

SYNTHESIS OF HIGHLY REACTIVE POLYISOBUTYLENES WITH BF₃·CYCLOHEXANOL INITIATING SYSTEM*

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Abstract The selective cationic polymerization of isobutylene (IB) initiated by a BF₃·cyclohexanol (CL) complex was carried out from the mixed C₄ fraction feed containing the 4C saturated and unsaturated hydrocarbons at –20°C. The effects of CL concentration, BF₃ concentration, solvent for preparing BF₃·CL complex and polymerization time on the chemical structure of end groups, number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the resulting polymers were investigated. The experimental results indicate that the BF₃·CL complex initiating system exhibited an extremely high selectivity toward the cationic polymerization of IB in the mixed C₄ fraction feed and low molecular weight (M_n = 900–3600) polyisobutylenes (PIBs) with large proportion of *exo*-double bond end groups were obtained. The *exo*-double bond content in PIB chain ends increased by increasing CL concentration or by decreasing solvent polarity in initiating system, BF₃ concentration and polymerization time. The M_n and MWD of the resulting PIBs were dependent on the concentrations of CL and BF₃. Highly reactive PIBs with around 90 mol% of *exo*-double bonds were successfully synthesized by the selective polymerization of IB from the mixed C₄ fraction feed, providing a potentially practical process for its simplicity and low costs.

Keywords: Reactivity; Polyisobutylene; Initiator; Cationic polymerization.

INTRODUCTION

Polyisobutylenes have excellent properties in chemical stability, thermal stability and resistance to oxidation, ozone and UV^[1]. Low molecular weight PIBs with more than 60 mol% of *exo*-double bonds at polymer chain ends are normally referred to as “highly reactive” PIBs (HRPIBs) since only this kind of terminal double bond has a sufficiently high reactivity. The high content of *exo*-double bonds is one of the most important quality criteria for HRPIBs^[2]. HRPIBs can directly react with maleic anhydride to synthesize polyisobutylene/maleic anhydride adduct which is used as fuel and lubricant additives.

Commercial HRPIBs with more than 80 mol% of *exo*-double bonds can be produced by a single-step process *via* cationic polymerization of pure isobutylene (IB) in hexane by using the complexes of BF₃ with secondary aliphatic alcohol and/or tertiary ether as initiating systems at temperatures from –60°C to 0°C and the content of *exo*-double bonds generally decreases with an increment in molecular weight^[3–7]. The tertiary complex of (BF₃)·L¹·L²·L³ with improved solubility in nonpolar medium has been developed for polymerization of isobutylene (IB), in which L¹ represents water or C₁–C₅ alkanol, L² represents aldehyde or ketone and L³ represents ether or alkanol with long chain^[8,9]. Recently, some other kinds of initiating systems, such as manganese^{II} or copper^{II} complexes with bulky non-coordinating borate counter anions and

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$t\text{BuCl}/\text{EtZnCl}$, have been reported for the synthesis of highly reactive PIBs by polymerizing IB in inert solvents^[10–15]. Since IB is produced by cracking methyl *tert*-butyl ether (MTBE) made from selective reaction of methanol with IB in C_4 fractions, many efforts have been made to synthesize HRPIBs by selective polymerization of IB in C_4 fractions directly. However, it is still difficult to synthesize highly reactive PIBs with more than 80 mol% of *exo*-double bonds directly *via* the selective cationic polymerization of IB in mixed C_4 fraction feed.

In this paper, a BF_3 -cyclohexanol (CL) complex initiating system has been explored to prepare highly reactive PIBs containing more than 90 mol% of *exo*-double bonds *via* IB polymerization from the mixed C_4 fraction feed. The structural characterization of resulting polymers was conducted by ^1H , ^{13}C (DEPT-135) NMR spectroscopy.

EXPERIMENTAL

Materials

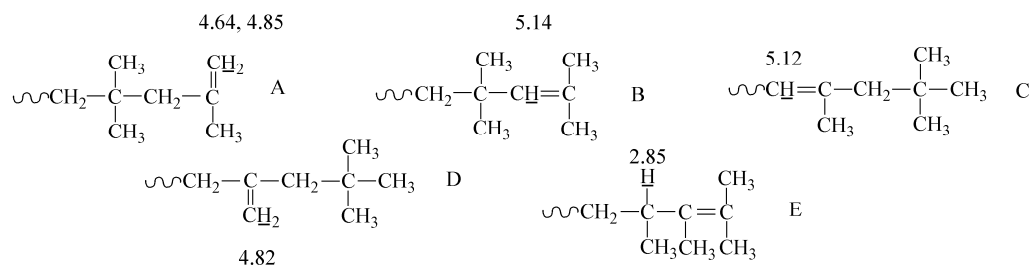
Dichloromethane (CH_2Cl_2 , AR, Beijing Yili Fine Chemical Co.) and *n*-hexane (*n*-Hex, AR, Beijing Yili Fine Chemical Co.) were freshly distilled from calcium hydride before use. Both IB (purity: 99.9%, Beijing Yanshan Petrochemical Co.) and the mixed C_4 fraction feed (Sino Petroleum Co.) were dried with 0.5 nm molecular sieves and cooled at -40°C before polymerization. The mixed C_4 fraction feed contains 24.5 wt% of isobutylene, 54.4 wt% of butane, 2.4 wt% of 2-butene, 18.6 wt% of 1-butene and 0.15 wt% of 1,3-butadiene. BF_3 (purity: 99.99%, Dalian Guangming Institute of Chemical Industry), cyclohexanol (CL, AR, Tianjin Jinke Fine Chemical Co.) and ethanol (98%, Beijing Yili Fine Chemical Co.) were used as received.

Procedures

General polymerization procedures were described as in our previous work^[16]. The representative cationic polymerization was carried out in a tube (120 mL) under a dry nitrogen atmosphere at -20°C . The mixed C_4 fraction feed or IB solution in *n*-Hex had the same IB concentration, *i.e.* $[\text{IB}]_0 = 2.73 \text{ mol}\cdot\text{L}^{-1}$. The mixed C_4 fraction feed or monomer solution in *n*-Hex was introduced into test tubes *via* a 20 mL volumetric pipette. The polymerization was started by addition of the pre-chilled BF_3 -CL complex solution in *n*-Hex/ CH_2Cl_2 solvent mixtures with different ratios and then terminated at a specific time by injection of 3 mL of ethanol with 1% NaOH. After evaporation of volatiles, the polymer product was washed with water until neutral and then dried in a vacuum oven at 40°C to a constant weight. Monomer conversion was determined gravimetrically.

Characterization

The polymer sample was dissolved in tetrahydrofuran (THF) with concentration of 2 g/L. The number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (MWD, M_w/M_n) of polymers were measured with a Waters 5151–2410 GPC instrument equipped with four Waters styragel columns connected in the following series: 500, 10^3 , 10^4 and 10^5 . THF was served as solvent of polymer and mobile phase. The measurements were carried out at room temperature. Molecular weight calibration was performed by several polystyrene standards with different molecular weights. ^1H - and ^{13}C -NMR spectra were recorded on a Varian 300 MHz spectrometer or on a Bruker AV 600 spectrometer (600 MHz) using CDCl_3 as solvent.



Scheme 1 The possible chemical structure of PIB chain ends and corresponding characteristic chemical shifts

The polymer chain ends may form several different structures of double bonds, such as *exo*-double bond (structure A), *endo*-double bond (structure B), tri-substituted double bond (structure C), di-substituted double bond (structure D) and tetra-substituted double bond (structure E), as shown in Scheme 1.

The fractional molar contents of different double bonds were quantified on the basis of integration of the corresponding characteristic signals in ^1H -NMR spectra.

RESULTS AND DISCUSSION

Effect of CL Concentration

All the cationic polymerizations of IB in the mixed C_4 fraction feed were conducted at -20°C , and the polymerization systems were homogeneous since the resulting polymers had low molecular weights and the unreacted C_4 hydrocarbons were good solvents even at low temperatures. The polymer products were subjected to ^1H -NMR and GPC analyses. The effect of CL concentration (expressed by molar ratios of CL/BF_3) on the cationic polymerization of IB, M_n , MWD and double bond structures is summarized in Table 1. The ^1H -NMR spectra of the resulting polymers synthesized at different molar ratios of CL/BF_3 are given in Fig. 1. The characteristic resonances for *exo*-double bond (structure A) appear at $\delta = 4.64$ and 4.85 . The characteristic resonances at $\delta = 5.14$, 5.12 , 4.82 and 2.85 are assigned to the *endo*-double bond (structure B), tri-substituted double bond (structure C), di-substituted double bond (structure D) and tetra-substituted double bond (structure E), respectively. On the basis of intensity integration of corresponding signals in ^1H -NMR spectra, the fractional molar amounts of various structures of double bonds (structure A–E) can be quantified. It can be clearly seen from Table 1 and Fig. 1 that the content of *exo*-double bond (structure A) in polymer chains was increased greatly up to *ca.* 89 mol% with increasing CL concentration or molar ratio of CL/BF_3 . At low concentration of CL, *i.e.* CL/BF_3 (molar ratio) = 0.62, the content of *exo*-double bond (structure A) was determined to be only 34.2 mol% and the contents of B, C and E were 36.1 mol%, 8.2 mol% and 21.5 mol% respectively, indicating heavy side transfer reactions. As shown in Scheme 2, the double bond isomers (structure B–E) formed *via* carbenium ion rearrangement hydride shift and methide shift^[17–19]. Very interestingly, the intensity of peaks at $\delta = 4.64$ and 4.85 (a_1 , a_2) for *exo*-double bond (structure A) was greatly enhanced by introduction of sufficient amounts of CL and its content was increased gradually to more than 80 mol%. The resonances at $\delta = 5.14$, 5.12 , and 2.85 gradually decreased with an increment in molar ratio of CL/BF_3 , indicating side transfer reactions *via* carbenium ion arrangement leading to the formation of different isomers could be effectively suppressed at high enough concentration of CL. The molecular weight decreased and molecular weight distribution narrowed with an increment in molar ratio of CL/BF_3 and GPC traces of polymer products were monomodal at $\text{CL}/\text{BF}_3 \geq 1.05$. Therefore, sufficient amounts of CL are needed to attain high content of *exo*-double bonds in polymer chains. Therefore, it can be supposed that CL played a very important role in suppressing side transfer reactions such as hydride shift and methide shift, and the growing polymer chain end cations were mainly terminated by normal β -proton abstraction from $-\text{CH}_3$.

Table 1. Effect of molar ratios of CL/BF_3 on cationic polymerization of IB, M_n , MWD and double bond structures

Run No.	CL/BF_3 (mol/mol)	t_p (min)	Conv. (%)	M_n by NMR	Double bonds mol% by NMR					M_n by GPC	M_w/M_n by GPC
					A	B	C	D	E		
1	1.27 ^a	20	19.1	900	83.8	11.6	2.5	2.1	0	900	1.8
2	1.22 ^a	20	35.2	1000	76.5	14.7	5.9	2.8	0	1000	1.8
3	1.05 ^a	5	67.1	1600	76.3	21.4	2.3	0	0	1800	2.8
4	0.62 ^a	5	81.3	2300	34.2	36.1	8.2	0	21.5	1600	3.8
5	1.10 ^b	5	41.5	2300	88.9	11.1	0	0	0	2200	2.3
6	1.05 ^b	5	62.3	2400	87.0	13.0	0	0	0	2400	2.4
7	1.00 ^a	5	67.0	2300	78.2	21.8	0	0	0	2300	2.9

^a CL was introduced into catalyst;

^b CL was introduced into catalyst ($\text{CL}/\text{BF}_3 = 1.0$, molar ratio), small amount of another CL was introduced into monomer solution solvent for initiating system: $n\text{-Hex}/\text{CH}_2\text{Cl}_2$ (V/V) = 60/40 (No. 1–4) and 80/20 (No. 5–7), IB/ $n\text{-Hex}$ solution, $[\text{BF}_3] = 0.014 \text{ mol}\cdot\text{L}^{-1}$, $T_p = -20^\circ\text{C}$.

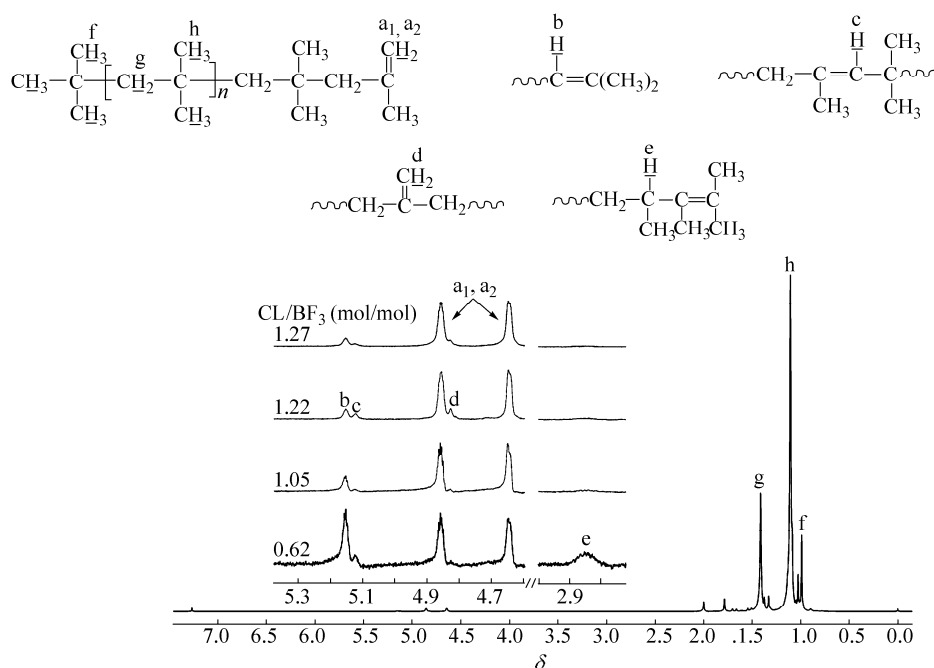
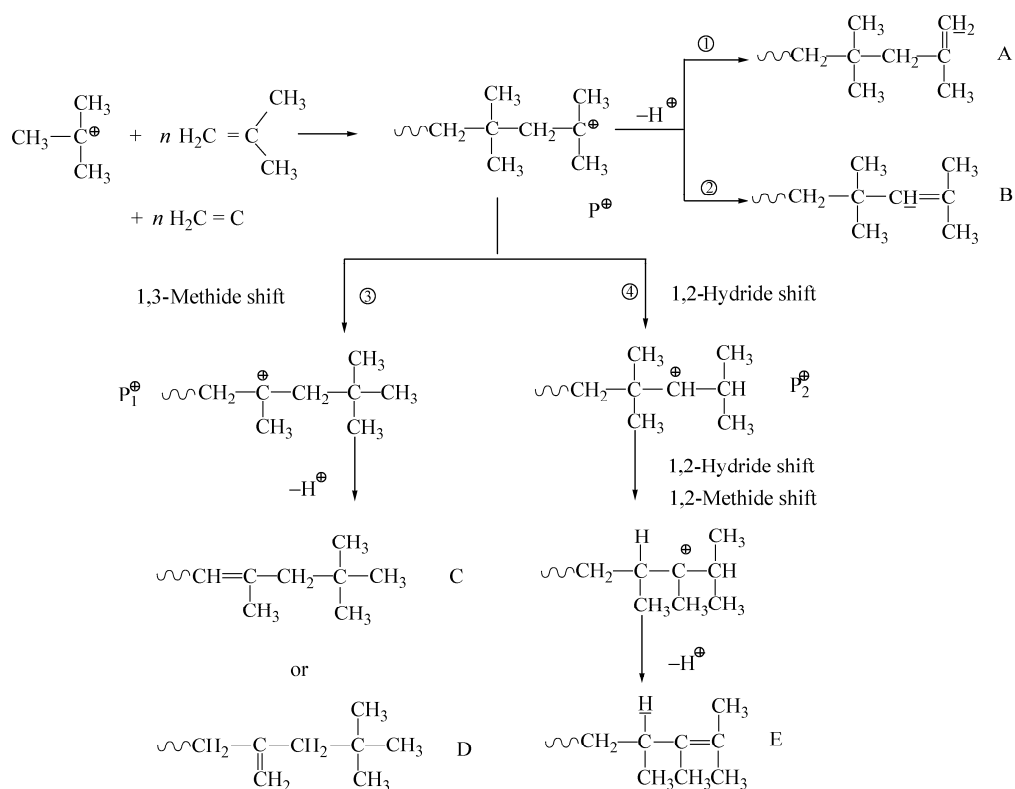


Fig. 1 ^1H -NMR spectra of PIB synthesized at different molar ratio of CL/BF_3



Scheme 2 Possible mechanism of termination and double bond isomer formation

Effect of Solvent in Initiating System

Solvent is necessary for the preparation of initiating system and plays an important role in the initiating species and its reactivity. The effect of solvent in initiating system on chain end groups and M_n of the resulting polymers was investigated, and the experimental results are given in Table 2 and Fig. 2. When the molar ratio of CL/BF₃ was set as 1.0, the content of *exo*-double bond (structure A) increased from 62.0 mol% to 77.1 mol% with decreasing solvent polarity from *n*-Hex/CH₂Cl₂ of 40/60 to 80/20 (*V/V*). The more ion pairs initiating active species formed in solvent mixture *n*-Hex/CH₂Cl₂ with lower polarity due to less solvation in the initiating system and the propagation subsequently proceeded *via* ion pairs species in the mixed C₄ hydrocarbons. The stabilization of the carbocations at the growing chain ends resulted in a decrease in the carbenium ion arrangements shown in Scheme 2 and in double bond isomer formation. PIBs with 91.5 mol% of *exo*-double bonds were successfully synthesized by initiating system of BF₃·CL complex (CL/BF₃ = 1.39) in *n*-Hex/CH₂Cl₂ solvent mixture (80/20, *V/V*) by polymerizing IB in the mixed C₄ fraction feed.

Table 2. The effect of solvent in initiating system on chain end groups and M_n of the resulting polymers

Run No.	CL/BF ₃ (mol/mol)	Catalyst solvent <i>n</i> -Hex/CH ₂ Cl ₂ (<i>V/V</i>)	t_p (min)	Conv. (%)	End-structure mol%			M_n^a
					A	B	D	
8	1.39	80/20	10	21.5	91.5	8.5	0	1600
9	1.2 ^b	80/20	20	30.4	80.8	13.1	4.1	2400
10	1.0	80/20	2	21.6	77.1	22.9	0	2900
11	1.0	60/40	2	27.4	65.0	35.0	0	3600
12	1.0	50/50	2	28.8	63.2	36.8	0	2800
13	1.0	40/60	2	22.5	62.0	38.0	0	2100

^a Calculated based on ¹H-NMR data;

^b *n*-Hex solution of IB, [IB]₀ = 2.73 mol·L⁻¹;

[IB]₀ (C₄ fractions) = 2.73 mol·L⁻¹, [BF₃] = 0.013 mol·L⁻¹, T_p = -20°C

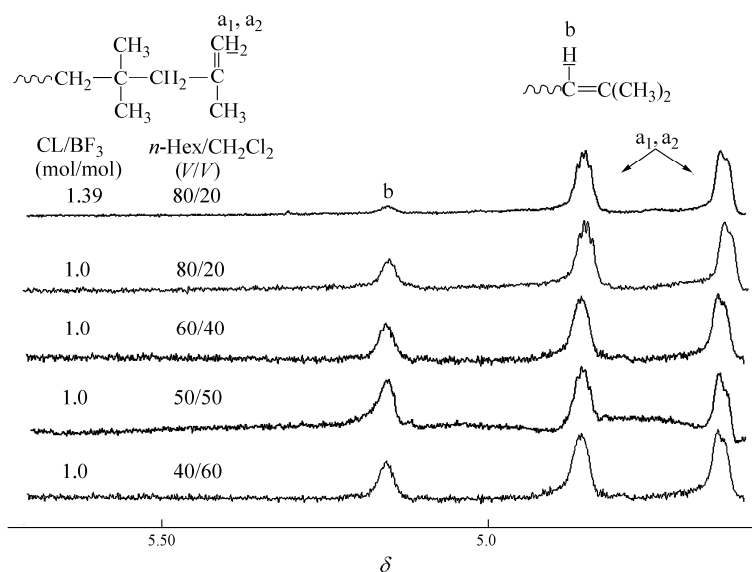


Fig. 2 ¹H-NMR spectra of PIBs synthesized from the mixed C₄ fraction feed with BF₃·CL complex initiating system in different *n*-Hex/CH₂Cl₂ solvent mixtures

On the other hand, the incorporation of other olefins or butadiene in C₄ mixed feed into polymer chains should be investigated. As reported recently in the cationic polymerizations^[20–22], isobutylene is *ca.* 17 times more reactive than butadiene, *ca.* 543 times more reactive than *n*-butene, *ca.* 294 times more reactive than *cis*-2-butene in 100% hexanes at 0°C. These results may help to understand the highly selective cationic polymerization of isobutylene in the mixed C₄ fraction feed. The ¹H-NMR spectra of the polymer samples

obtained from the mixed C_4 fraction feed are shown in Fig. 2. It can be seen that exclusive formation of the addition of butadiene to the growing chain essentially occurred for the undetectable characteristic resonances at $\delta = 5.2\text{--}5.7$. No observation of the characteristic resonance signals for *n*-butene structural unit indicates that no copolymerization of *n*-butene occurred even at its high concentration in the mixed C_4 fraction feed.

In order to get further insight into the resulting polymer structure, ^{13}C -NMR characterization was performed on both the polymer sample obtained using the mixed C_4 fraction feed with BF_3 ·CL initiating system in this paper and the commercial HPIB (Glissopal® 1000, BASF, *exo*-double bond = 90.1 mol%) obtained from IB polymerization in hexane for comparison. The DEPT-135 (distortionless enhancement by polarization transfer) technique was also used to analyze the chemical structure of the resulting polymers. In DEPT spectra, only the lines of carbons bonded to hydrogen are detected. Moreover, lines of methine and methylene carbons exhibit a different phase in DEPT-135 spectra, which simplifies the investigation of chemical structures. The ^{13}C -NMR spectra and DEPT-135 spectra of a representative polymer product obtained from the mixed C_4 fraction feed (sample 8 in Table 2) and Glissopal® 1000 are given in Figs. 3 and 4, respectively. The strong characteristic signals at $\delta = 114.3$ and 143.8 are assigned to *exo*-double bond (structure A) and the weak characteristic signals at $\delta = 128.0$ and 135.3 are assigned to *endo*-double bond (structure B). No other signals observed in the olefinic area further confirm the absence of 1,3-butadiene incorporation in polymer chains. The homopolymer or copolymer of 1-butene and 2-butene could also be undetected from the ^{13}C -NMR spectra. The comparison from the ^{13}C -NMR characterization indicates that the polymer product synthesized from IB polymerization in the mixed C_4 fraction feed has almost the same carbon skeleton as that of commercial HPIB (Glissopal® 1000) by polymerizing IB in hexane. Consequently, the initiating system of BF_3 ·CL complex in *n*-Hex/ CH_2Cl_2 solvent mixture with low polarity exhibits very high selectivity to the cationic polymerization of isobutylene in the mixed C_4 fraction, resulting in the formation of highly reactive polyisobutylenes with *ca.* 90 mol% of *exo*-double bonds.

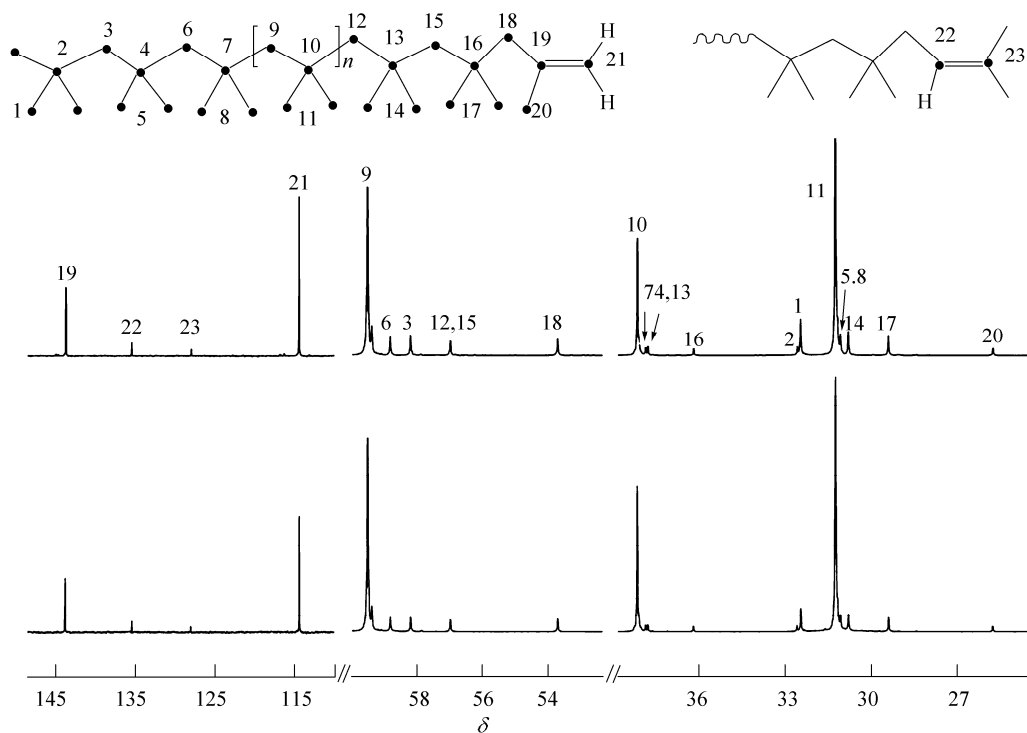


Fig. 3 ^{13}C -NMR spectra of polymer prepared from the mixed C_4 fraction feed (Sample 8, top) and commercial HPIB (Glissopal® 1000, bottom)

Sample 8: $F_A = 91.5$ mol%, $F_B = 8.5$ mol%, $M_n = 1600$;

Glissopal® 1000: $F_A = 90.1$ mol%, $F_B = 6.3$ mol%, $F_D = 3.6$ mol%, $M_n = 1000$

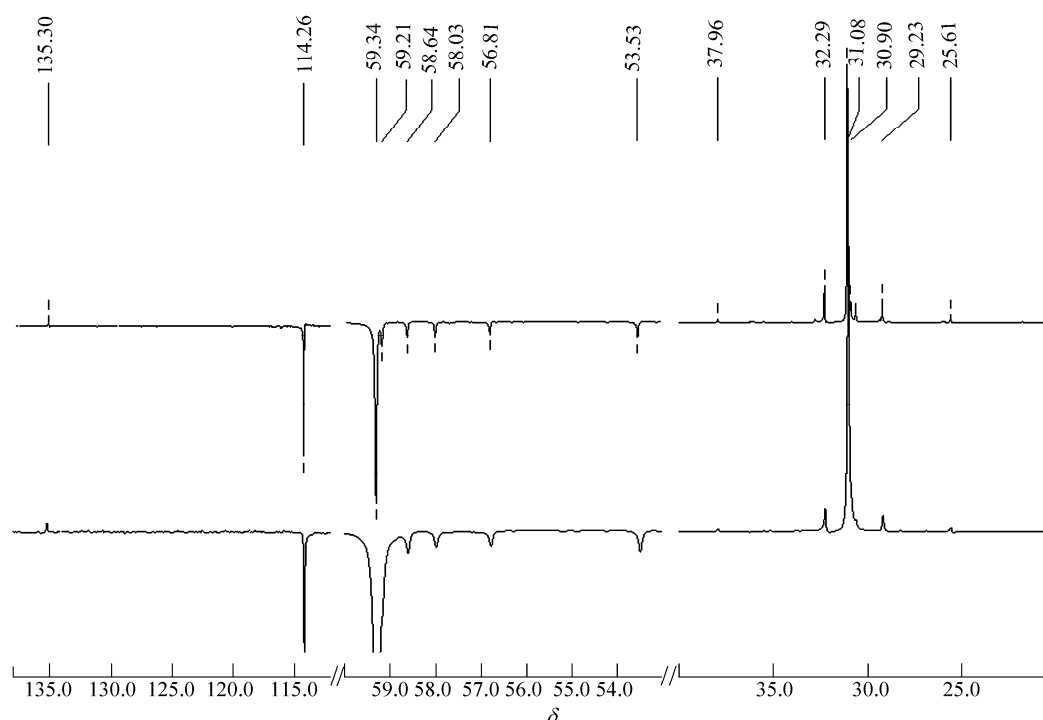


Fig. 4 DEPT-135 spectra of PIB prepared from the mixed C₄ fraction feed (Sample 8, top) and commercial HRPIB (Glissopal® 1000, bottom)

Effect of Polymerization Time

Polymerization time is one of the most important variables in controlling polymerization, molecular weight and unsaturated structures. The effect of polymerization time on chain end groups, M_n and MWD of the resulting polymers was investigated, and the experimental results are summarized in Table 3. It can be seen that the cationic polymerization of IB initiated by $\text{BF}_3 \cdot \text{CL}$ complex in the mixed C₄ fraction feed proceeded with a relatively rapid polymerization rate, and monomer conversion gradually increased with polymerization time. The M_n and MWD of PIBs changed slightly with polymerization time and the *exo*-double bond content was *ca.* 90 mol% in 20 min, suggesting that the polymerization was dominantly terminated by β -H elimination. The content of *exo*-double bond (structure A) decreased slightly to 87.3 mol% by prolonging reaction time to 30 min, which is ascribed to the formation of 2.4 mol% of di-substituted double bond (structure D) *via* carbenium ion rearrangement shown in Scheme 2. It has been reported that the *exo*-double bond migration happened even in living cationic polymerization of IB at high Lewis acid, leading to the formation of more substituted double bonds with prolonging polymerization time^[23].

Table 3. Effect of polymerization time on chain end groups, M_n and MWD of the resulting polymers

Run No.	t_p (min)	Conv. (%)	Double bonds mol% by NMR					M_n by GPC	M_w/M_n by GPC	M_n by NMR
			A	B	C	D	E			
15	30	56.1	87.3	10.3	0	2.4	0	1000	2.0	1000
16	20	30.8	90.0	10.0	0	0	0	1100	2.1	1100
17	10	16.0	90.1	9.9	0	0	0	1100	2.0	1000

$[\text{BF}_3] = 0.017 \text{ mol} \cdot \text{L}^{-1}$, $\text{CL}/\text{BF}_3 = 1.2$, cyclohexane/ $\text{CH}_2\text{Cl}_2 = 80/20$ (V/V), other conditions are shown as in Table 2.

CONCLUSIONS

The initiating system of BF_3 -cyclohexanol (CL) complex in hexane/ CH_2Cl_2 solvent mixtures with low polarity has been successfully developed to polymerize isobutylene with an extremely high selectivity in the mixed C_4 fraction feed and to synthesize low molecular weight ($M_n = 900\text{--}3600$) polyisobutylenes with large contents of *exo*-double bonds. The content of *exo*-double bond end groups in polyisobutylene chains greatly increased with increasing concentration of cyclohexanol or decreasing the solvent polarity for preparing the initiating system. The synthesis of the desirable highly reactive polyisobutylenes with around 90 mol% of *exo*-double bonds (structure A) could be achieved by selective cationic polymerization of isobutylene in mixed C_4 fraction feed with BF_3 -cyclohexanol initiating system in the presence of sufficient amounts of cyclohexanol. This research work provides a potentially practical process for production of highly reactive polyisobutylenes by using the mixed C_4 fraction feed directly.

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