Initiation via Haloboration in Living Cationic Polymerization. 1. The Polymerization of Isobutylene

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ABSTRACT: We have discovered that, using polar solvents in the presence of a proton trap, BCl_3 alone can initiate the polymerization of isobutylene. The polymerization rate increased in the order methyl chloride, methylene chloride, 1,2-dichloroethane. Increasing the BCl_3 concentration increases the rate; however the molecular weights are similar at similar conversions. Change in temperature in the studied range −25 to −60 °C had no effect on the polymerization rate or on the molecular weights. The products are low molecular weight asymmetric telechelic polymers carrying a BCl_2^- head group and a tertiary chloro end group. A new initiation mechanism via haloboration is proposed to explain the apparent livingness of the polymerization and the structure of the polymers.

Introduction

Although cationic polymerization may be induced by a variety of chemical as well as physical methods, the most important initiating system from a scientific as well as a practical point of view is the cationogen/Friedel–Crafts acid system. The need for a cationogen to bring about cationic polymerization was clarified by the discovery of cocatalysis, i.e., that most Friedel–Crafts acids, particularly some halides of boron, titanium, and tin, require an additional cation source to initiate polymerization. Several authors claimed however that cationic polymerization and particularly that of isobutylene (IB) can be started by $AlBr_3$ or $AlCl_3$,[1] $TiCl_4$,[2] $AlEtCl_2$,[3] and BCl_3[4] even in the absence of a separate cation source. Depending on the suggested mechanism, the initiation was classified as "self", "direct", "spontaneous", "ion radical", and "nonprotonic". On the basis of conductivity studies of the $TiCl_4/CH_2Cl_2$ system Plesch et al.[5] concluded that there is no ionogenic reaction between $TiCl_4$ and CH_2Cl_2. The observed conductivity was interpreted by self-ionization of $TiCl_4$. A similar mechanism was proposed for the polymerization of IB by $AlCl_3$,[1] i.e., self-ionization of $AlCl_3$ generating $AlCl_2^+$ cations that immediately add to the double bond of the monomer. Marechal et al.[4] have reported the polymerization of IB, that was assumed to proceed by direct initiation, with BCl_3 in CH_2Cl_2 at −30 °C when $[BCl_3] \geq 0.01$ M, and they reported high molecular weights ($\sim 10^5$) and high polymerization rates (60–84% conversions in 30 min) under high vacuum conditions. Moulis[6] et al. and later Gandini and Martinez[7] reported that sterically hindered pyridines may discriminate effectively between initiation by protons and initiation by species formed from $TiCl_4$, BF_3, $SnCl_4$, and $EtAlCl_2$ in the polymerization of IB and α-methylstyrene. From Kennedy's published results on the polymerization of α-methylstyrene in the presence of 2,6-di-*tert*-butylpyridine (DTBP)[8] they concluded that BCl_3 behaves similarly.[7]

It is important to note that although initiation by metal halides has been assumed with the above Lewis acids, "direct initiation was postulated but not proved satisfactory".[9] With $TiCl_4$ attempts have been made to observe the corresponding intermediates by ^1H NMR but without success, which was explained by the known instability of the organotitanium compounds.[10]

Recently, we reported the living polymerization of IB and styrene (St) by the alkyl halide, ether, ester/$TiCl_4$, or BCl_3 initiating systems in the presence of proton trap DTBP in concentrations slightly higher than the concentration of protic impurities in the system.[11-13] We suggested that the polymerizations are living because of the absence of chain transfer and reversible termination and that the purpose of DTBP and that of the externally added electron donors are similar, i.e., to trap protic impurities in the polymerization systems. In the absence of a proton trap proton induced chain transfer prevents living polymerization with $TiCl_4$. With BCl_3 there is a fast polymerization by the protons from impurities, which masks the much slower living polymerization, and most of the monomer is consumed by this process, unless protic impurities are scavenged.

The synthesis of PIB with methacrylate and isobutyrate end groups has recently been accomplished by living polymerizations initiated by novel functional initiators carrying primary methacrylate or primary isobutyrate groups in conjunction with $TiCl_4$ in the presence of DTPB.[14] When BCl_3 is used instead of $TiCl_4$ (to obtain low molecular weight polymers, for which BCl_3 is the preferred Lewis acid), however, the molecular weights and the methacrylate or isobutylate functionalities were much lower than the theoretical results, although the absence of terminal double bonds indicated the absence of chain transfer to the monomer. By the use of proton traps initiation by protons was eliminated. Since this finding pointed toward initiation by a hitherto unknown mechanism, we decided to study polymerizations by BCl_3 in the absence of a separately added initiator and in the presence of DTBP. Unexpectedly, polymers were formed even in the absence of a separately added cation source.

In the present publication we report on the polymerization of IB with BCl_3.

Experimental Section

A. Materials. 1,2-Dichloroethane was washed with water, dried over $MgSO_4$, and stored over KOH. The dried 1,2-dichloroethane was refluxed over P_2O_5 for 24 h and distilled twice from fresh P_2O_5 just before use. All other materials have already been described.[11-13]

Model Compounds. Isobutyldichloroborane was prepared by hydroboration of IB with $BCl_2H{\cdot}SMe_2$ in pentane at room

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Table 1. Polymerization of IB in CH_3Cl[a]

sample no.	reacn time (h)	M_n	M_w/M_n	conversion (%)
1	2.5	900	1.35	2
2	5.0	1500	1.40	8
3	10	2700	1.38	37
4	20	3900	1.35	78

[a] $[BCl_3] = 0.512$ M, [DTBP] = 4.7×10^{-3} M, [IB] = 0.938 M, -35 °C.

Table 2. Polymerization of IB in CH_2Cl_2[a]

sample no.	reacn time (min)	M_n	M_w/M_n	conversion (%)
1	10	810	1.26	2
2	30	2200	1.29	27
3	60	3200	1.30	80
4	120	3500	1.29	95

[a] Temperature: -40 °C. Other reaction conditions as in Table 1.

Table 3. Polymerization of IB in $ClCH_2CH_2Cl$[a]

sample no.	reacn time (min)	M_n	M_w/M_n	conversion (%)
1	10	2300	1.24	42
2	20	2500	1.19	60
3	30	2500	1.18	67
4	40	2500	1.18	79
5	50	2500	1.17	83
6	120	2600	1.16	90

[a] Temperature: -25 °C. Other reaction conditions as in Table 1.

temperature, using a procedure reported for the synthesis of *n*-octyldichloroborane.[15] It was purified by distillation (bp = 94–96 °C). NMR: ^{11}B δ 67.47 ppm; ^{13}C δ 33.10; ^{1}H δ 1.00 (CH_3), 1.51 (CH_2), 2.12 (CH) ppm.

Methanolysis of this compound with excess methanol gave isobutyldimethoxyborane that was recovered following the removal of the solvent (CH_3Cl or CH_2Cl_2[8]), the excess methanol, and the hydrogen chloride generated. NMR: ^{11}B δ 31.34 ppm; ^{13}C δ 33.10 ppm; ^{1}H δ 0.95 (CH_3), 0.74 (CH_2), 1.85 (CH), 3.58 (OCH_3) ppm.

Trimethoxyboron was prepared in methyl chloride at -40 °C from BCl_3 and methanol followed by evaporation of the solvent and HCl under dry nitrogen. NMR: ^{11}B δ 14.50 (neat), 18.44 (reaction mixture) ppm; ^{13}C δ 50.76 ppm; ^{1}H δ 3.39 ppm.

B. Procedures. Polymerizations were carried out in an MBraun 150M stainless steel glovebox already described. Large (75-mL) test tubes were used as polymerization reactors. The total volume of the reaction mixture was 25 mL. The addition sequence of the reactants was the following: (a) solvent, (b) proton trap (DTBP), (c) monomer, (d) Lewis acid. After the last component was added, the reaction mixture was stirred vigorously by a vortex stirrer and placed back into the temperature controlled heptane bath. The polymerizations were terminated by adding prechilled methanol. The polymers were purified by repeated dissolution–precipitation in hexane/methanol and dried in vacuo prior to GPC measurements. Molecular weights were measured using a Waters HPLC system. Absolute molecular weights of representative samples measured using a miniDawn (Wyatt Technologies Inc.) GPC on line multiangle laser light scattering detector were in good agreement with molecular weights determined on the basis of linear PIB calibration. ^{1}H, ^{13}C, and ^{11}B NMR measurements were carried out by a Bruker 270-MHz multinuclear spectroscope equipped with a temperature controller.

Results and Discussion

In the preliminary experiments methyl chloride, methylene chloride, 1,2-dichloroethane, and mixtures of 1,2-dichloroethane and *n*-hexanes were used as the solvent for the polymerization of isobutylene by BCl_3. The results are in Tables 1–4. Low molecular weight polymers with narrow molecular weight distributions were obtained in all solvents. The polymerization rate increased strongly with polarity in the order methyl chloride, methylene chloride, 1,2-dichloroethane. Adding *n*-hexane to 1,2-dichloroethane reduced the rates substantially, and with the 40/60 v/v mixture no polymer formed in 2 h at -25 °C. Further kinetic experiments have been carried out with methyl chloride and methylene chloride. The conversion–time, ln($[M_0]/[M]$)–time and M_n–conversion plots can be seen in Figures 1–6.

Table 4. Polymerization of IB in $ClCH_2CH_2Cl$/*n*-hexane[a]

sample no.	$ClCH_2CH_2Cl$/ hexane (v/v)	M_n	M_w/M_n	conversion (%)
1	90/10	2500	1.16	83
2	80/20	2300	1.25	54
3	40/60			0

[a] Temperature: -25 °C. Polymerization time: 2 h. Other reaction conditions as in Table 1.

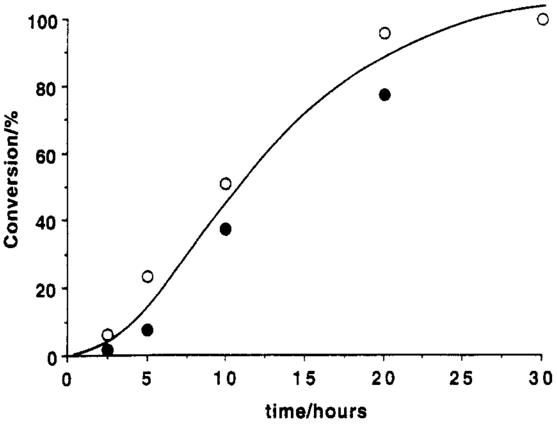


Figure 1. Conversion vs time plot for the polymerization of IB with the BCl_3/MeCl/-35 °C system. The two symbols represent two separate sets of experiments, indicating the degree of reproducibility. Conditions: $[BCl_3] = 0.512$ M, [DTBP] = 4.7×10^{-3} M, [IB] = 0.948 M.

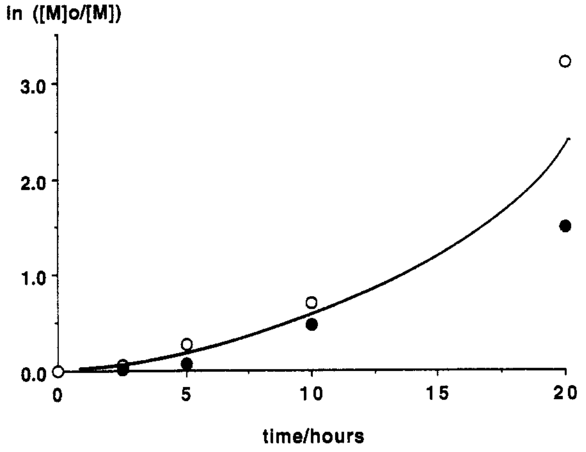


Figure 2. ln($[M_0]/[M]$) vs time plot for the polymerization of IB with the BCl_3/MeCl/-35 °C system. The two symbols represent two separate sets of experiments, indicating the degree of reproducibility. Conditions: $[BCl_3] = 0.512$ M, [DTBP] = 4.7×10^{-3} M, [IB] = 0.948 M.

Much higher rates were obtained with methylene chloride, but generally the conversion–time (Figures 1 and 4), ln($[M_0]/[M]$)–time (Figures 2 and 5), and M_n–conversion plots (Figures 3 and 6) are similar. According to Figures 2 and 5, $k_p[M_n^+]$ (the first derivatives of the ln($[M_0]/[M]$)–time curve) increases with time, which suggests that the cation concentration is increasing. The curved M_n–conversion plots (Figures 3, 6) indicate that the mole concentration of PIB also increases with conversion.

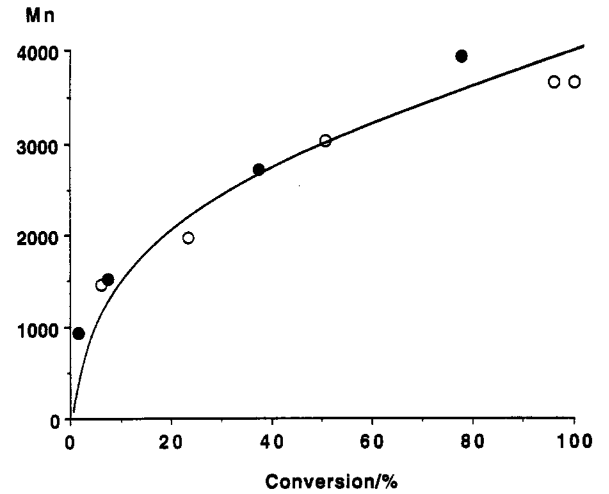


Figure 3. M_n-conversion plot for the polymerization of IB with the BCl_3/MeCl/−35 °C system. The two symbols represent two separate sets of experiments, indicating the degree of reproducibility. Conditions: $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.948$ M.

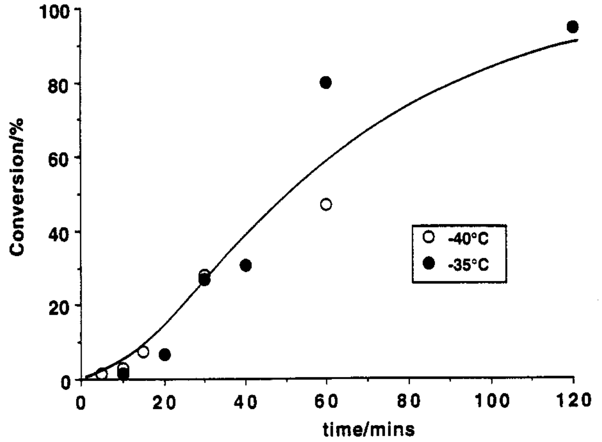


Figure 4. Conversion vs time plot for the polymerization of IB with the BCl_3/CH_2Cl_2/−40 and −35 °C system. Conditions: $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.938$ M.

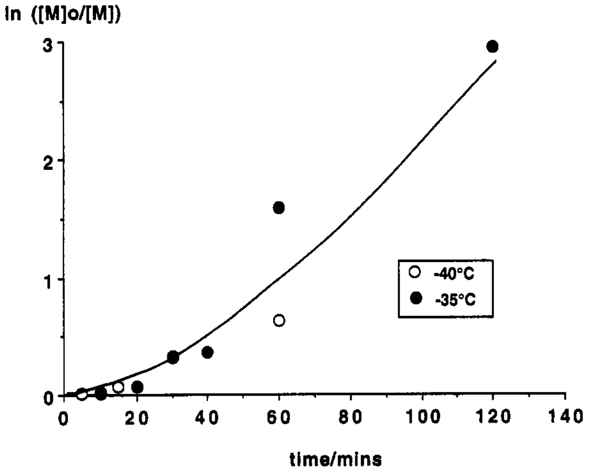


Figure 5. $\ln([M_0]/[M_t])$ vs time plot for the polymerization of IB with the BCl_3/CH_2Cl_2/−40 and −35 °C system. Conditions: $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.938$ M.

Interestingly, a change in temperature in the −25 to −60 °C range had no effect on the polymerization rate or on the molecular weights (Figures 7 and 8).

In agreement with former results[11,12] demonstrating that the only role of the DTBP is to trap protic impurities, increasing the DTBP concentration does not affect the yields or the molecular weights (Table 5).

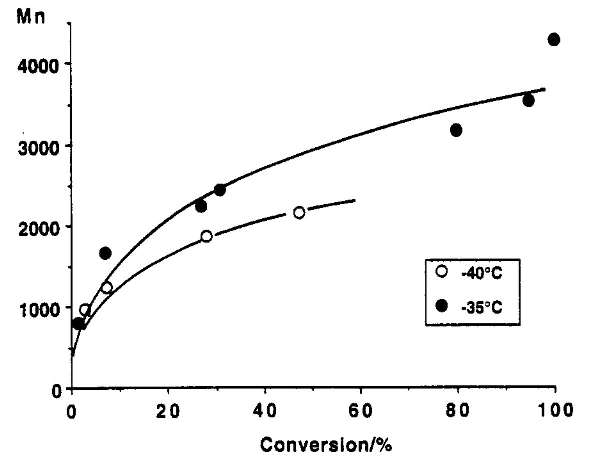


Figure 6. M_n vs conversion plot for the polymerization of IB with the BCl_3/CH_2Cl_2/−40 and −35 °C system. Conditions: $[BCl_3] = 0.512$ M, $[DTBP] = 4.7 \times 10^{-3}$ M, $[IB] = 0.938$ M.

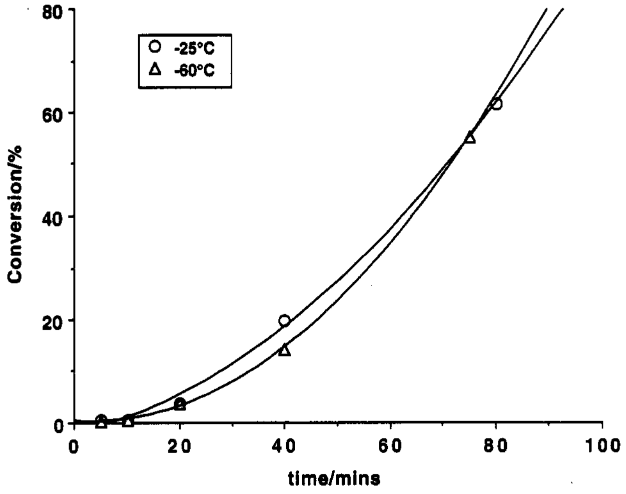


Figure 7. Conversion vs time plot for the polymerization of IB with the BCl_3/methylene chloride/−25 and −60 °C system. Conditions: $[BCl_3] = 0.25$ M, $[4\text{-MeDTBP}] = 4.0 \times 10^{-3}$ M, $[IB] = 0.938$ M.

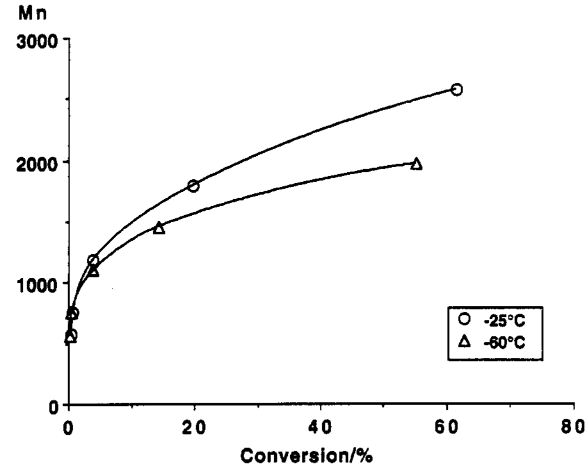


Figure 8. M_n-conversion plot for the polymerization of IB in methylene chloride at −25 and −60 °C. Conditions: $[BCl_3] = 0.25$ M, $[4\text{-MeDTBP}] = 4.0 \times 10^{-3}$ M, $[IB] = 0.93$ M.

The effect of the BCl_3 concentration is shown in Figures 9–11. Increasing $[BCl_3]$ increases the rate of polymerization, but the molecular weights are similar at simmilar conversions. It is important to point out that the extremely high BCl_3 concentrations are not necessary for the polymerization to occur, but at lower $[BCl_3]$ the polymerization time to reach high monomer conversions will be higher.

Table 5. Polymerization of IB at Different DTBP Concentrations[a]

sample no.	[DTBP] (M)	M_n	M_w/M_n	conversion (%)
1	4.7×10^{-3}	2300	1.29	56
2	1×10^{-2}	2600	1.32	53
3	5×10^{-2}	2700	1.33	51

[a] Solvent: CH_2Cl_2. Temperature: -40 °C. Time: 45 min.

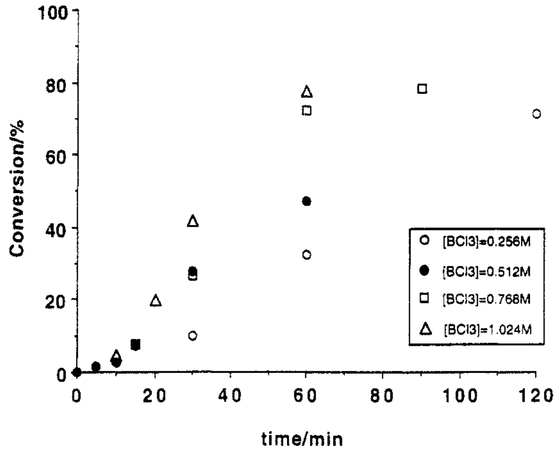


Figure 9. Conversion vs time plot for the polymerization of IB with the BCl_3/CH_2Cl_2/-40 °C system.

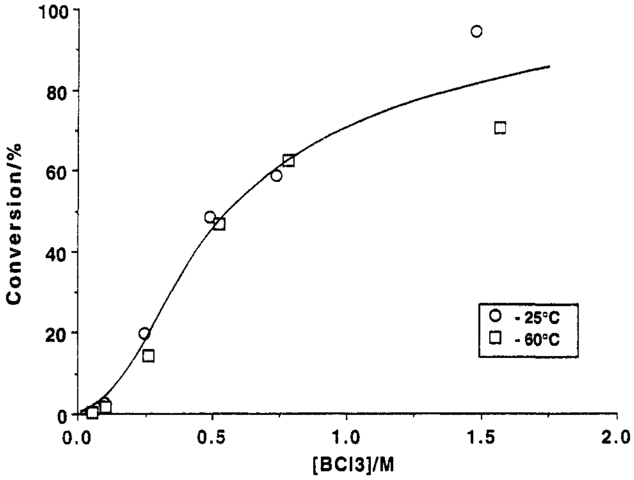


Figure 10. Effect of BCl_3 concentration on the rate of IB polymerization using methylene chloride at -25 and -60 °C. Conditions: $[BCl_3] = 4.9 \times 10^{-2}$ to 1.47 M and 5.2×10^{-2} to 1.56 M, $[4\text{-MeDTBP}] = 4.0 \times 10^{-3}$ M, [IB] = 0.93 M. Polymerization time: 40 min.

Representative PIB samples were characterized by ^1H (Figure 12), ^{13}C, and ^{11}B NMR (Figure 13). The ^{13}C spectra were unrevealing. According to the ^1H NMR spectrum the polymer is (PIB)Cl with 100% tertiary chloro end functionality. Terminal unsaturation is absent, which indicates the absence of chain transfer. The ^1H NMR spectrum of the polymer quenched with MeOH reveals a peak at about 3.5 ppm that can be attributed to the $-B(OCH_3)_2$ head group (Figure 12), because that peak was absent when the polymerization was quenched with CD_3OD. The ^{11}B NMR spectrum of the polymer quenched with MeOH shows a broad peak at ~32 ppm (BF_3 etherate as internal reference) which can be assigned to a boron atom with two neighboring oxygen atoms. It can be easily distinguished from the trimethoxyboron signal at 18 ppm (Figure 13), which shows that it is not due to traces of trimethoxyboron formed in the quenching with MeOH. This assignment was confirmed by the ^{11}B NMR spectrum of the model compound isobutyldimethoxyboron obtained by the methanolysis of isobutylboron dichloride that was synthesized according to ref 15. When isobutyldimethoxyboron was added to this polymer solution, the peak due to the dimethoxyboron compound appears on top of this broad peak. The results of elemental analysis (Table 6) also corroborate our suggested structure:

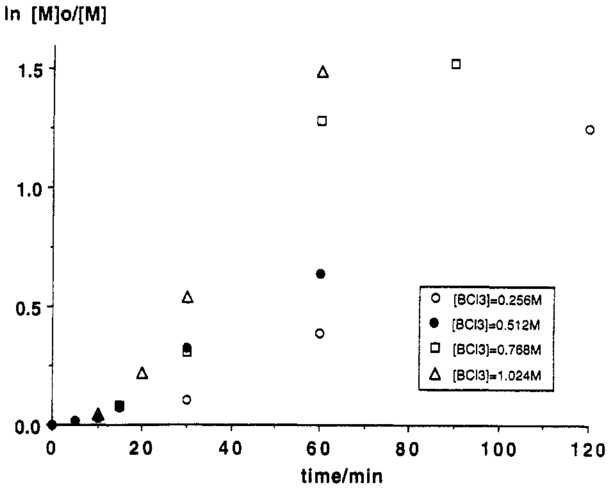


Figure 11. $\ln([M]_0/[M])$-time plot for the polymerization of IB with the BCl_3/CH_2Cl_2/-40 °C system.

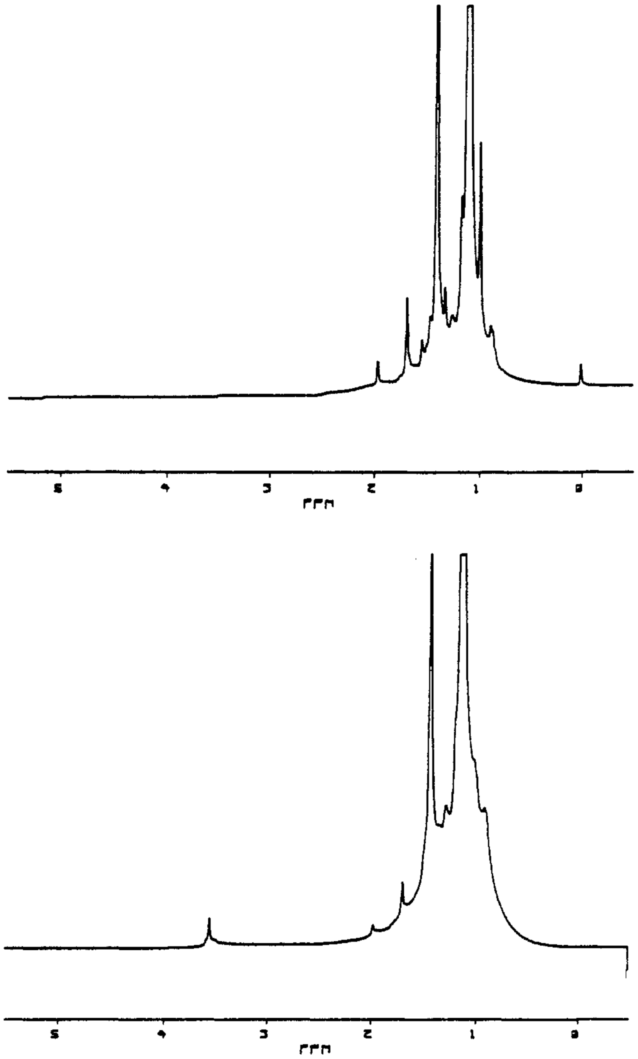


Figure 12. ^1H NMR spectrum of $(CH_3O)_2B-CH_2C(CH_3)_2-PIB-CH_2C(CH_3)_2Cl$ formed by direct initiation (B) in comparison with (PIB)Cl (A).

$$(CH_3O)_2B-CH_2-C(CH_3)_2-[CH_2-C(CH_3)_2]_n-CH_2-C(CH_3)_2-Cl$$

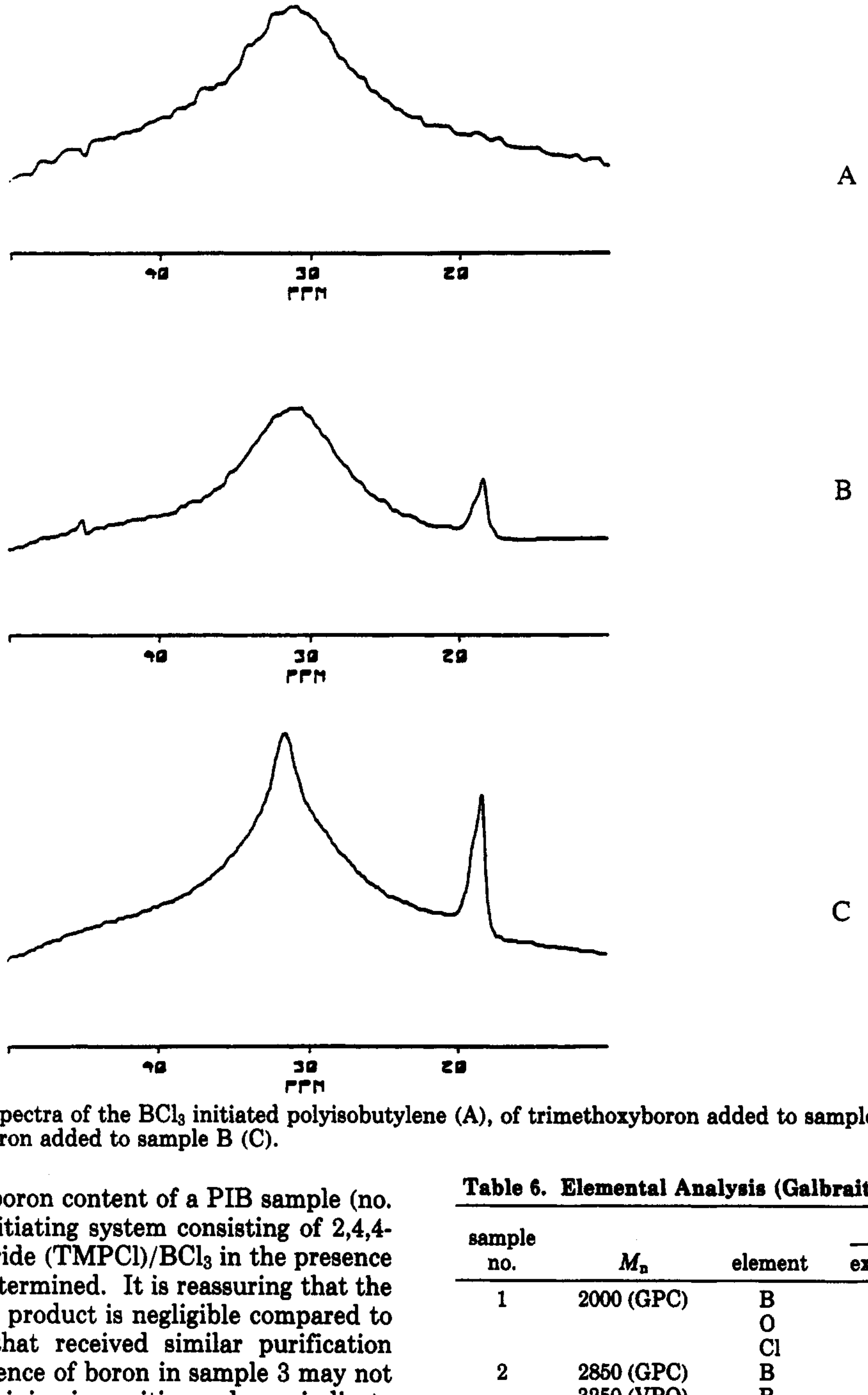


Figure 13. ^{11}B NMR spectra of the BCl_3 initiated polyisobutylene (A), of trimethoxyboron added to sample A (B), and of 2.5 μL of isobutyldimethoxyboron added to sample B (C).

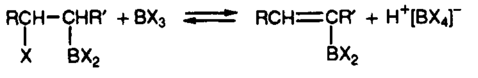
For comparison the boron content of a PIB sample (no. 3) obtained by an initiating system consisting of 2,4,4-trimethylpentyl chloride (TMPCl)/BCl_3 in the presence of DTBP was also determined. It is reassuring that the boron content of this product is negligible compared to the other samples that received similar purification treatment. The presence of boron in sample 3 may not be due to boron containing impurities and may indicate that some polymer was formed by direct initiation which competes with initiation from (TMP)Cl. It will be recalled that with initiators carrying primary methacrylate, or primary isobutyrate, groups the ester functionality (~0.6) was much lower than the theoretical value of 1.0. Evidently, the initiation with these initiators is very slow and direct initiation started about 40% of polymer molecules.

Polymerization Mechanism. The results of the preliminary experiments could be explained by self-ionization of BCl_3 (Scheme 1a) or by haloboration followed by BCl_3 coinitiation (Scheme 1b). Both processes would lead to PIB^+ carbenium ions and BCl_4^- anions. IB polymerizations involving these species have been shown[12] to be living, albeit slow by cationic standards. With the present system however new polymer chains would be started continuously during the polymerization until the monomer is depleted. This continuous initiation could explain the increasing cation and polymer concentration and could account for the M_w/M_n of 1.2–1.4.

Table 6. Elemental Analysis (Galbraith Laboratories Inc.)

sample no.	M_n	element	content of element exptl (%)	theor (%)
1	2000 (GPC)	B	0.52	0.55
		O	1.41	1.60
		Cl	1.38	1.77
2	2850 (GPC)	B	0.38	0.34
	3250 (VPO)	B	0.38	0.39
2	2850 (GPC)	Cl	0.99	1.08
	3250 (VPO)	Cl	0.99	1.26
3	1800 (GPC)	B	0.039	0

The haloboration of olefins (4) is well documented and has been reviewed by Lappert.[16] For example, norbornadiene was almost quantitatively converted to the nortricyclene derivative by BCl_3.[17] 1-Olefins have also been transformed by boron trihalides to the corresponding (2-haloalkyl)boron derivatives.[17-19] To account for residues assumed to be halogenated hydrocarbons, the following reaction through a carbenium ion intermediate has been postulated:[17]



$$\underset{X}{RCH}-\underset{BX_2}{CHR'} + BX_3 \rightleftharpoons RCH{=}\underset{BX_2}{CR'} + H^+[BX_4]^-$$

Since route b is based on well-established chemistry, but there is no evidence for equilibrium 1, route b is more likely at present. Kinetic and mechanistic investigations[20]

Scheme 1

Initiation

$$\text{(a)}\qquad 2\mathrm{BCl_3} \overset{K_1}{\rightleftarrows} \mathrm{BCl_2{}^{+}BCl_4{}^{-}} \qquad (1)$$

$$\mathrm{BCl_2{}^{+}BCl_4{}^{-} + CH_2{=}C(CH_3)_2} \xrightarrow{k_1} \mathrm{BCl_2{-}CH_2{-}{}^{+}C(CH_3)_2BCl_4{}^{-}} \qquad (2)$$

$$\mathrm{BCl_2{-}[CH_2{-}C(CH_3)_2]^{+}BCl_4{}^{-}} \rightleftarrows \mathrm{BCl_3 + BCl_2{-}CH_2{-}C(CH_3)_2{-}Cl} \qquad (3a)$$

$$\text{or (b)}\qquad \mathrm{BCl_3 + CH_2{=}C(CH_3)_2} \xrightarrow{k_2} \mathrm{BCl_2{-}CH_2{-}C(CH_3)_2{-}Cl} \qquad (4)$$

$$\mathrm{BCl_3 + BCl_2{-}CH_2{-}C(CH_3)_2{-}Cl} \rightleftarrows \mathrm{BCl_2{-}[CH_2{-}C(CH_2)_2]^{+}BCl_4{}^{-}} \qquad (3b)$$

Propagation

$$\mathrm{BCl_2{-}CH_2{-}C^{+}(CH_3)_2BCl_4{}^{-} + M} \xrightarrow{k_p} \mathrm{BCl_2{-}[CH_2{-}C(CH_3)_2]_{\mathit{n}}{}^{+}BCl_4{}^{-}} \qquad (5)$$

Termination and Reinitiation

$$\mathrm{BCl_2{-}[CH_2{-}C(CH_3)_2]_4n^{+}BCl_4{}^{-}} \overset{K_2}{\rightleftarrows} \mathrm{BCl_3 + BCl_2{-}[CH_2{-}C(CH_3)_2]_{\mathit{n}}{-}Cl} \qquad (3c)$$

carried out to clarify which mechanism is operational also favor mechanism b.

Synthetic Prospects. The polyisobutenyl dimethoxyboron is formed from the dichloroboron derivative by quenching with methanol. Alkyldichloroboranes can be methanolyzed easily and yield the methyl esters of the corresponding alkylboronic acids.[15] They are also easily hydrolyzable by cold water to the corresponding boronic acid [$(HO)_2B$–].[15] Chemistry is also available, pioneered by Brown,[21] to convert the Cl_2B–, $(HO)_2B$–, or $(CH_3O)_2B$– head groups to a variety of functional groups, most notably to a primary hydroxyl group upon oxidation. In most of these reactions the yields are close to 100%. The results of research directed toward these functionalization reactions leading to novel asymmetric telechelic PIBs will be published shortly.

Conclusion

Some distinguished scientists in the field of ionic polymerizations recently concluded on direct initiation: "Notwithstanding their academic interest, it has to be admitted that such an initiation plays only a minor role in cationic polymerizations, provided that it does occur, and even then it offers little advantage from the synthetic point of view"[9] and "it will certainly not progress to the industrial-technological arena in the foreseeable future".[22] It is apparent from the results presented in this paper not only that direct initiation does occur but also that it plays a major role in cationic polymerization, especially with the recently discovered living systems in which propagation is much slower compared to conventional systems. Direct initiation therefore may compete with controlled initiation, and the careful selection of experimental conditions is necessary to minimize its effect.

In the absence of initiator on the other hand, direct initiation, by BCl_3, leads to valuable asymmetric telechelic polymers that are difficult to obtain otherwise, and as such offers a distinct synthetic advantage that may lead to new polymeric materials and processes.[23]

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