

Cationic polymerizations at elevated temperatures by novel initiating systems having weakly coordinating counteranions

2. Isobutylene/isoprene copolymerizations

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Abstract

As a sequel to our studies on isobutylene (IB) homopolymerizations, we have investigated the copolymerization of IB/isoprene (IP) mixtures containing up to ~20 mole% IP in the feed by the use of the *in situ* $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating system in close-to-*neat* monomers in the temperature range from -35 to -8 (reflux)°C. The effects of temperature and IB/IP feed ratio on copolymer molecular weights were determined and compared with those produced by AlCl_3 . The molecular weights of butyl rubbers obtained by the novel initiating system under a variety of conditions are invariably and significantly higher than those made with AlCl_3 . High molecular weight gel-free rubbers containing up to ~5 mol% unsaturation can be obtained at relatively high temperatures. Copolymer compositions can be controlled by the IB/IP ratio in the feed. Product molecular weights decrease with increasing IP content. To gain insight into the copolymerization mechanism, the activation enthalpy of molecular weights ($\Delta H^\ddagger = -5.9$ kcal/mol, -24.7 kJ/mol) and the reactivity ratios ($r_{\text{IB}} = 1.8$, $r_{\text{IP}} = 1.5$) have been determined.

Introduction

In the first paper of this series (1) we have demonstrated the synthesis of very high molecular weight polyisobutylene (PIB) by the use of *in situ* prepared $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating systems under close-to-*neat* conditions at uncommonly high temperatures (up to reflux). In subsequent research we have proceeded to explore isobutylene (IB)/isoprene (IP) copolymerizations (butyl rubbers) under essentially the same conditions. The driving force for the latter investigations was to explore the possibility of butyl rubber synthesis in the absence of noxious chlorinated solvents (methyl chloride, methylene chloride) and without cryogenic cooling. Introductory scouting investigations have shown that such polymerizations are indeed feasible and that very high molecular weight IB/IP copolymers can be produced by our new initiating system under desirable conditions. Surprisingly, we also found that high molecular weight gel-free IB/IP copolymers can be prepared in the presence of up to 12 mole% IP in the feed. This finding is of particular interest since conventional IB/IP slurry copolymerizations (2-5) are well known to produce useless crosslinked gels in the presence of IP concentrations above ~4 mole% IP in the charge.

This paper describes our IB/IP copolymerization studies with up to 30 mole% IP by the *in situ* $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating system under close-to-*neat* conditions in the -35 to -8 (reflux)°C range. We have determined that gel-free butyl rubbers having substantially

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superior molecular weights and IP-incorporation levels can be obtained by the use of our novel initiator system in homogeneous media in the absence of cryogenic cooling, than are obtained by conventional Friedel-Crafts acids, e.g., AlCl_3 , in conventional methyl chloride slurries at cryogenic temperatures.

Experimental

Materials, equipment used and overall conditions have been described in the first paper of this series (1). Isoprene (Aldrich) was purified by distillation under reduced pressure prior to use.

A typical IB/IP copolymerization was carried out in the $-35\text{ }^\circ\text{C}$ to $-8\text{ }^\circ\text{C}$ (reflux range) as follows: Into a 250 mL three-neck flask, IB (71.2 mL, 0.852 mol), Me_3SiCl (0.244 g, 2.25 mmol), and IP (1.2 g, 17.8 mmol (2.1 mol%)) were added with stirring and polymerization was induced by the addition of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.232 g, 0.34 mmol dissolved in 3.8 mL CH_3Cl ; the small amounts of methyl chloride were needed to dissolve the lithium salt (1)): total volume of the charge = 76 mL. Samples (10 mL) were withdrawn and quenched by pre-chilled methanol at predetermined time intervals. The viscosity of the charges increased with increasing conversion, but did not affect the efficiency of agitation. After 210 min. the polymerization was quenched by methanol and the products were isolated by precipitation in methanol, purified (redissolving in hexanes and washing with water and methanol) and dried in vacuum at $40\text{ }^\circ\text{C}$. Copolymerizations were carried out with 4, 6, 8, 12, 15, 20 and 30 mol% of IP in the feed at $-35\text{ }^\circ\text{C}$. Copolymerizations in refluxing mixtures ($-8\text{ }^\circ\text{C}$) were carried out in a flask equipped with a cold-finger condenser (filled with a mixture of n-pentane and Dry Ice).

Molecular weights were determined by GPC (Waters Co.) using established procedures (6). ^1H NMR spectra were recorded ($\sim 30\text{ mg}$ in CDCl_3 , 256 FIDs) by a Varian 300 spectrometer using standard 5 mm tubes at room temperature; details have been described (7).

Results and Discussion

Tables 1 and 2 show the results of representative copolymerization experiments in terms of overall IB/IP conversions, copolymer molecular weights, molecular weight distributions (Mw/Mn), and copolymer compositions (IP incorporation), and Figure 1 shows the ^1H NMR spectrum of a representative IB/IP copolymer containing 8.5 mol % of IP. Specifically, Table 1 highlights the effects of temperature (in the -35 to -8 (reflux) $^\circ\text{C}$ range) and conversion, and Table 2, the effect of IP concentration at $-35\text{ }^\circ\text{C}$ on copolymer characteristics. It is quite apparent that butyl rubbers with commercially desirable property parameters, i.e., Mn ($\sim 100,000\text{ g/mol}$), molecular weight distributions (Mw/Mn ~ 2.2), and IP contents ($\sim 1.2\text{ mol}\%$), can be readily prepared with the new initiating system under environmentally more benign conditions (substantially less amounts of noxious methyl chloride solvent) and at much higher temperatures than practiced by contemporary industrial processes ($\sim 100\text{ }^\circ\text{C}$).

Conventional butyl rubber contains only $\sim 1.2\text{ mole}\%$ unsaturation which necessarily gives rise to "slow curing" rubbers (2-4). The two limiting reasons why the level of unsaturation in the rubber cannot be much raised is because above $\sim 1.2\text{ mole}\%$ unsaturation the molecular weights start to decrease to technologically unacceptable levels and undesirable gel starts to appear. As shown by the data in Table 2, by the use of the $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating system we have prepared high molecular weight (Mn $> 100,000\text{ g/mol}$) gel-free rubbers having $\sim 5.0\text{ mole}\%$ unsaturation at $-35\text{ }^\circ\text{C}$.

Table 1. IB and IP (2.1 mol %) copolymerization*

Time min	Temp. °C	Conv. %	$\bar{M}_n \times 10^{-3}$ g/mol	$\bar{M}_w \times 10^{-3}$ g/mol	\bar{M}_w / \bar{M}_n **	IP incorp. mol %
50	-8	13.6	47	103	2.2	1.20
20	-20	2.2	80	176	2.2	
40	-20	4.1	81	179	2.2	1.20
60	-20	6.6	85	193	2.3	
80	-20	9.5	90	204	2.3	1.22
100	-20	12.4	92	199	2.2	
120	-20	17.2	91	202	2.2	1.22
140	-20	22.3	92	201	2.2	
150	-35	13.5	170	370	2.2	1.20

* $\text{Me}_3\text{SiCl} = 3 \times 10^{-2} \text{ M}$; $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4] = 4.5 \times 10^{-4} \text{ M}$; IB = 71.2 mL; IP = 1.76 mL;
 $\text{CH}_3\text{Cl} = 3.8 \text{ mL}$ needed to dissolve the Li salt, total volume = 76 mL

** Monomodal distributions

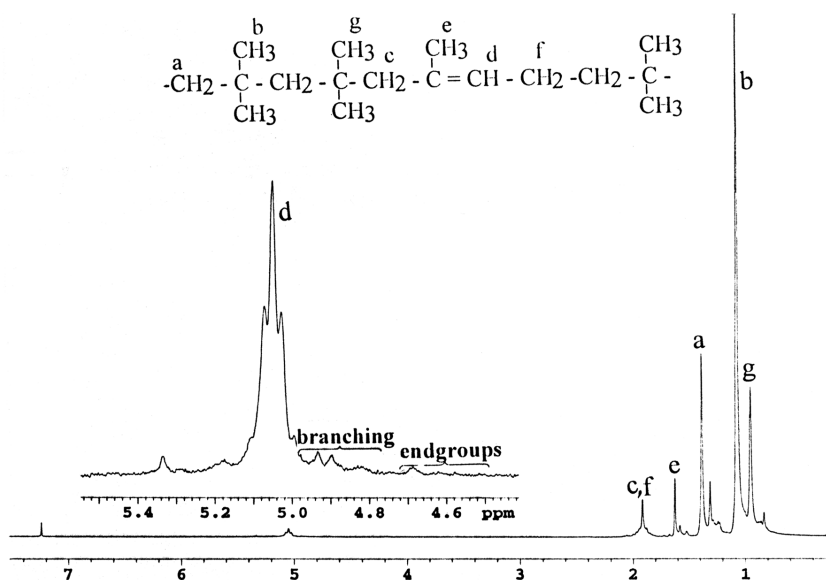


Figure. 1. ^1H NMR spectrum of a representative IB/IP copolymer prepared at -35°C ($M_n = 84,000 \text{ g/mol}$).

Table 2. IB and IP copolymerization at different feed compositions at -35°C .*

IP in feed mol %	Time min	Conv. %	$\overline{M}_n \times 10^{-3}$ g/mol	$\overline{M}_w \times 10^{-3}$ g/mol	$\overline{M}_w/\overline{M}_n^{**}$	IP incorp. mol %	Gel
2.1	150	13.5	170	370	2.2	1.20	gel free
4.0	50	5.2	123	294	2.4	2.51	gel free
6.0	50	6.2	117	290	2.4	3.69	gel free
8.0	50	7.9	108	257	2.4	4.85	gel free
12	40	13.0	84	218	2.6	8.5	gel free
15	40	12.6	74	201	2.7	10.6	~5 % gel
20	40	10.6	45	167	3.7	14.3	>10 % gel

*Polymerization conditions same as Table 1 except total volume = 10 mL.

**Monomodal distributios

Figure 2A shows the results of a representative kinetic study carried out with 2.1 mole% IP in the charge at -20°C . In contrast to conventional IB/IP copolymerizations carried out in methyl chloride slurries at cryogenic temperatures where the rates are immeasurably high and polymerization heat removal is process limiting (2-3), the rates observed in our systems are conveniently controllable by adjusting reagent concentrations.

Figure 2B shows the corresponding molecular weight profile. Similarly to IB homopolymerizations (1), the molecular weights increase with conversions and reach a plateau at $\sim 10\%$ conversion. In line with earlier observations (2-5, 8, 9), we were not surprised that the molecular weight of IB/IP copolymers were lower than those of IB homopolymers synthesized under similar conditions and that they decreased with increasing IP contents in the charge. Remarkably, the copolymerization charges remained homogeneous (and the products gel-free) in the presence of even 12 mole% IP in the feed; above this level, gel starts to form. Copolymerizations carried out under common slurry conditions in methyl chloride invariably gel above ~ 4 mole% IP in the charge (2,3)

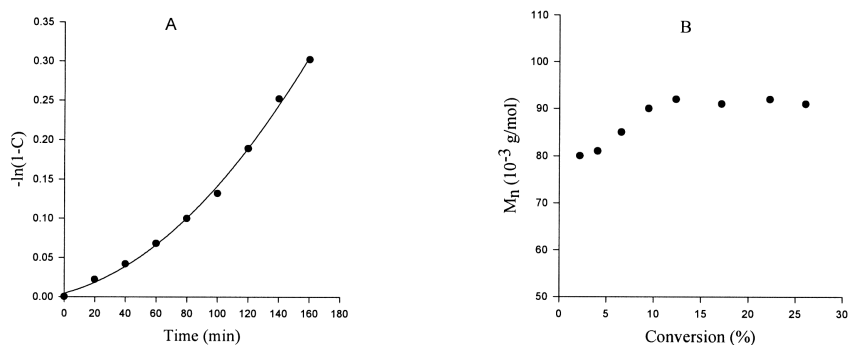


Figure 2. First order rate (A) and M_n vs. conversion (B) plots for close-to-neat IB and IP (2.1 mol % in feed) copolymerizations at -20°C . For conditions see Table 1.

Copolymer composition can be readily controlled by the IB/IP feed ratio. As shown by Figure 3A, IP incorporation in IB/IP copolymers is a linear function of the IP concentration in the feed at least up to ~20 mole% IP. The molecular weights decrease as a function of IP concentration as shown by the data in Figure 3B. These observations are in line with earlier findings (2-5) and indicate that IP is a powerful chain transfer agent in IB/IP copolymerizations.

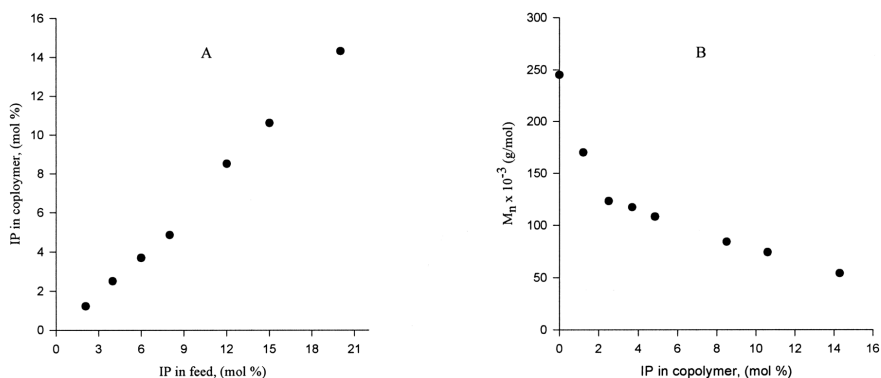


Figure 3. Incorporation of IP in the copolymer (A) and copolymer molecular weight (B) as a function of feed composition at -35°C ($\text{Me}_3\text{SiCl} = 3.0 \times 10^{-2} \text{ M}$; $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4] = 4.5 \times 10^{-3} \text{ M}$; $\text{IB} = 10 \text{ mL} - (\text{vol IP} + 0.5 \text{ mL CH}_3\text{Cl})$, total volume = 10 mL).

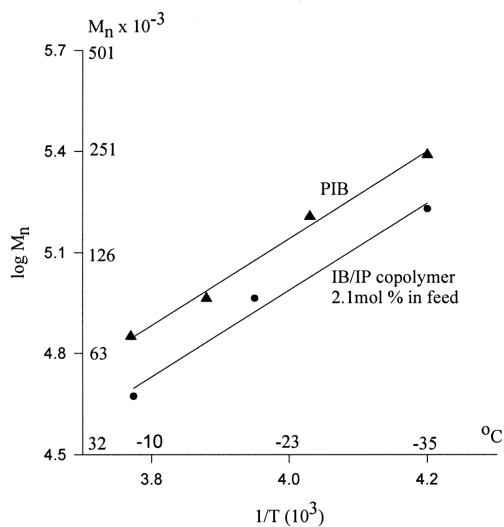


Figure 4. Effect of temperature on copolymer molecular weight in the -8 to -35°C range.

Figure 4 shows the effect of temperature on the molecular weights of IB/IP copolymers in the -35 to -8°C range. The activation enthalpy difference of molecular weights calculated from the slope of the Arrhenius plot is $\Delta H^{\ddagger} = -5.9$ kcal/mol (24.7 joule/mol) which is virtually identical to that calculated for similar IB homopolymerizations (1).

The purpose of Figure 5 is to illustrate dramatically the improvement in molecular weights obtained by the $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating system over that of AlCl_3 . The solid line of the $\log M_n$ vs. $1/T$ plot shows the M_n 's produced by the AlCl_3 system with 12 mole% IP in the charge in the -120 to -87°C range (5). The broken line extrapolates these data to -35°C and indicates the M_n ($\sim 11,000$ g/mol) that would be obtained at this temperature with AlCl_3 . The solid triangle indicates the M_n ($\sim 84,000$ g/mol) that has in fact been obtained by the new initiating system under the same conditions.

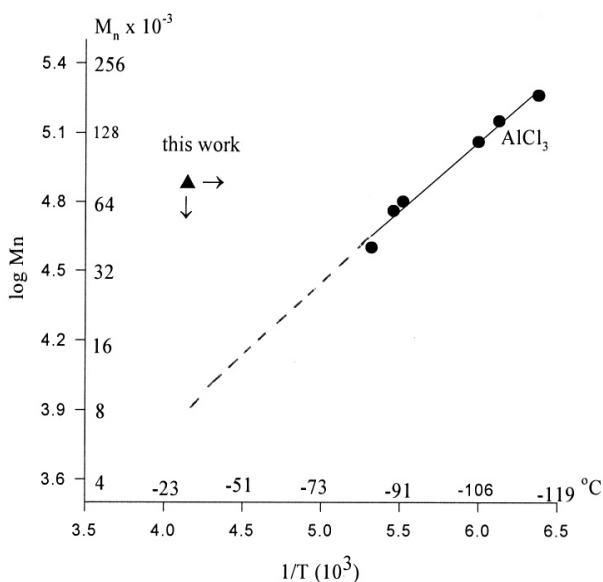


Figure 5. Comparison of copolymer molecular weights obtained by AlCl_3 (ref. 5) and $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ (this work, see Table 2) initiators with 12 mol% IP in the feed.

Evidently the M_n 's produced by the $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ system at -35°C and by AlCl_3 at -100°C are about the same.

Figure 6 shows the Kelen-Tudos plot (10) to calculate the reactivity ratios for IB and IP. According to the satisfactory correlation obtained (including index reversion), the quality of the system can be classified by category I (2), and yields $r_{\text{IB}} = 1.8$, and $r_{\text{IP}} = 1.5$.

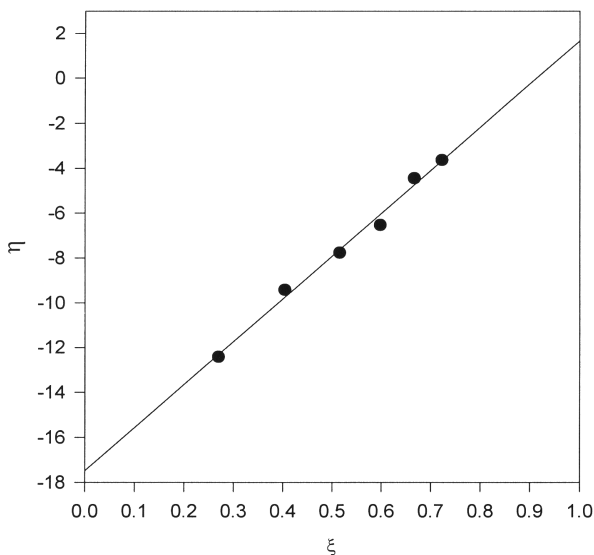


Figure 6. Determination of reactivity ratios by K-T plot ($\alpha = 0.1$). (For conditions see Table 2).

Conclusions

The *in situ* $(\text{CH}_3)_3\text{Si}[\text{B}(\text{C}_6\text{F}_5)_4]$ initiating system produces much higher molecular weight IB/IP copolymers (butyl rubbers) than AlCl_3 . Moreover, the copolymerizations can be conducted by the use of close-to-neat monomer charges at relatively high temperatures (up to reflux). Gel-free butyl rubbers with $M_n > 100,000$ g/mol and up to ~5 mol% unsaturation can readily be made at -35°C .

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