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Initiation via Haloboration in Living Cationic Polymerization. 4. The Polymerization of α-Methylstyrene

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ABSTRACT: The polymerization of α-methylstyrene was studied in the absence of a separately added cationogen (i.e., initiator) and in the presence of a proton trap, using boron halides (BX_3, X = Cl, Br, and I). The effect of the monomer and BX_3 concentration, solvent polarity, and temperature was examined. The polymerization rates increased with decreasing temperature and with increasing solvent polarity. The molecular weight (M_n) of the products also increased with decreasing temperature; however it was relatively independent of solvent polarity. Under identical conditions the M_n's were highest with BCl_3, lower with BBr_3, and lowest with BI_3. Kinetic experiments support that initiation is by haloboration, but direct proof was only obtained for BI_3. For polymers made with BI_3 the presence of one boron per chain was confirmed by elemental analysis, while the high M_n's obtained with BCl_3 and BBr_3 prevented quantitative analysis of head and end groups.

Introduction

Recently we reported that boron halides (BX_3) alone can initiate the living polymerization of isobutylene (IB)[1] and styrene (St)[2] in polar solvents in the presence of a proton trap (2,6-di-*tert*-butylpyridine; DTBP) to prevent initiation by protic impurities. On the basis of kinetic and mechanistic studies with IB, the initiation mechanism was found to be haloboration (Scheme 1b).[3] The results of these studies did not support direct initiation by self-ionization of BX_3 (Scheme 1a).

The products are low molecular weight asymmetric telechelic polymers, carrying X_2B- head groups and halo end groups. The head groups were quantitatively converted to other functionalities, most notably to primary alcohols upon oxidation by alkaline hydrogen peroxide in tetrahydrofuran at room temperature.[2]

Contrary to some past views,[4,5] it is now apparent that direct initiation can play a major role in cationic polymerization, especially with the recently discovered living systems where propagation is much slower than in conventional systems.[6] Direct initiation therefore may compete with controlled initiation, and the careful selection of experimental conditions is necessary to minimize its effect, to obtain the desired well-defined polymers. On the other hand, in the absence of any other ionogen direct initiation yields valuable asymmetric telechelic polymers that are difficult to obtain by other methods.

On the basis of results obtained with IB and St, it is likely that haloboration initiation also takes place with other monomers such as α-methylstyrene (α-MeSt). The effect of DTBP on the polymerization of α-MeSt using BCl_3 has already been investigated.[7] In a series of publications Kennedy et al. reported much lower yields, much higher molecular weights, and narrower molecular weight distributions (MWDs) than those obtained in the absence of DTBP. Similar to our observations with IB and St, yields, molecular weights, and MWDs were independent of DTBP concentrations at [DTBP] > 0.001 M. These findings however were explained by proposing that DTBP scavenges the protons emerging during counteranion-assisted chain transfer to a monomer, but that other elementary events remain unaffected by the presence of DTBP. Thus it was concluded that adventitious H_2O is the initiating cationogen. To avoid an apparent conflict that DTBP is able to trap the protons arising in counteranion-assisted chain transfer but not during initiation, it was proposed that initiation proceeds by a concerted route in the absence of protons. This view was questioned by Moulis et al.,[8] and later by Gandini and Martinez.[9] It was suggested that the polymerization of α-MeSt using BCl_3 in the presence of DTBP is due to direct initiation; however evidence was not given.

Scheme 1. Direct Initiation by Self-ionization (a) and by Haloboration (b) When the Active Species Are Ion Pairs

Initiation

a) $$2BX_3 \overset{K_1}{\rightleftarrows} BX_2^+BX_4^-$$

$$BX_2^+\ BX_4^- + CH_2{=}C(R_1)R_2 \xrightarrow{k_1^{\pm}} BX_2\text{-}CH_2\text{-}C^+(R_1)R_2\ \ BX_4^-$$

or b) $$BX_3 + CH_2{=}C(R_1)R_2 \xrightarrow{k_2} BX_2\text{-}CH_2\text{-}C(R_1)(R_2)\text{-}X$$

$$BX_3 + BX_2\text{-}CH_2\text{-}C(R_1)(R_2)\text{-}X \rightleftarrows BX_2\text{-}CH_2\text{-}C^+(R_1)R_2\ \ BX_4^-$$

Propagation

$$BX_2\text{-}CH_2\text{-}C^+(R_1)R_2\ \ BX_4^- + (n\text{-}1)M \xrightarrow{k_p^{\pm}} BX_2\text{-}[CH_2\text{-}C(R_1)R_2]_n^+\ BX_4^-$$

Termination-reinitiation

$$BX_2\text{-}[CH_2\text{-}C(R_1)R_2]_n^+\ BX_4^- \overset{K_2}{\rightleftarrows} BX_3 + BX_2\text{-}[CH_2\text{-}C(R_1)(R_2)]_n\text{-}X$$

In light of the recently discovered haloboration initiation, we reexamined the polymerization of α-MeSt in the presence of DTBP using different boron halides and in the present report attempt to identify the polymerization mechanism.

Experimental Section

Materials. α-MeSt was purified by washing it with 10% aqueous sodium hydroxide solution, followed by distilled water until it became neutral, and then dried over M_gSO_4. Traces of water remaining after treatment with M_gSO_4 were removed by treatment with dibutylmagnesium (1.0 M solution in

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heptane, Aldrich). This was followed by vacuum distillation in which the first fraction containing the heptane solvent was discarded. Methyl chloride (MeCl, Air Products) was dried by passing the gas through in-line gas purifier columns packed with BaO/Drierite and condensed in the cold bath of the glovebox prior to polymerization. Hexane (Hex) was refluxed for 2 days with concentrated sulfuric acid, washed with distilled water until it became neutral, dried over $M_{g}SO_4$, refluxed for 24 h over CaH_2, and distilled under nitrogen atmosphere.

Boron trichloride (BCl_3, 99.9%, Aldrich), boron tribromide (BBr_3, 99.9%, Aldrich), boron triiodide (BI_3, 99.8+%, Aldrich), and the proton trap 2,6-di-*tert*-butylpyridine (DTBP, 99.1% by GC, Aldrich) were used as received.

Procedures. Polymerizations were carried out in an MBraun 150M stainless steel glovebox (Innovative Technology Inc.) equipped with a gas purification system (15 lb molecular sieves and 11 lb copper catalyst) which provides a dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm). The moisture content of the gas phase in the glovebox was monitored by an MBraun moisture analyzer. Large (75 mL) test tubes were used as polymerization reactors. The reagents were added in the following sequence: (1) solvents, (2) proton trap (DTBP), (3) BX_3, and (4) α-MeSt. Following the addition of α-MeSt the solutions were vigorouosly stirred by a Vortex stirrer and placed back to the constant temperature bath. After predetermined times, the polymerizations were quenched by the addition of prechilled methanol.

The polymers were purified by repeated precipitation in methanol and dried under vacuum. The polymer obtained with BI_3 was slightly colored possibly due to the presence of free I_2. This was removed by dissolving the polymer in distilled methylene chloride and washing with 1 wt % sodium thiosulfate solution containing NH_3, followed by washing with distilled water and being precipitated in methanol.

The molecular weights and polydispersities (M_w/M_n's) were determined by gel permeation chromatography (GPC) using a Waters HPLC system equipped with a Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line multiangle laser light-scattering (MALLS) detector (miniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. Tetrahydrofuran was used as an eluent at a rate of 1.0 mL/min.

^1H NMR spectroscopy was carried out on a Bruker's 250 MHz instrument.

Results and Discussion

We postulated that in the presence of DTBP and in the absence of a separately added cation source α-MeSt also undergoes haloboration initiation and theorized that previously reported results of Kennedy et al. are a manifestation of haloboration initiation. To test our hypothesis, polymerizations were carried out in the presence of DTBP and the results were compared to findings with IB and St such as *S*-shaped conversion−time curves, indicating increasing cation concentration, evolution of the molecular weight, and narrow MWDs when termination and chain transfer are absent. To corroborate that the polymerization is by haloboration initiation we were also seeking direct proof, by qualitative and quantitative identification of the head and end groups of the polymer. Contrary to the findings with IB and St, the living polymerization of α-MeSt by boron halides as co-initiators has not yet been demonstrated. The living polymerization of α-MeSt initiated by the cumyl chloride/BCl_3 initiating system in a CH_2Cl_2:toluene 1:7 v:v solvent mixture at −78 °C in the presence of *n*-Bu_4NCl was claimed by Matyjaszewski et al.[10] However, diagnostic plots were not shown to prove the absence of chain transfer and termination. In the absence of *n*-Bu_4NCl, lower than theoretical M_n and broad MWD ($M_w/M_n = 3.4$) were obtained. Termination is reportedly absent using the BCl_3/CH_2Cl_2:methylcyclohexane 25:75 v:v/ 50 °C polymerization system, but chain transfer to monomer is operational.[11] Under the reported conditions (i.e., low temperature and low solvent polarity) indanyl ring formation is suppressed, and chain transfer results in the exclusive formation of olefinic terminus. Then the addition of BX_3 may also occur on the terminal olefin end. A similar phenomenon that AlX_3 quantitatively adds to the terminal double bond of PIB has been reported.[12] Thus the presence of boron in the polymer would not be sufficient proof that the polymerization took place by haloboration initiation. Therefore additional identification and quantification of the end groups would be required. We recently discovered, however, that chain transfer to a monomer is absent in a mixed polar (MeCl or CH_2Cl_2)/nonpolar (Hex or methylcyclohexane) solvent system at −80 °C;[13] accordingly the polymerization is living at this temperature, and thus, this system is well suited for studying direct initiation. The polymerization is also living at −60 °C and the concentration of growing cationic centers remains constant during polymerization. Under a monomer-starved condition (i.e., after the completion of the polymerization) however the lifetime of the cationic centers was found to be limited at −60 °C.[13]

Table 1. Polymerization of α-MeSt Initiated by BCl_3 ($[\alpha\text{-MeSt}]_0 = 0.62$ M, [DTBP] = 0.003 M)

$[BCl_3]$ (M)	temp (°C)	solvent	reaction time	conversion (%)	M_n ($\times10^{-3}$)	M_w/M_n
0.512	−40	CH_2Cl_2	3 h	100	54	2.6
0.512	−40	CH_2Cl_2/Hex, 40:60 v/v	6 h	91	64	2.4
0.01	−40	CH_2Cl_2	0.5 h	14	43	1.9
			1.0 h	19	45	2.0
			2.0 h	26	49	1.8
			4.0 h	39	50	1.7
			6.0 h	48	44	1.9
			27 h	75	41	1.8
0.01	−60	CH_2Cl_2	0.5 h	49	219	2.6
0.01	−80	CH_2Cl_2	0.5 h	100	811	1.4
0.01	−80	MeCl/Hex, 40:60 v/v	5 min	9.1	193	1.3
			15 min	11	294	1.7
			30 min	15	414	1.7
			60 min	24	464	1.9

Results of polymerizations by BCl_3 with different solvent composition and temperature are summarized in Table 1.

The polymerization of α-MeSt was much faster than that of IB or St, and contrary to the polymerization of IB, also proceeded, although more slowly, in nonpolar solvent mixtures. The M_n's and M_w/M_n's were independent of solvent composition. Moderate rates are obtained even at a low 0.01 M BCl_3 concentration. The polymerization rates and molecular weights increase sharply with the decrease of temperature, as is commonly found in cationic polymerizations. The negative apparent activation energies reported in cationic polymerization for monomers such as IB, St, α-MeSt, and indene were recently compiled by Sigwalt.[14] The generally accepted view is, that higher ionization of the chain ends at lower temperature may explain the negative apparent activation energy. The M_w/M_n's are close to the most probable distribution at −40 and −60 °C, but decrease to 1.4 at −80 °C. Kinetic results at −40 °C (Table 1) indicate that termination, most probably by terminative chain transfer (i.e., proton elimination followed by trapping with DTBP), is operational, since the first-order plot (not shown) is curved downward,

Table 2. Polymerization of α-MeSt initiated by BBr_3 ($[\alpha\text{-MeSt}]_0 = 0.62$ M, [DTBP] = 0.003 M)

$[BBr_3]$ (M)	temp (°C)	solvent	reaction time	conversion (%)	M_n ($\times 10^{-3}$)	M_w/M_n
0.01	−40	CH_2Cl_2	1 h	100	12.0	2.3
0.005	−40	CH_2Cl_2				
			10 min	64	23.8	2.0
			30 min	67	23.9	1.9
			2 h	63	22.8	1.8
0.005	−40	MeCl				
			10 min	59	39.3	1.7
			30 min	71	37.6	1.8
			1 h	73	43.1	1.6
0.01	−80	CH_2Cl_2	5 min	100	186	2.1

Table 3. Polymerization of α-MeSt Initiated by BI_3 ($[\alpha\text{-MeSt}]_0 = 0.35$ M, $[BI_3]_0 = 0.005$ M, [DTBP] = 0.003 M)

temp (°C)	solvent	time (min)	conversion (%)	M_n ($\times 10^{-3}$)	M_w/M_n
−40	MeCl	4	19	6.9	1.3
−60	MeCl	4	53	15.4	1.2
−80	MeCl	4	100	24.8	1.1
−80	MeCl/Hex, 80/20 v/v	3	95	24.6	1.1
−80	MeCl/Hex, 60/40 v/v	3	87	25.2	1.2
−80	MeCl/Hex, 40/60 v/v	4	50	25.4	1.1

indicating that the active end concentration decreases during the polymerization. At −80 °C this may be absent, but at all three temperatures the polymers had molecular weights that are too high for accurate head and end group analysis.

By a kinetic treatment of Scheme 1 for IB, eq 1 was obtained for the number average degree of polymerization, DP_n:

$$DP_n = \{k_p^{\pm}[M]_0 C/(2k_2K_2)\}^{1/2} \qquad (1)$$

where C is conversion.[3] Compared to BCl_3 lower molecular weight PIBs were obtained with BBr_3, suggesting that k_2 and/or K_2 is higher with BBr_3 (BBr_3 is a stronger Lewis acid than BCl_3,[15,16] and BBr_4^- is probably much less stable than BCl_4^-, since K_2 is higher with BBr_4^-). Thus, in order to obtain lower molecular weight Pα-MeSt to verify the presence of boron-containing head groups, we decided to use BBr_3 and BI_3 instead of BCl_3. Results with BBr_3 are tabulated in Table 2.

In agreement with theoretical considerations lower M_n's were obtained. Interestingly, in contrast with the polymerization of IB and St, the polymerization of α-MeSt is much faster with BBr_3 than with BCl_3. Similar to the results with BCl_3, termination (most probably by terminative chain transfer) is operational at −40 °C. As a result, the polymerization stops short of completion after 10 min in a CH_2Cl_2 solvent. Thus, assuming that initiation is by haloboration, all available BBr_3 is consumed and further initiation is absent. The concentration of polymer chains at this point is $\sim 2 \times 10^{-3}$ M; apparently the remaining BBr_3 is consumed in a reaction with impurities, such as H_2O ($\sim 1-2 \times 10^{-3}$ M, see also Figure 6). Termination may be absent at −80 °C, but the M_n is still too high for head and end group analysis that may prove that initiation occurs by haloboration.

Results obtained with BI_3 at different temperatures (−40 to −80°C) and solvent polarities (MeCl/Hex, 100/0 to 40/60 v/v) are listed in Table 3. Results obtained using CH_2Cl_2 are not listed in Table 3, because in CH_2Cl_2 the polymerizations were so fast that complete conversions were reached in less than 1 min. At −40 °C the polymers had multimodal MWDs with large amounts of low molecular weight oligomers. At −80 °C the MWDs were monomodal ($M_n \sim 7-9000$, $M_w/M_n \sim 2.3$); nevertheless the presence of a long low molecular weight tail suggested chain transfer and/or termination (though complete conversions were still reached).

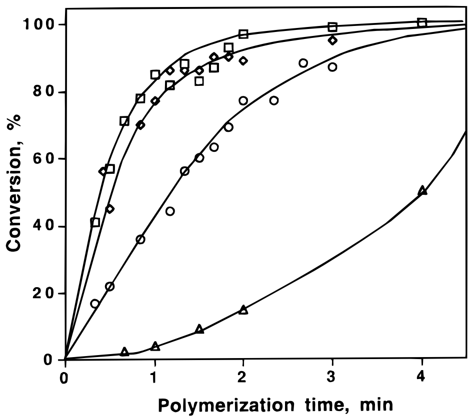

Figure 1. Conversion vs time plots for polymerizations carried out at −80° C in different solvent polarity. $[\alpha MeSt]_0 = 0.35$M, $[BI_3]_0 = 0.005$M, [DTBP] = 0.003 M. □, MeCl; ◇, MeCl/Hex, 80:20 v/v; ○, MeCl/Hex, 60:40 v/v; △, MeCl/Hex, 40:60 v/v.

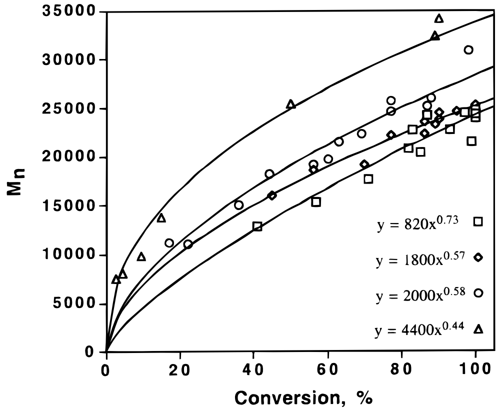

Figure 2. Molecular weight vs conversion plots obtained at −80° C in different solvent polarity. $[\alpha MeSt]_0 = 0.35$ M, $[BI_3]_0 = 0.005$ M, [DTBP] = 0.003 M. □, MeCl; ◇ MeCl/Hex, 80:20 v/v, ○, MeCl/Hex, 60:40 v/v; △, MeCl/Hex, 40:60 v/v.

According to the results in Table 3, the polymerization rate increases with the increase of solvent polarity and with the decrease of temperature. The M_n's however are similar, generally in the range of $M_n \approx 25000-30000$ g/mol, at close to complete monomer conversions and thus suitable for head and end group analysis. Importantly, the MWDs are very narrow ($M_w/M_n \sim 1.1$), suggesting the absence of termination and chain transfer. Encouraged by these results, further kinetic measurements were carried out with BI_3.

The conversion−time plots for experiments conducted at −80 °C in MeCl/Hex, 100/0 to 40/60 v/v are shown in Figure 1. The polymerization rate increases strongly with increasing solvent polarity. The plots, especially at lower solvent polarity, are clearly *S*-shaped, indicating an increase of growing center concentration with time. Figure 2 shows the M_n vs conversion plots. Interestingly, at a constant conversion somewhat higher M_n's are obtained at lower solvent polarity, indicating that change in polarity affects the rate of direct initiation more than that of propagation. The M_n vs conversion plots are similar and generally follow the $M_n = f(\text{conversion})^{\sim 0.5}$ relationship (see curve fitting, Figure 2). Figure 3 shows the M_n vs conversion plots for $[M]_0$=

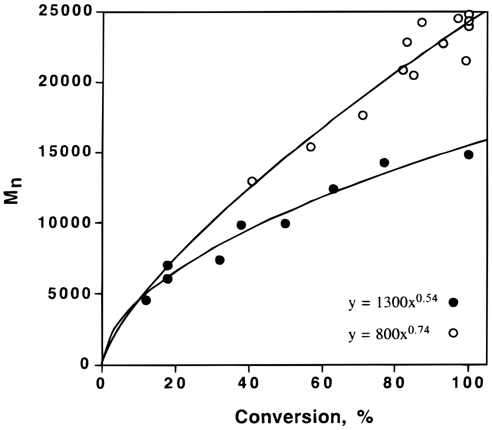

Figure 3. Molecular weight vs conversion plots obtained in MeCl at −80° C at different monomer concentrations. $[BI_3]_0 = 0.005$ M, [DTBP] = 0.003 M. ●, $[\alpha MeSt]_0 = 0.05$ M, ○, $[\alpha MeSt]_0 = 0.35$ M.

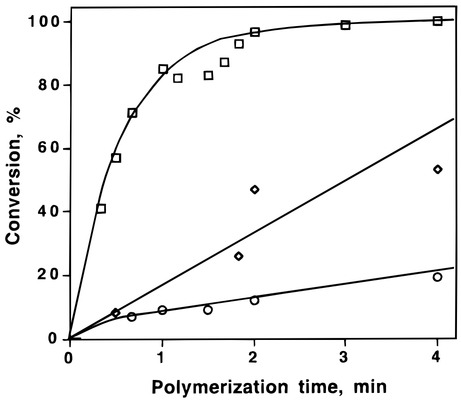

Figure 4. Conversion vs polymerization time at different temperatures in MeCl. $[\alpha MeSt]_0 = 0.35$ M, $[BI_3]_0 = 0.005$ M, [DTBP] = 0.003 M. □ −80 °C; ◊ −60 °C; ○, −40 °C.

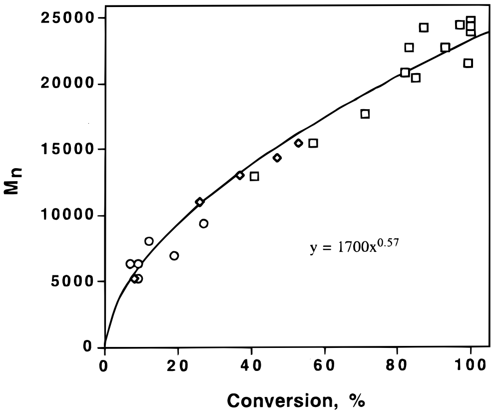

Figure 5. M_n vs conversion plot obtained at different temperatures in MeCl. $[\alpha MeSt]_0 = 0.35$ M, $[BI_3]_0 = 0.005$ M, [DTBP] = 0.003 M. □ −80 °C; ◊ −60 °C; ○, −40 °C.

0.35 $\{M_n = f(\text{conversion})^{0.54}\}$ and 0.05 M $\{M_n = f(\text{conversion})^{0.74}\}$.

Decreasing the temperature significantly increases the rate of polymerization (Figure 4). However, at the same conversion, the M_n's are similar, independent of the temperature in the studied range (Figure 5). A similar negligible temperature dependence has been found with IB, indicating that the activation energies of propagation and haloboration as well as the reaction heat of the ion pair formation is small.[3]

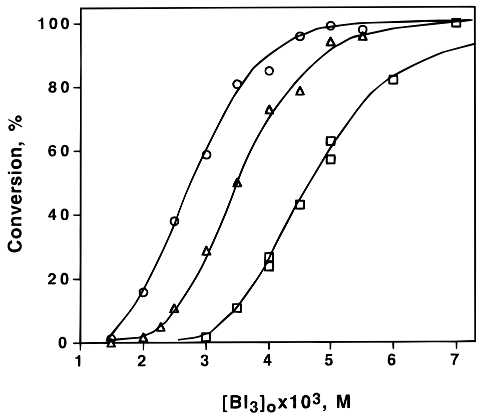

Figure 6. Conversion as a function of BI_3 concentration. [DTBP] = 0.003 M, $[\alpha MeSt]_0 = 0.35$ M, −80 °C. ○, MeCl, 40 s; △, MeCl/Hex, 80:20 v/v, 2 min; ○, MeCl/Hex, 40:60 v/v, 30 min.

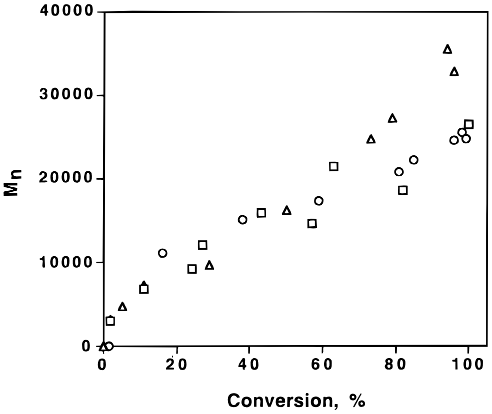

Figure 7. Molecular weight vs conversion as a function of BI_3 concentration. [DTBP] = 0.003 M, $[\alpha MeSt]_0 = 0.35$ M, −80 °C. □ MeCl, 40 s; △, MeCl/Hex, 80:20 v/v, 2 min; ○, MeCl/Hex, 40:60 v/v, 30 min.

Increasing the concentration of BI_3 leads to higher polymerization rates (Figure 6), but the M_n−conversion plots, shown in Figure 7, are similar to those shown on Figure 2. Interestingly, the conversion−$[BI_3]_0$ plots show that polymerization is absent at $[BI_3] \leq 0.0015$ M, which is about the concentration of protic impurities in our system.

While the presented kinetic data strongly support our hypothesis, that the polymerization with boron halides is by direct initiation, structural analysis provided unequivocal proof. ^{1}H NMR spectroscopy of relatively low molecular weight polymers obtained with BI_3 revealed the presence of about 75% external double bonds (4.55 and 4.95 ppm) at the chain end and suggested the presence of $(CH_3O)_2B-$ headgroup (3.35 ppm), as shown in Figure 8. Elimination of HI most probably occured during workup. The remaining ∼25% end groups are likely internal double bonds and methoxy groups. In agreement with previous findings with other initiating systems,[17,18] the polymer is predominantly syndiotactic (>90%) (Figure 8). The ^{1}H NMR assignments were made in accordance with those by Kennedy et al.[17] Representative samples have been analyzed for boron content, and the results are listed in Table 4. According to the results of elemental analysis, the polymer contains one boron atom per chain. These results verify that the polymerization is by direct initiation that may take place via self-ionization or haloboration. To identify which mechanism is operational, a kinetic treatment similar to that reported for the direct initiation of IB may be used. Assuming that propagation is exclusively

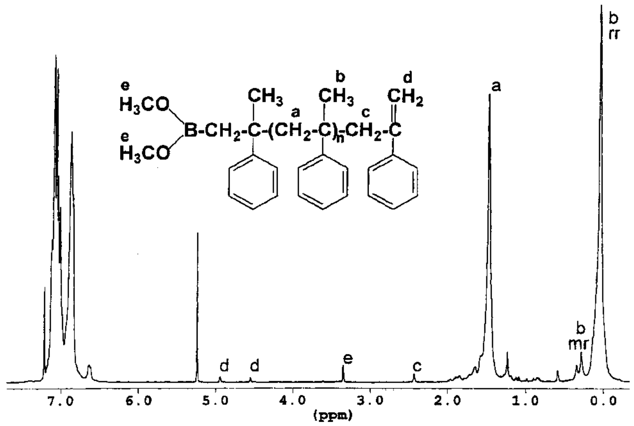

Figure 8. ^{1}H NMR spectrum of a representative Pα-MeSt sample ($M_n = 7700$, $M_w/M_n = 1.19$).

Table 4. Calculated and Experimental Boron Contents Determined by Elemental Analysis of Pα-MeSt Samples Obtained with BI$_3$ at −80 °C

		boron content (wt %)	
M_n ($\times 10^{-3}$)	M_w/M_n	theoretical[d]	experimental
21.9[a]	1.40	0.05	0.06
11.6[b]	1.19	0.10	0.12
11.3[b]	1.22	0.10	0.10
6.7[c]	1.32	0.16	0.16

[a] Polymerization conditions: $[BI_3]_0 = 0.02$ M, $[\alpha MeSt]_0 = 0.35$ M, [DTBP] = 0.004 M, MeCl/Hex (40:60 v/v), 4 min. [b] Polymerization conditions: $[BI_3]_0 = 0.005$ M, $[\alpha MeSt]_0 = 0.35$ M, [DTBP] = 0.003 M, MeCl/Hex (40:60 v/v), 1.5 min. [c] Polymerization conditions: $[BI_3]_0 = 0.01$ M, $[\alpha MeSt]_0 = 0.35$ M, [DTBP] = 0.01 M, MeCl/Hex (20:80 v/v), 32 min. [d] Based on one boron per chain.

by ion pairs, for self-ionization eq 2a and for haloboration eq 2b were obtained:[3]

$$\mathrm{DP_n} = \{k_p^{\pm}[M]_0C/(2k_1^{\pm}K_2[BX_3])\}^{0.5} \tag{2a}$$

$$\mathrm{DP_n} = \{k_p^{\pm}[M]_0C/(2k_2K_2)\}^{0.5} \tag{2b}$$

According to both equations $\mathrm{DP_n} = f(C)^{0.5}$; however eq 2a predicts that at constant conversion, $\mathrm{DP_n}$ will be inversely proportional to $[BX_3]^{0.5}$. In contrast, according to eq 2b, at constant conversion the $\mathrm{DP_n}$ is independent of $[BX_3]$. Thus the two mechanisms can be distinguished.

While for IB we have shown that propagation is by ion pairs, we extended our kinetic treatment to systems where propagation is exclusively by free ions. Scheme 2 shows the polymerization mechanism when free ions are involved.

By kinetic treatment of self-ionization (Scheme 2a) assuming that $[BX_3]$ is constant, the following differential equation was derived:

$$-d[M]/d[PX] = k_p^{+}[PX]/k_1^{+}K_1K_1'K_2K_2'[BX_3] \tag{3}$$

Solving the differential eq 3, eq 4a was obtained, which is essentially identical to eq 2a:

$$\mathrm{DP_n} = \{k_p^{+}[M]_0C/(2k_1^{+}K_1K_1'K_2K_2'[BX_3])\}^{0.5} \tag{4a}$$

Similarly, from Scheme 2b (haloboration) the following differential equation can be obtained:

$$-d[M]/d[PX] = k_p^{+}[PX]^{1/2}/k_2(K_2K_2'[BX_3])^{1/2} \tag{5}$$

Solving eq 3, eq 4b is obtained, which is different from 2b:

$$\mathrm{DP_n} = \{4k_p^{+2}[M]_0C/(9k_2^{2}K_2K_2'[BX_3])\}^{1/3} \tag{4b}$$

The experimental $\mathrm{DP_n}$ vs conversion plots $\{\mathrm{DP_n} = f(\text{conversion})^{\sim 0.5}$ in Figure 2−3$\}$ are compatible with eqs 2a, 2b, and 4a, but not with 4b. The deviations from the predicted 0.5 exponent are due to the fact that $[BI_3]$, assumed to be constant in the derivations, decreases. In MeCl, due to the lowest molecular weights obtained, this decrease is the highest (~50% of BI$_3$ is consumed at 100% conversion). Therefore the rate of haloboration initiation decreases with conversion, and the plot approaches that of a living polymerization with instantaneous initiation $\{M_n = f(\text{conversion})\}$. According to eqs 2a, 2b, and 4a, at constant conversion $\mathrm{DP_n} = f([M]_0)^{0.5}$; thus a decrease of $[M]_0$ does not bring about a similar decrease in $\mathrm{DP_n}$. Therefore at lower $[M]_0$ the decrease in $[BI_3]$ during polymerization will be lower. Figure 3 shows the M_n vs conversion plots for $[M]_0 = 0.35$ and 0.05 M. The plot for $[M]_0 = 0.05$ M now follows $\mathrm{DP_n} = f(\text{conversion})^{0.5}$, since $[BI_3]$ can be considered constant. (The polymer concentration at 100% conversion is only 4×10^{-4} M, much less than $[BI_3]_0 = 0.005$ M.)

Equations 2a and 4a predict that at a constant conversion $\mathrm{DP_n}$ will be inversely proportional to $[BX_3]^{0.5}$. In contrast, according to eq 2b, $\mathrm{DP_n}$ is independent of $[BX_3]$ at a constant conversion. In Table 5, the M_n's of Pα-MeSt obtained at −80 °C, in different solvents and $[BI_3]$, at similar conversion are shown. Apparently the

Scheme 2. Direct Initiation by Self-ionization (a) and by Haloboration (b) When the Active Species Are Free Ions

Initiation

a)

$$2BX_3 \underset{}{\overset{K_1}{\rightleftarrows}} BX_2^{+}\,BX_4^{-} \overset{K_1'}{\rightleftarrows} BX_2^{+} + BX_4^{-}$$

$$BX_2^{+} + CH_2{=}C(R_1)R_2 \xrightarrow{k_1^{+}} BX_2\text{-}CH_2\text{-}C^{+}(R_1)R_2$$

or b)

$$BX_3 + CH_2{=}C(R_1)R_2 \xrightarrow{k_2} BX_2\text{-}CH_2\text{-}C(R_1)(R_2)\text{-}X$$

$$BX_3 + BX_2\text{-}CH_2\text{-}C(R_1)(R_2)\text{-}X \rightleftarrows BX_2\text{-}CH_2\text{-}C^{+}(R_1)R_2\ \ BX_4^{-} \rightleftarrows BX_2\text{-}CH_2\text{-}C^{+}(R_1)R_2 + BX_4^{-}$$

Propagation

$$BX_2\text{-}CH_2\text{-}C^{+}(R_1)R_2 + (n\text{-}1)M \xrightarrow{k_p^{+}} BX_2\text{-}[CH_2\text{-}C(R_1)R_2]_n^{+}$$

Termination-reinitiation

$$BX_2\text{-}[CH_2\text{-}C(R_1)R_2]_n^{+} + BX_4^{-} \overset{K_2'}{\rightleftarrows} BX_2\text{-}[CH_2\text{-}C(R_1)R_2]_n^{+}\ BX_4^{-} \overset{K_2}{\rightleftarrows} BX_3 + BX_2\text{-}[CH_2\text{-}C(R_1)(R_2)]_n\text{-}X$$

Table 5. Polymerization of α-MeSt Initiated by BI_3 at −80 °C ($[\alpha\text{-MeSt}]_0$ = 0.35 M, [DTBP] = 0.003 M)

$[BI_3]$ (M)	solvent	conversion (%)	M_n ($\times 10^{-3}$)	M_w/M_n
0.005	MeCl	100	24.8	1.1
0.007	MeCl	100	26.4	1.1
0.01	MeCl	100	26.2	1.1
0.0035	MeCl/HeX, 80/20 v/v	50	16.2	1.1
0.005	MeCl/HeX, 80/20 v/v	50	17.1	1.1
0.005	MeCl/HeX, 40/60 v/v	100	32.4	1.1
0.01	MeCl/HeX, 40/60 v/v	100	30.3	1.2

M_n's in a given solvent are independent of $[BI_3]$, and therefore initiation is by haloboration.

Conclusion

The polymerization of α-MeSt was examined using different boron halides, in the absence of a separately added ionogen and in the presence of DTBP, to verify that initiation is by direct initiation. Results obtained with BCl_3, BBr_3, and BI_3 are consistent with this proposition, yet direct proof could only be obtained with BI_3. With BCl_3 and BBr_3, the high molecular weights prevented identification of the head and end groups. When BI_3 was used, the relatively low molecular weights allowed qualitative and quantitative analysis of the head $\{(CH_3O)_2B-\}$ and end groups $\{-CH_2C(Ph)=CH_2\}$, and thus proved that the polymerization is by direct initiation. Kinetic results obtained with BI_3 suggest that the mechanism of initiation is haloboration and that propagation is by ion pairs.

While direct proof was not obtained with BCl_3 and BBr_3, it is reasonable to infer that initiation occurs similarly by haloboration and not by adventitious H_2O proceeding by a concerted route in the absence of free protons, as formerly suggested.

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