}^{+} + \mathrm{MtX}_n\mathrm{H}^-$$

All three theories imply that the polymerization system is free of protogenic impurities. Kennedy cautioned, however, that even the most exhaustive drying may not remove the last traces of protogenic materials, and initiation may be due to their presence.

It is important to note that, although initiation by metal halides has been postulated with the above Lewis acids, evidence was presented only for aluminum halides.[1] With $TiCl_4$ attempts have been made to observe the corresponding intermediates by ^{1}H NMR but without success, which was explained by the known instability of the organotitanium compounds.[5]

We have recently discovered that using polar solvents (CH_3Cl, CH_2Cl_2, $ClCH_2CH_2Cl$) in the presence of the proton trap di-*tert*-butylpyridine (DTBP) or 4-methyl-di-*tert*-butylpyridine (4-MeDTBP), BCl_3 alone can initiate the polymerization of isobutylene (IB).[6] The products are low molecular weight asymmetric telechelic polyisobutylenes (PIBs) carrying a BCl_2 head group and a tertiary chloro end group, intermediates to a variety of valuable asymmetric telechelic PIBs, which are difficult to obtain by traditional methods.

Two mechanisms were proposed in the first publication of this series[6] to explain the kinetics of the polymerization and the structure of the polymers, i.e., self-ionization of BCl_3 (Scheme 1a) and haloboration followed by BCl_3 coinitiation (Scheme 1b). Both would lead to $PIB^+BCl_4^-$ growing centers. It was postulated that chain transfer to monomer and irreversible termination are absent, since IB polymerizations involving these species have been shown to be living. Thus, living polymerization with continuous initiation may explain the observed increase

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[‖] This paper is dedicated to the memory of Prof. Tibor Kelen, who passed away on October 9, 1993.

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Scheme 1

Initiation

a)

$$2BCl_3 \xrightleftharpoons{K_1} BCl_2^+BCl_4^-$$

$$BCl_2^+\,BCl_4^- + CH_2{=}C(CH_3)_2 \xrightarrow{k_1} BCl_2\text{-}CH_2\text{-}\overset{+}{C}(CH_3)_2\,BCl_4^-$$

$$BCl_2\text{-}[CH_2\text{-}C(CH_3)_2]^+\,BCl_4^- \rightleftharpoons BCl_3 + BCl_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}Cl$$

or b)

$$BCl_3 + CH_2{=}C(CH_3)_2 \xrightarrow{k_2} BCl_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}Cl$$

$$BCl_3 + BCl_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}Cl \rightleftharpoons BCl_2\text{-}[CH_2\text{-}C(CH_3)_2]^+\,BCl_4^-$$

Propagation

$$BCl_2\text{-}CH_2\text{-}C^+(CH_3)_2\,BCl_4^- + M \xrightarrow{k_p} BCl_2\text{-}[CH_2\text{-}C(CH_3)_2]_n^+\,BCl_4^-$$

Termination-reinitiation

$$BCl_2\text{-}[CH_2\text{-}C(CH_3)_2]_n^+\,BCl_4^- \xrightleftharpoons{K_2} BCl_3 + BCl_2\text{-}[CH_2\text{-}C(CH_3)_2]_n\text{-}Cl$$

Table 1. Polymerization of IB in CH_2Cl_2 in the Absence of n-Bu_4NCl[a]

reactn time/h	M_n	M_w/M_n	conv/%
0.17	800	1.26	2
0.5	2200	1.29	27
1	3200	1.30	80
2	3500	1.29	95

[a] $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.957$ M, temperature = −40 °C.

in cation and polymer concentration during the polymerization and could account for the 1.2–1.4 molecular weight distributions.

Haloboration of olefins is well documented and the results have been compiled by Lappert.[7] On the other hand, self-ionization of BCl_3 (route 1a) has not been demonstrated.

In the present publication, using kinetic considerations, we attempt to identify which mechanism is operational.

Experimental Section

n-Bu_4NCl was made anhydrous by refluxing its CH_2Cl_2 solution on CaH_2. All other materials, polymerization, and characterization methods have been described.[6]

Results and Discussion

Although the identification of the nature of the growing centers is not the objective of this publication, for the kinetic treatment of Scheme 1 we need to establish the nature of the growing centers. Scheme 1 postulates that propagation is by $PIB^+BCl_4^-$. This symbolism represents ion pairs and in the present context any other growing species toward (but not including) the covalent species on the Winstein spectrum. However, if free ions are also present, a further equilibrium would exist between free ions and ion pairs, and Scheme 1 would not satisfactorily describe the polymerization. In this case the concentration of free ions and the rate of propagation could be decreased by the use of a common ion salt. In the presence of a common ion, the free ion–ion pair equilibrium is shifted toward the ion pairs. Accordingly, polymerization rates would be lowered. For haloboration–initiation the haloboration (first step of initiation) would not be affected; therefore the presence of a common ion would also result in lower molecular weights. Tables 1 and 2 list the results of experiments carried out in the absence and presence of a common ion salt. Comparison of the molecular weights shows that PIBs obtained in the presence of a common ion salt have a somewhat lower molecular weight at similar conversion. Increasing the [n-Bu_4NCl]/[polymer] ratio resulted in lower molecular weights but the difference is small. Importantly, the polymerization rates are similar in the presence and absence of n-Bu_4NCl, suggesting that our postulate is valid, i.e., propagation is not by free ions.

Table 2. Polymerization of IB in CH_2Cl_2 in the Presence of n-Bu_4NCl[a]

[nBu_4NCl]/[polymer]	reactn time/h	M_n	M_w/M_n	conv/1%
1/2	5	2800	1.28	96
1/1	1	2700	1.28	91
1/1	2	2700	1.27	96
1/1	3	2700	1.28	90
1/1	5	2700	1.28	92
1/1	8	2800	1.34	100
3/1	5	2500	1.27	98

[a] $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.957$ M, temperature −40 °C.

It was suggested by one of the reviewers that besides the self-ionization of BCl_3, a limited equilibrium of monomeric BCl_3 with its polarized dimeric donor–acceptor complex could be considered. We have recently published that in the living polymerization of IB with the *tert*-alkyl chloride/BCl_3 system, propagation is first order in BCl_3;[8] therefore BCl_3 is mostly monomeric. Nevertheless, if the proposed limited equilibrium existed, $BCl_2^+BCl_4^-$ should be replaced by the dimeric donor–acceptor complex; however, the kinetic equations obtained from Scheme 1a would still be valid.

Using simplifying notations, P^+ for all carbenium ions and PCl for all dormant chlorides, one can write the following differential equations for Scheme 1a:

$$d([PCl] + [P^+])/dt = k_1[BCl_2^+BCl_4^-][M] \qquad (1)$$

and assuming that $[P^+]$ is negligible compared to [PCl]

$$d[PCl]/dt = k_1[BCl_2^+BCl_4^-][M] \qquad (2)$$

Assuming fast self-ionization equilibrium and that $[BCl_3] \sim$ constant ($[BCl_2^+BCl_4^-] = K_1[BCl_3]^2$)

$$d[PCl]/dt = k_1[BCl_2^+BCl_4^-][M] = k_1K_1[BCl_3]^2[M] \qquad (3)$$

Since first-order monomer dependency was found with the *tert*-alkyl chloride/BCl_3 system using the same solvents,[8] first-order dependency is assumed with the present system:

$$-d[M]/dt = k_p[P^+][M] = k_p[PCl][BCl_3][M]/K_2 \qquad (4)$$

$$-d[M]/d[PCl] = k_p[PCl]/(k_1K_1K_2[BCl_3]) \qquad (5)$$

Solving the differential eq 5 gives

$$[M]_0 - [M] = k_p[PCl]^2/(2k_1K_1K_2[BCl_3]) \qquad (6)$$

With the assumption that $[P^+]$ is negligible compared to [PCl]

$$DP_n = ([M]_0 - [M])/[PCl] = k_p[PCl]/(2k_1K_1K_2[BCl_3]) \qquad (7)$$

where DP_n is the degree of polymerization. Since using fractions the conversion $C = ([M]_0 - [M])/[M]_0$,

$$DP_n^{\,2} = k_p[M]_0C/(2k_1K_1K_2[BCl_3]) \qquad (8a)$$

or

$$M_n = 56\{k_p[M]_0C/(2k_1K_1K_2[BCl_3])\}^{1/2} \qquad (8b)$$

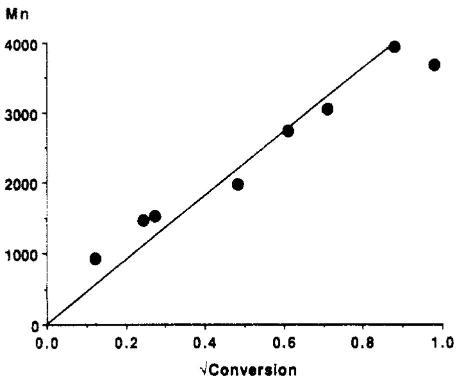

Figure 1. Polymerization of IB using CH_3Cl at −35 °C. $[BCl_3]$ = 0.512 M, [DTBP] = 4.7 × 10^{-3} M, $[IB]_0$ = 0.948 M.

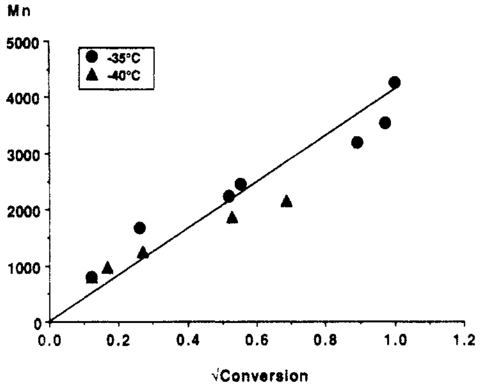

Figure 2. Polymerization of IB using CH_2Cl_2 at −40 and −35 °C. $[BCl_3]$ = 0.512 M, [DTBP] = 4.7 × 10^{-3} M, $[IB]_0$ = 0.938 M.

According to eq 8b, the M_n versus square root of conversion plot will be linear starting at the origin. For Scheme 1b

$$d[PCl]/dt = k_2[BCl_3][M] \tag{9}$$

$$-d[M]/dt = k_p[P^+][M] \tag{10}$$

$$-d[M]/d[PCl] = k_p[PCl]/k_2K_2 \tag{11}$$

Similarly to obtaining eq 8 through eqs 6 and 7, the conversion can be written as follows:

$$DP_n^{\,2} = k_p[M]_0C/(2k_2K_2) \tag{12a}$$

or

$$M_n = 56\{k_p[M]_0C/(2k_2K_2)\}^{1/2} \tag{12b}$$

Similarly to eq 8b, eq 12b predicts that the M_n versus square root of conversion plot will be linear starting at the origin. The results plotted in Figure 1 for methyl chloride and in Figure 2 for methylene chloride are in agreement with this prediction.

Equation 8b predicts that at the same conversion the M_n will be inversely proportional to $[BCl_3]^{1/2}$. In contrast to eq 8b, however, according to eq 12b at a constant conversion, M_n is independent of $[BCl_3]$. Molecular weights obtained at −25 °C using 0.25 M $[BCl_3]$ and different polymerization times to obtain different conversions and those that were obtained using increasing $[BCl_3]$ and a constant, 40 min polymerization time leading to increasing conversions are plotted in Figure 3. Similar results at −60 °C are plotted in Figure 4. According to these results, DP_n is independent of $[BCl_3]$; i.e., initiation is by haloboration (Scheme 1b).

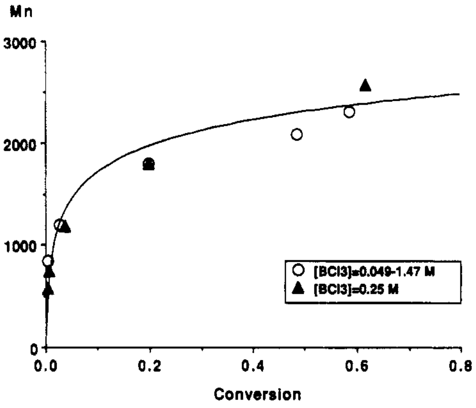

Figure 3. Polymerization of IB using CH_2Cl_2 at −25 °C. $[IB]_0$ = 0.93 M, [4-MeDTBP] = 4.0 × 10^{-3} M.

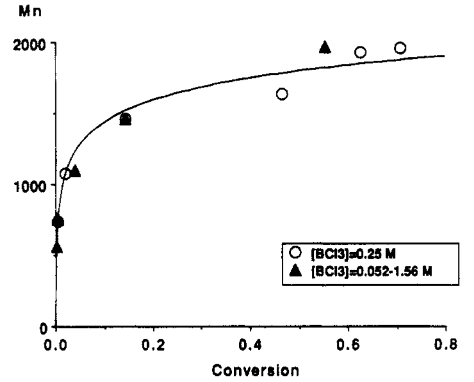

Figure 4. Polymerizationn of IB using CH_2Cl_2 at −60 °C. $[IB]_0$ = 0.93 M, [4-MeDTBP] = 4.0 × 10^{-3} M.

The time dependence of the conversion and its dependence on $[BCl_3]$ can be obtained by solving eq 4:

$$-d[M]/dt = k_p[P^+][M] = k_p[PCl][BCl_3][M]/K_2 \tag{4}$$

Substitution of

$$[PCl] = \{([M]_0 - [M])2K_2k_1K_1[BCl_3]/k_p\}^{1/2} \tag{13}$$

for Scheme 1a and

$$[PCl] = \{([M]_0 - [M])2K_2k_2/k_p\}^{1/2} \tag{14}$$

for Scheme 1b followed by integration yields eq 15 for Scheme 1a and eq 16 for Scheme 1b:

$$\ln\{(1 + C^{1/2})/(1 - C^{1/2})\} = (2[M]_0k_1K_1k_p/K_2)^{1/2}[BCl_3]^{3/2}t \tag{15}$$

$$\ln\{(1 + C^{1/2})/(1 - C^{1/2})\} = (2[M]_0k_2k_p/K_2)^{1/2}[BCl_3]t \tag{16}$$

where the conversion $C = ([M]_0 - [M])/[M]_0$.

Equations 15 and 16 predict the same conversion vs time plot, but different conversion (at a constant polymerization time) vs $[BCl_3]$ dependences. If self-ionization is operational, according to eq 15 the $\ln\{(1 + C^{1/2})/(1 - C^{1/2})\}$ versus $[BCl_3]^{3/2}$ plot is linear starting at the origin. If the initiation mechanism is haloboration, eq 16 predicts that the $\ln\{(1 + C^{1/2})/(1 - C^{1/2})\}$ versus $[BCl_3]$ plot will be linear starting at the origin. The two plots are shown in Figures 5 (eq 15) and 6 (eq 16). Only the plot in Figure 6 is linear; consequently initiation is by haloboration.

Using eqs 12 and 16, one can calculate k_2 and k_p/K_2. For methylene chloride in the −25 to −60 °C temperature range, $k_2 = 8.1 \times 10^{-6}$ L mol^{-1} s^{-1} and $k_p/K_2 = 9.4 \times 10^{-2}$ s^{-1}. The

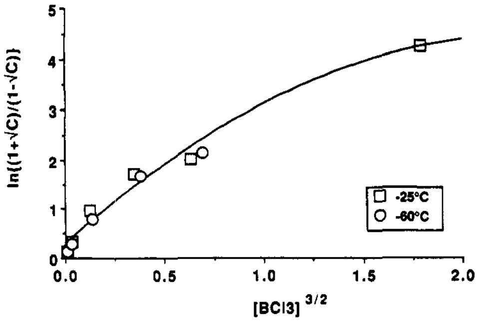

Figure 5. Polymerization of IB using CH_2Cl_2. $[IB]_0 = 0.93$ M, [4-MeDTBP] = 4.0×10^{-3} M, polymerization time = 40 min.

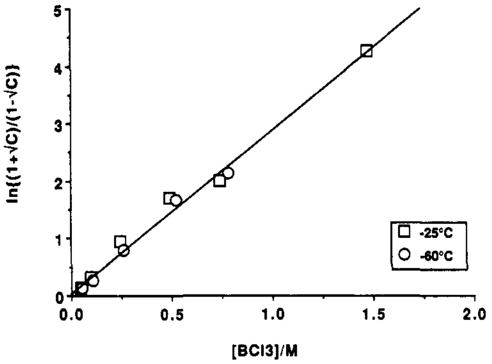

Figure 6. Polymerization of IB using CH_2Cl_2. $[IB]_0 = 0.93$ M, [4-MeDTBP] = 4.0×10^{-3} M, polymerization time = 40 min.

negligible temperature dependence in the −25 to −60 °C temperature range indicates that the activation energies of propagation and haloboration as well as the reaction heat of the ion pair formation is small. Data are unavailable for CH_3Cl to use eq 16; however, the k_p/K_2 value can be calculated using the first-order plots obtained with the 2,4,4-trimethylpentyl chloride (TMPCl)/BCl_3/IB/CH_3Cl/ −40 °C system.[8] Since $-d[M]/dt = k_p[P^+][M]$,

$$\{\ln([M]_0/[M])\}/t = k_p[P^+] \qquad (17)$$

Using the termination–reinitiation equilibrium to express $[P^+]$ one can write eq 17 as follows:

$$\{\ln([M]_0/[M])\}/t = k_p[PCl][BCl_3]/K_2 \qquad (18)$$

From eq 18 ([PCl] = [TMPCl]) $k_p/K_2 = 8.8 \times 10^{-3}$ s^{-1} was obtained. Evidently the concentrationn of active centers and/or k_p is much lower in CH_3Cl. Interestingly, k_2, the rate constant of haloboration calculated from eq 12 with $k_p/K_2 = 8.8 \times 10^{-3}$ s^{-1}, is also lower in CH_3Cl ($k_2 = 8.7 \times 10^{-7}$ L mol^{-1} s^{-1}), and therefore the molecular weights of PIBs obtained by haloboration–initiation using CH_3Cl or CH_2Cl_2 are similar.

Conclusion

Two polymerization mechanisms were presented to account for direct initiation of IB by BCl_3, (a) self-ionization and (b) haloboration. Kinetic equations obtained using the two polymerization schemes predicted different molecular weight–$[BCl]_3$ and conversion–$[BCl_3]$ dependencies. Results obtained using CH_3Cl or CH_2Cl_2 at −25 and −60 °C confirmed that the mechanism is according to the Sigwalt–Olah theory, i.e., haloboration–initiation.

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