



A cost-effective process for highly reactive polyisobutylenes via cationic polymerization cointiated by AlCl_3

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ARTICLE INFO

Article history:

Received 10 April 2010

Received in revised form

30 September 2010

Accepted 10 October 2010

Available online 16 October 2010

Keywords:

Cationic polymerization

Isomerization

Initiators

ABSTRACT

The initiating system consisting of AlCl_3 with dialkyl ether such as di-*n*-butyl ether or diisopropyl ether has been successfully developed for providing a cost-effective process of synthesis of highly reactive polyisobutylenes (HRPIBs) with large proportion of *exo*-olefin end groups up to 93 mol% at temperatures ranging from -20 to $+20$ °C. The above dialkyl ethers played very important roles in promoting the directly rapid β -proton elimination from $-\text{CH}_3$ of the growing chain ends to create *exo*-olefin end groups and decreasing or even suppressing the carbenium ion rearrangements to form the double bond isomers. Very importantly, the highly reactive PIBs with 80–92 mol% of *exo*-olefin end groups, having low M_n s of 1300–2300 g mol^{-1} and monomodal molecular weight distribution ($M_w/M_n = 1.7\text{--}2.0$) could be achieved at $0\text{--}20$ °C. These results are comparable to those of commercial HRPIBs produced industrially by the best BF_3 -based initiating system at far below 0 °C.

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1. Introduction

Polyisobutylenes (PIBs) are important materials with excellent properties, such as low gas permeability and high chemical stability, and have been applied in many fields. PIBs are commercially produced by two processes with aluminum trichloride (AlCl_3) and boron trifluoride (BF_3) cointiating systems respectively. The conventional PIBs with low content (<10 mol%) of *exo*-olefin end groups are industrially produced using H_2O as initiator and AlCl_3 as cointiator, which having low reactivity for further functionalization reactions [1–4]. The PIBs with large proportion of *exo*-olefin end groups more than 60 mol%, preferably more than 75 mol%, are normally referred to as highly reactive PIBs (HRPIBs). HRPIBs with number-average molecular weight (M_n) of 500–5000 g mol^{-1} are of great interest due to their applications as intermediates for production of the additives to lubricants and fuels, such as surfactants or dispersants [5–7]. Large proportion of *exo*-olefin end groups is favored to produce the additives since they have high reactivity in chemically modification with maleic anhydride. Commercial low molecular weight HRPIBs (M_n s = 800–2500 g mol^{-1} ; $M_w/M_n \sim 2.0$) with more than 80 mol% of *exo*-olefin end groups can be only produced by a single-step process via cationic polymerization of

isobutylene initiated by BF_3 -based system at temperatures far below 0 °C [7]. Recently, the initiating systems consisting of solvent-ligated $[\text{M}(\text{NCMe})_6]^{2+}$ ($M^{\text{II}} = \text{Mn, Cu}$) complexes with the bulky, non-coordinating counter ions such as $[\text{C}_3\text{H}_3\text{N}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ have been reported for preparing HRPIBs with M_n s of 1400–7000 g mol^{-1} at ambient temperatures by a single-step process and the polymerization process induced by these kinds of initiating systems sometimes required long time to get high monomer conversions [8,9]. However, these solvent-ligated manganese(II) and Copper(II) complexes are not commercially available and need to be synthesized by several reactions [8,9]. And these complexes are kept at room temperature for short periods of time and need to be stored at -35 °C under argon atmosphere to prevent decomposition and oxidation over long storage periods [8,9]. Another initiating system consisting of alkyl zinc chloride (e.g. EtZnCl) and alkyl halide (e.g. *t*-BuCl) was also reported to produce medium molecular weight HRPIBs with M_n s of 10000–29000 g mol^{-1} and M_w/M_n of 1.9–2.5 at room temperature [10]. On the other hand, HRPIBs could also be prepared by specific termination reaction after completion of cationic polymerization or by modification from *tert*-chloro terminated functional PIB chains [11–14].

This research thinking about the potentially practical utilization of our initiating systems in industry in the future has led us to explore the AlCl_3 -based system for providing a cost-effective and simple process of synthesis of highly reactive PIBs since AlCl_3 , of greatest economic significance, is commonly applied in industrial

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production of conventional PIBs. To the best of our knowledge, no polymerization reaction to prepare highly reactive PIBs with such a high content of *exo*-olefinic groups (~90 mol%) by using AlCl_3 as coinitiator at 0 °C or above has been described so far. In this paper, we will report our investigation on the cationic polymerization of isobutylene (IB) by the initiating system consisting of H_2O , AlCl_3 and dialkyl ethers such as dibutyl ether (OB_2) or diisopropyl ether (OP_2) to prepare highly reactive PIBs containing large content of *exo*-olefin end groups even up to 93 mol% by a single-step process. The effects of polymerization conditions on monomer conversion, number-average molecular weight (M_n), molecular weight distribution (MWD, M_w/M_n) and end group structures of the resulting PIBs were investigated.

2. Experimental

2.1. Materials

Dichloromethane (CH_2Cl_2 , analytical reagent, Beijing Yili Fine Chemical Co.) was purified as described previously [15]. Di-*n*-butyl ether (99%, OB_2 , Tianjin Fuchen Chemical Co.) and diisopropyl ether (99%, OP_2 , Tianjin Guangfu Chemical Co.) were distilled from CaH_2 under nitrogen before use. Anhydrous aluminum trichloride (AlCl_3 , 99%, Acros; packaging under nitrogen), isobutylene (99.9%, IB, Beijing Yanshan Petroleum Chemical Co.) and ethanol (analytical reagent, Beijing Yili Fine Chemical Co.) were used as received.

2.2. Polymerization procedure

All the manipulation, reactions and cationic polymerizations of isobutylene were carried out under a dry nitrogen atmosphere. Specific reaction conditions are listed in the Figure captions and Tables. A representative procedure was described as follows: The monomer solution in CH_2Cl_2 was prepared in a chilled 1000 mL round-bottom flask at -40 °C. The monomer solution was airtightly transferred to 20 mm × 200 mm test tubes (polymerization reactors) via a 20 mL volumetric pipette and cooled at the desired reaction temperature for more than 30 min. The solutions of dialkyl ether and AlCl_3 were added into monomer solutions to initiate the polymerization. After predetermined time, the polymerization was terminated by injection of 4 mL of prechilled ethanol containing 1% NaOH. After evaporation of the volatiles, the polymer was purified two times by reprecipitation from hexanes/ethanol and finally washed with ethanol and water. The polymer products were dried thoroughly in a vacuum oven at 40 °C. The monomer conversion was determined gravimetrically.

2.3. Characterization

The H_2O concentrations in the components and polymerization systems were monitored electrochemically with an SF-6 water determination apparatus in conjunction with a Karl–Fischer reagent for coulometric titration according to the method described previously [15]. The molecular weight and its distribution of polymers were determined with a Waters 5151-2410 gel permeation chromatography (GPC) system equipped with three Styragel GPC columns (HT3, HT5, and HT6E) at 30 °C. Tetrahydrofuran (THF) served as solvent of PIB with a concentration of 20 mg of PIB/10 mL of THF and was also used as mobile phase at a flow rate of 1.0 mL min^{-1} . ^1H NMR spectroscopy of the polymer solution in CDCl_3 was carried out on a Bruker spectrometer (300 MHz and 600 MHz) and the spectrum was recorded by calibrating to tetramethylsilane ($\delta_{\text{H}} = 0.00$) as internal standard.

3. Results and discussion

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–Craft acids, particularly some halides of boron, titanium and tin, require an additional cation source to initiate polymerization (cointiation mechanism). Some authors claimed that cationic polymerization and particularly that of isobutylene (IB) can be started by AlBr_3 or AlCl_3 , AlEtCl_2 , TiCl_4 or BCl_3 even in the absence of a separate cation source (direct initiation mechanism via halometalation or self-ionization). The direct initiation might generally operated in the absence of proton either by using a large amount of proton trap, e.g. 2,6-di-*tert*-butylpyridine, or by using vacuum line and high vacuum with completely sealed apparatus [16]. Therefore, the mechanism of initiation of cationic polymerization by metal halide may include the simultaneous cointiation and direct initiation. It has been concluded on direct initiation that “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” [17].

The control experiment of cationic polymerization of isobutylene (IB) with the conventional $\text{H}_2\text{O}/\text{AlCl}_3$ initiating system was carried out in CH_2Cl_2 in the absence of dialkyl ether at 0 °C for comparison in this research. Fig. 1 gives a typical ^1H NMR spectrum of this resulting PIB. On the basis of intensity integration of corresponding signals in ^1H NMR spectrum, the fractional molar amounts of head group, structural units and various structures of end groups including double bonds can be quantified. The strong resonance signals at $\delta = 1.11$ (z) and 1.42 (y) are assigned to the $-\text{CH}_3$ and $-\text{CH}_2$ protons in the main chain of PIB respectively. AlCl_3 was mainly in conjunction with a small amount of water to create an initiating active center H^+ (AlCl_3OH^-) to induce the cationic polymerization of IB and then form *t*-butyl head group in the PIB chain, which resonance appears at $\delta = 0.99$ (x) [9,18]. The β -proton abstraction from the tertiary cation (I) of the growing PIB chain normally leads to *exo*- or *endo*- double bond end groups, i.e. $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ (structure A) or $-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$ (structure B). The expansion of the olefin region (inset in Fig. 1) at $\delta = 4.64$ and 4.84 (a_1 , a_2) shows that only 11.8 mol% of *exo*-olefin end groups ($-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$, structure A) existed in the PIB chains. The expected vinylidene route to produce highly reactive PIBs (structure A) is the minor one for the conventional cationic polymerization with $\text{H}_2\text{O}/\text{AlCl}_3$ initiating system, which is similar to the observations of commercial conventional PIB products in ^1H NMR spectra reported [2,4,19]. The fraction of *endo*-olefin end groups ($-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$, structure B) was negligible or undetectable in this conventional PIB sample. A variety of internal unsaturated bonds can also be formed by isomerization via hydride and/or methide shifts [1,3]. The two strong quartet resonances at $\delta = 5.17$ and 5.37 (c_1 , c_2) are definitely attributed to $-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)$ end groups in PIB chains (structure C) for *Z*- and *E*-configuration respectively and the content of structure C was determined to be 48.1 mol%. In addition, the intensive multiple resonances at $\delta = 2.85$ (e) are attributed to $-\text{CH}-$ proton in *tetra*-substituted unsaturated end groups ($-\text{CH}_2\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$, structure E) in PIB chains and its content was determined to be 40.1 mol% [19]. The large proportions of the internal unsaturated bonds (C and E) suggest the serious transfer side reactions from the normal tertiary cation (I) of the growing PIB chain end via carbenium ion rearrangements. Scheme 1 illustrates the possible mechanism of the transfer reactions. The carbenium ion rearrangements from tertiary cation (I) via 1,2-hydride and subsequent 1,2-methide shifts

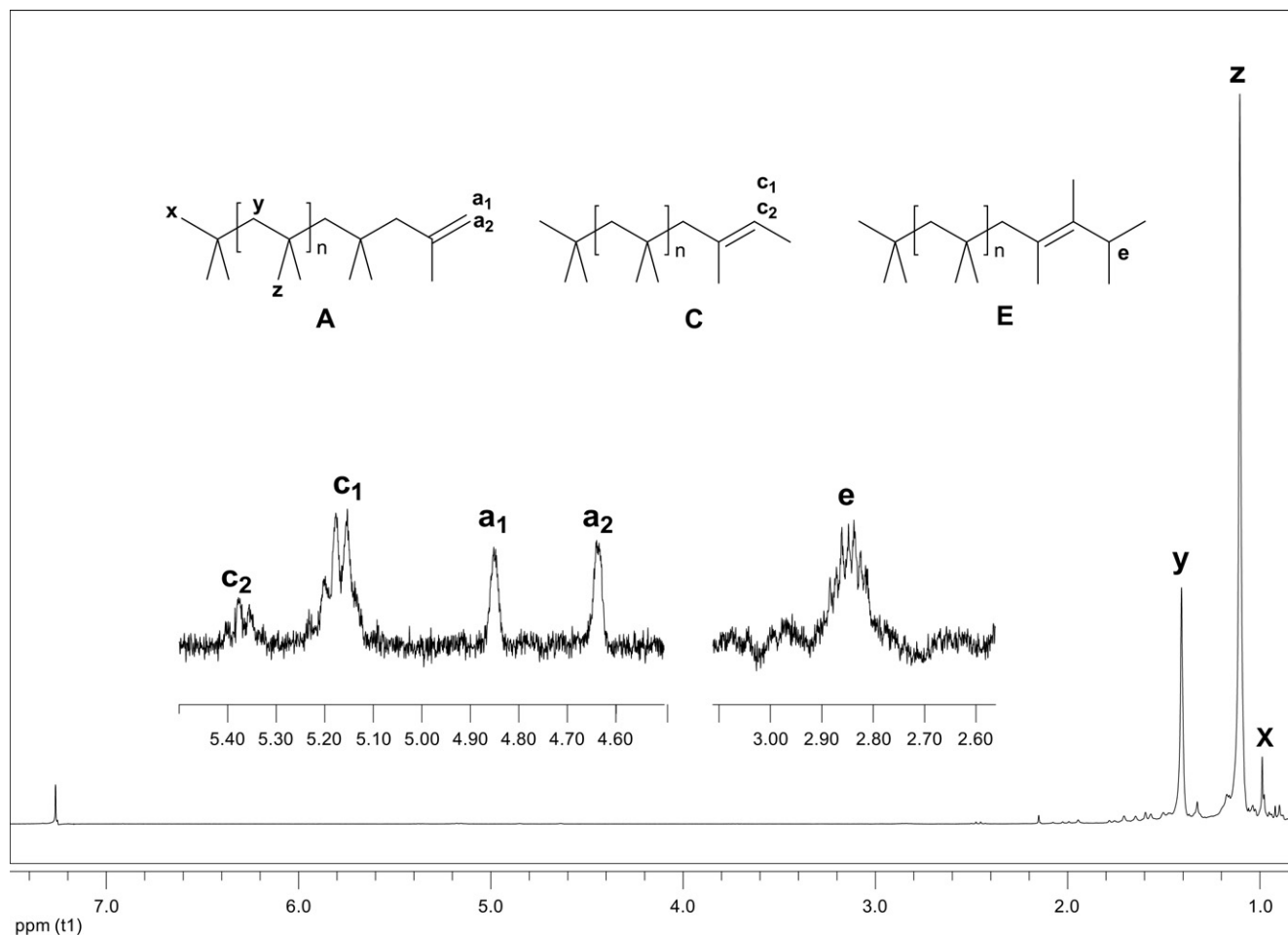
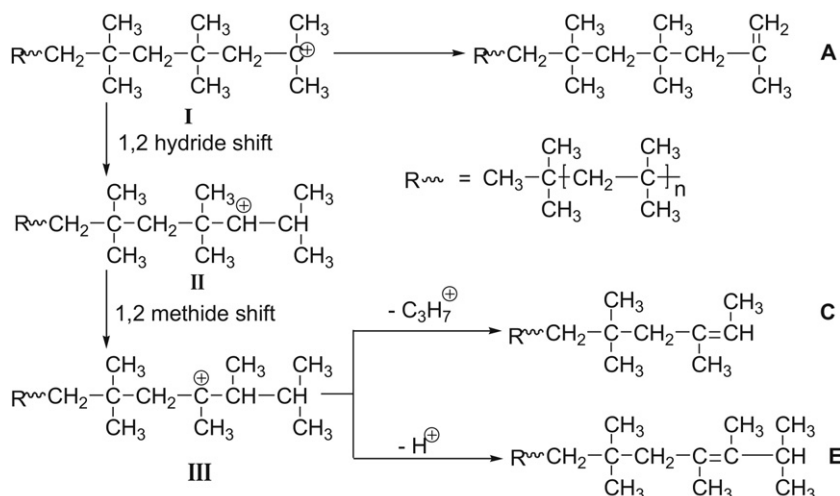


Fig. 1. ^1H NMR spectrum of PIB obtained with $\text{H}_2\text{O}/\text{AlCl}_3$ initiating system (300 MHz). Conditions: $[\text{AlCl}_3] = 0.002 \text{ mol L}^{-1}$; $[\text{IB}] = 1.82 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}] = 0.0007 \text{ mol L}^{-1}$; CH_2Cl_2 ; $T = 0^\circ\text{C}$; $t = 20 \text{ min}$.

to generate the carbenium ion (III), followed by the formation of *tetra*-substituted double bond (structure E) and *tri*-substituted double bond (structure C) respectively [3,20,21]. The strongly coordinating anion (AlCl_3OH^-) facilitates H- and CH_3 -shifts followed by proton or isopropyl elimination to create the internal

unsaturated bonds (structures E and C). These two internal unsaturated structures (C and E) have also been obviously observed in commercial conventional low molecular weight PIBs [2,4,19]. Furthermore, the absence of characteristic resonance signals at $\delta = 1.68$ and 1.96 [22], corresponding to $-\text{CH}_2-$ and $-\text{CH}_3$ protons



Scheme 1. The possible mechanism of formation of *exo*-olefin end groups and transfer side reactions.

in PIB-CH₂-C(CH₃)₂-Cl respectively, indicates that the conventional PIB chains were free of *tert*-Cl terminal groups and the termination via chlorine transfer from counter anion did not take place during polymerization.

We have purposefully sought to produce highly reactive PIBs with *exo*-olefin end groups by exploring the initiating system based on AlCl₃ as coinitiator to optimize β-proton abstraction and to reduce the unexpected transfer side reactions. Further investigations were conducted by introducing dialkyl ether, such as di-*n*-butyl ether (OB₂) or diisopropyl ether (OP₂) into the above conventional IB polymerization system initiated by H₂O/AlCl₃.

The cationic polymerizations of IB were carried out by using H₂O/AlCl₃/OB₂ as initiating system at three different concentrations of OB₂ while keeping other experimental conditions constant. A representative ¹H NMR spectrum of PIB obtained at [OB₂] = 0.021 mol L⁻¹ is shown in Fig. 2. Compared to the expansion of the olefin region shown in Fig. 1, it can be clearly observed from Fig. 2 that the characteristic resonance signals for *exo*-olefin end groups (structure A) appeared obviously at δ = 4.64 and 4.84, whereas both the characteristic resonance signals for internal unsaturated structure C (δ = 5.15 and 5.35) and E (δ = 2.85) are almost undetectable. The content of *exo*-olefin end groups in polymer chains increased greatly to around 88 mol% when [OB₂] was in the range of 0.020–0.022 mol L⁻¹. Therefore, this H₂O/AlCl₃/OB₂ initiating system presented an excellent property for producing the desired highly reactive PIBs (structure A) with results comparable to those in

commercial HRPIB products with the best BF₃-based initiating system. OB₂ played very important roles in promoting the directly rapid β-proton elimination from -CH₃ of the growing chain ends to create *exo*-olefin end groups and decreasing the carbenium ion rearrangements to form the double bond isomers. It has been pointed out that OB₂ (Lewis base) may have some interaction with AlCl₃ (Lewis acid) to moderate the Lewis acidity of AlCl₃ [33]. The weakly coordinating counter anion [AlCl₃(OB₂)OH⁻] would result in more rapid β-proton abstraction from -CH₃ group in the tertiary cation (I) of the growing PIB chain to predominantly produce the *exo*-double bond end groups (structure A). On the other hand, small amount of excess OB₂ probably could act as a Lewis base to suppress the above isomerizations. The transfer side reactions via carbenium ion rearrangements to form the structures of C and E isomers could be almost suppressed in the presence of sufficient amounts of OB₂. The very weak resonance signal (b) at δ = 5.14 for *endo*-olefin end groups (structure B) can be still observed, which is attributed to β-proton abstraction from -CH₂- group in the tertiary cation (I) of growing polymer chain end, as shown in Scheme 2 [13]. Consequently, the directly rapid β-proton abstraction from -CH₃ of the growing PIB chain ends should be responsible for termination of the growing PIB chains and highly reactive PIBs with large amount of *exo*-olefin end groups could be produced with this H₂O/AlCl₃/OB₂ initiating system.

Additionally, there are two visible shoulder peaks (f₂, f₁) at δ = 4.82 and 4.80 to the downfield *exo*-olefin peak (a₁) at δ = 4.84. This weak resonance at δ = 4.82 may be assigned either to CH₂=

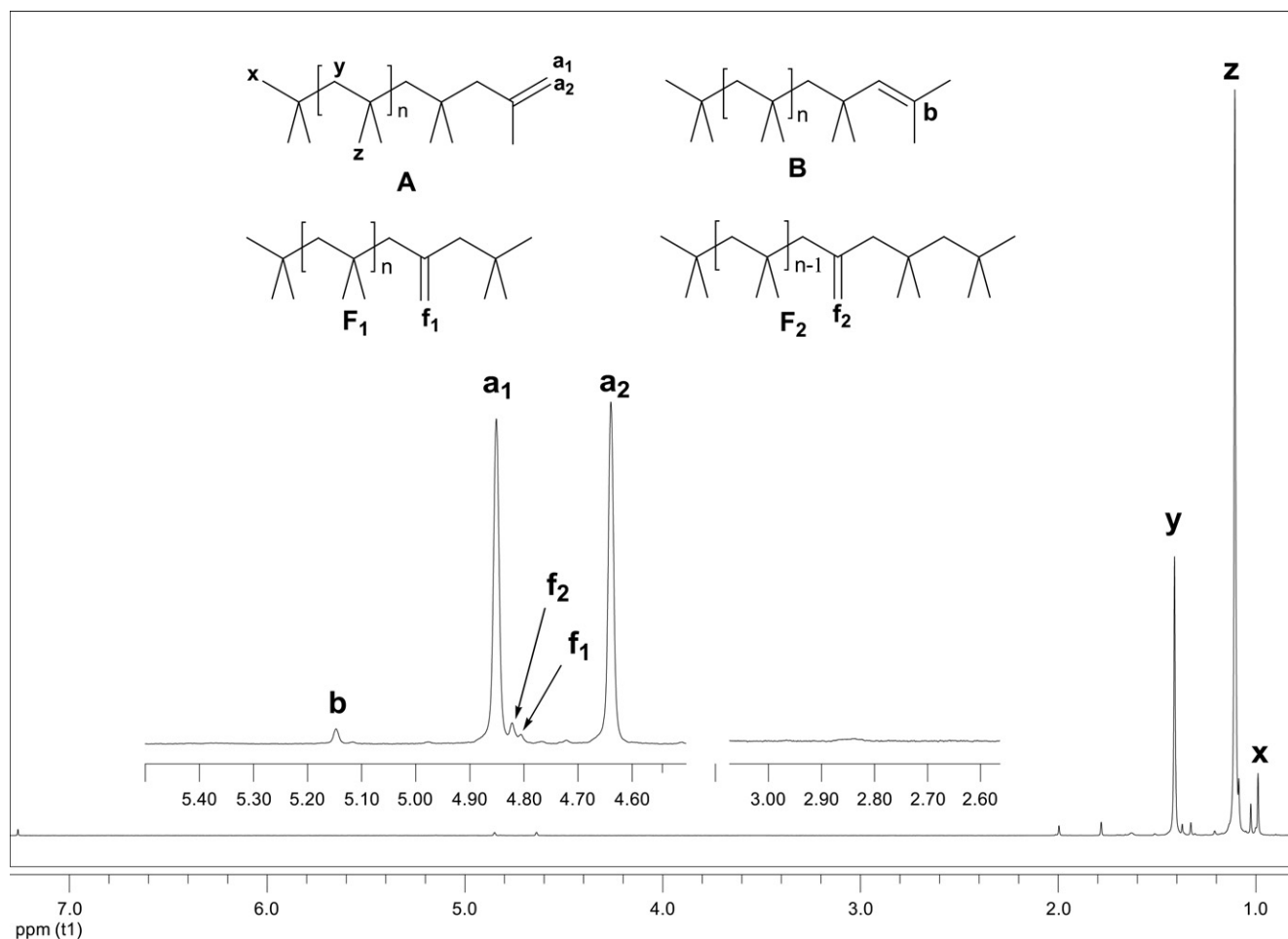
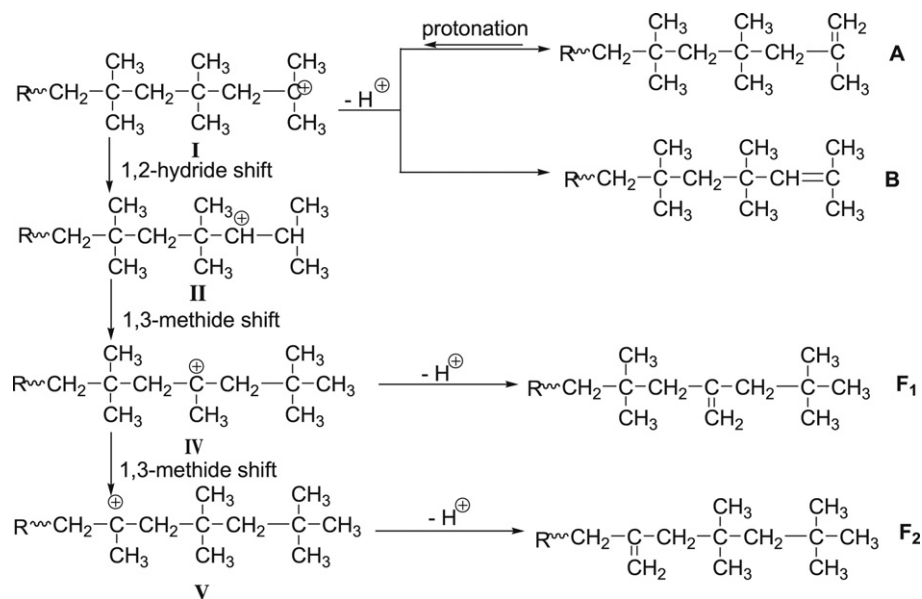


Fig. 2. ¹H NMR spectrum of PIB obtained with H₂O/AlCl₃/OB₂ initiating system (600 MHz). [OB₂] = 0.021 mol L⁻¹; [AlCl₃] = 0.02 mol L⁻¹; [IB] = 1.82 mol L⁻¹; [H₂O] = 0.0012 mol L⁻¹; CH₂Cl₂; T = 0 °C; t = 20 min.



protons of internal vinylenes (structure F₂ in Scheme 2) resulting from carbenium ion rearrangements [1,23] or to the two identical protons of CH₂= in the coupled PIBs formed by the addition of a growing PIB carbenium ion (I) to the *exo*-olefinic end group (A) in another PIB chain [13,24]. If the chain coupling reactions occurred during polymerization, these formed coupled PIBs should be observed as a shoulder in GPC traces corresponding to approximately twice the molecular weight of the main peak and thus leading to broad molecular weight distribution. Actually, it can be seen from Fig. 3 that all the three GPC traces exhibit monomodal and symmetrical distributions ($M_w/M_n \sim 1.8$) with expected low molecular weights. The coupling reactions could be avoided when β -proton abstraction from the growing carbenium ions (I) was sufficiently rapid, which prevents them from reacting with the *exo*-olefin end groups (A) in another PIB chains. Therefore, the resonance signals at $\delta = 4.80$ and 4.82 are unambiguously attributed to the internal vinylenes structures of F₁ and F₂ formed via carbenium

ion rearrangements respectively. As shown in Scheme 2, the tertiary cation (I) of the growing PIB chain end may undergo 1,2-hydride and 1,3-methide shifts to create carbenium ion (IV) followed by formation of structure F₁ via subsequent β -proton elimination. Moreover, the carbenium ion (IV) may further undergo 1,3-methide shift to create carbenium ion (V) followed by formation of structure F₂. These two structures of F₁ and F₂ are very similar and differ only by a shift of the double bond of one monomer unit inside the polymer chain.

In order to support the above experimental results, the cationic polymerizations of IB were further carried out using diisopropyl ether (OP₂) instead of OB₂ at four different concentrations of OP₂ under the other identical conditions as illustrated in Fig. 2. The GPC traces and corresponding data of M_n , M_w/M_n and *exo*-olefin (A) content of the resulting PIBs are presented in Fig. 4. It can be found that all the GPC traces of the PIBs obtained at different OP₂

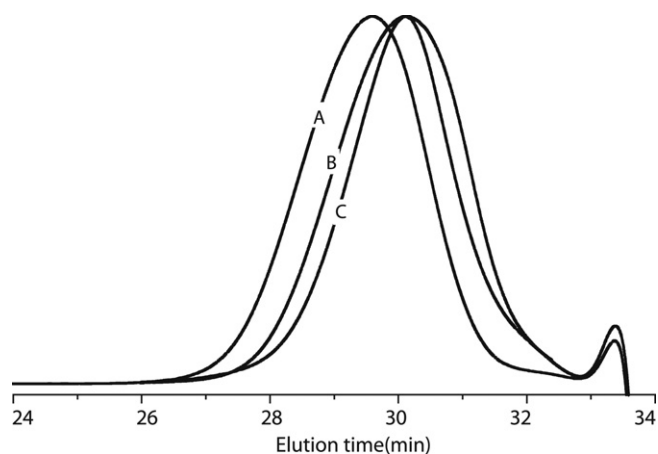


Fig. 3. GPC traces of PIBs obtained with H₂O/AlCl₃/OB₂ initiating system at different OB₂ concentrations. A: [OB₂] = 0.020 mol L⁻¹, $M_n = 2900$ g mol⁻¹, $M_w/M_n = 1.8$, structure A = 87.2 mol%; B: [OB₂] = 0.021 mol L⁻¹, $M_n = 1900$ g mol⁻¹, $M_w/M_n = 1.8$, structure A = 88.5 mol%; C: [OB₂] = 0.022 mol L⁻¹, $M_n = 1800$ g mol⁻¹, $M_w/M_n = 1.8$, structure A = 88.5 mol%.

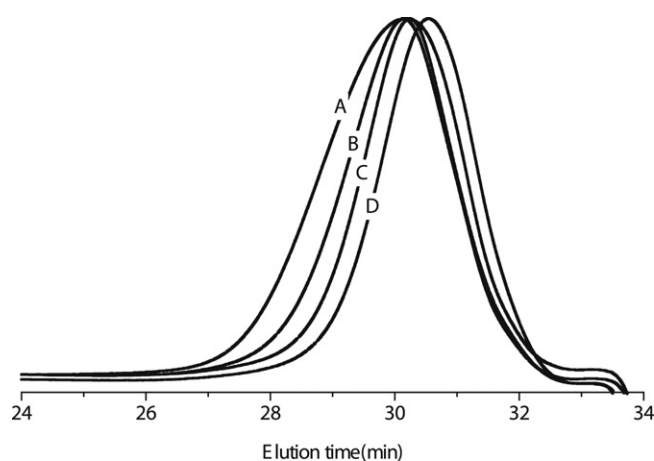


Fig. 4. GPC traces of PIBs obtained with H₂O/AlCl₃/OP₂ initiating system at different OP₂ concentrations. A: [OP₂] = 0.020 mol L⁻¹, $M_n = 1900$ g mol⁻¹, $M_w/M_n = 2.0$, structure A = 88.5 mol%; B: [OP₂] = 0.023 mol L⁻¹, $M_n = 1900$ g mol⁻¹, $M_w/M_n = 1.8$, structure A = 90.1 mol%; C: [OP₂] = 0.025 mol L⁻¹, $M_n = 1700$ g mol⁻¹, $M_w/M_n = 1.7$, structure A = 92.2 mol%; D: [OP₂] = 0.027 mol L⁻¹, $M_n = 1300$ g mol⁻¹, $M_w/M_n = 1.7$, structure A = 92.4 mol%.

concentrations exhibit monomodal and symmetrical distributions ($M_w/M_n = 1.7\text{--}2.0$) with low molecular weight ($M_n = 1300\text{--}1900\text{ g mol}^{-1}$). It has been established that, the propagation rate being first order in monomer concentration, when transfer to monomer is predominant among the chemical events leading to the interruption of chain growth, the number average molar mass is approximately constant or decreased slightly with time and the polydispersity index is equal to 2.0 [16g]. It should also be mentioned that the polydispersity index (PDI, M_w/M_n) of commercial highly reactive PIBs produced industrially by the initiating system consisting of secondary alcohol and/or *tert*-ether with BF_3 is around 2.0, which is a typical of a polymerization process during which the chain propagation process is interrupted by transfer or termination reactions. The HRPIBs having PDIs of $M_w/M_n \sim 1.7$ were obtained via controlled cationic polymerization of isobutylene (IB) using Manganese(II) complexes as initiators (Ref. [8]) and Copper(II) complexes as initiators [8,9]. Therefore, the desired highly reactive PIBs containing 88.5–92.4 mol% of *exo*-olefin end groups could also be successfully prepared with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OP}_2$ initiating system. Fig. 5 gives the representative ^1H NMR spectrum of highly reactive PIB obtained with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OP}_2$ initiating system at $[\text{OP}_2] = 0.027\text{ mol L}^{-1}$.

Therefore, highly reactive PIBs with large contents of *exo*-olefin end groups (structure A, 87.2–92.4 mol%) could be successfully synthesized via the cationic polymerization of IB with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ or OP_2 initiating system. It should be noted that these bulky weakly coordinating counter anions consisting of OB_2 or OP_2 caused much more β -proton abstraction from $-\text{CH}_3$ group than that from $-\text{CH}_2-$ group in the normal tertiary cations (I) and thus led to the dominant formation of *exo*-olefin end groups (structure A)

rather than *endo*-olefin (structure B). On the other hand, dialkyl ethers (OB_2 or OP_2) play a very important role to moderate the Lewis acidity of AlCl_3 and the cationicity of the normal tertiary cation (I) of growing PIB chain and thus to decrease greatly the unexpected transfer side reactions (isomerizations) to form structures of C, E, F_1 and F_2 .

According to the above observations, this is an indication of a chain transfer dominated polymerization process involving serious β -proton elimination from $-\text{CH}_3$ group in the normal tertiary cations (I). Therefore, the role of bulky OB_2 or OP_2 in this AlCl_3 -coinitiated polymerization system has probably some differences from the mechanistic roles of external Lewis base in the living cationic polymerization of isobutylene or styrene, in which led to the formation of dormant species with chloro-end groups [25]. To elucidate the polymerization mechanism, further investigations on the cationic polymerization of IB with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ initiating system were conducted with a special focus on the influences of AlCl_3 concentration, polymerization time and temperature on monomer conversion, M_n , M_w/M_n and unsaturated structures in PIB chains.

The influences of AlCl_3 concentration and polymerization time were investigated and the experimental results are summarized in Table 1. Figs. 6 and 7 give the typical ^1H NMR spectra in the $\delta = 4.5\text{--}5.3$ olefin region of PIB products obtained at different AlCl_3 concentrations from 0.005 to 0.04 mol L^{-1} ($t = 20\text{ min}$) and at different polymerization times from 2 to 60 min ($[\text{AlCl}_3] = 0.04\text{ mol L}^{-1}$) respectively. AlCl_3 concentration is one of the most important variables in controlling polymerization degree, molecular weight and different unsaturated structures as mentioned above. The monomer conversion increased while M_n decreased and MWD narrowed with

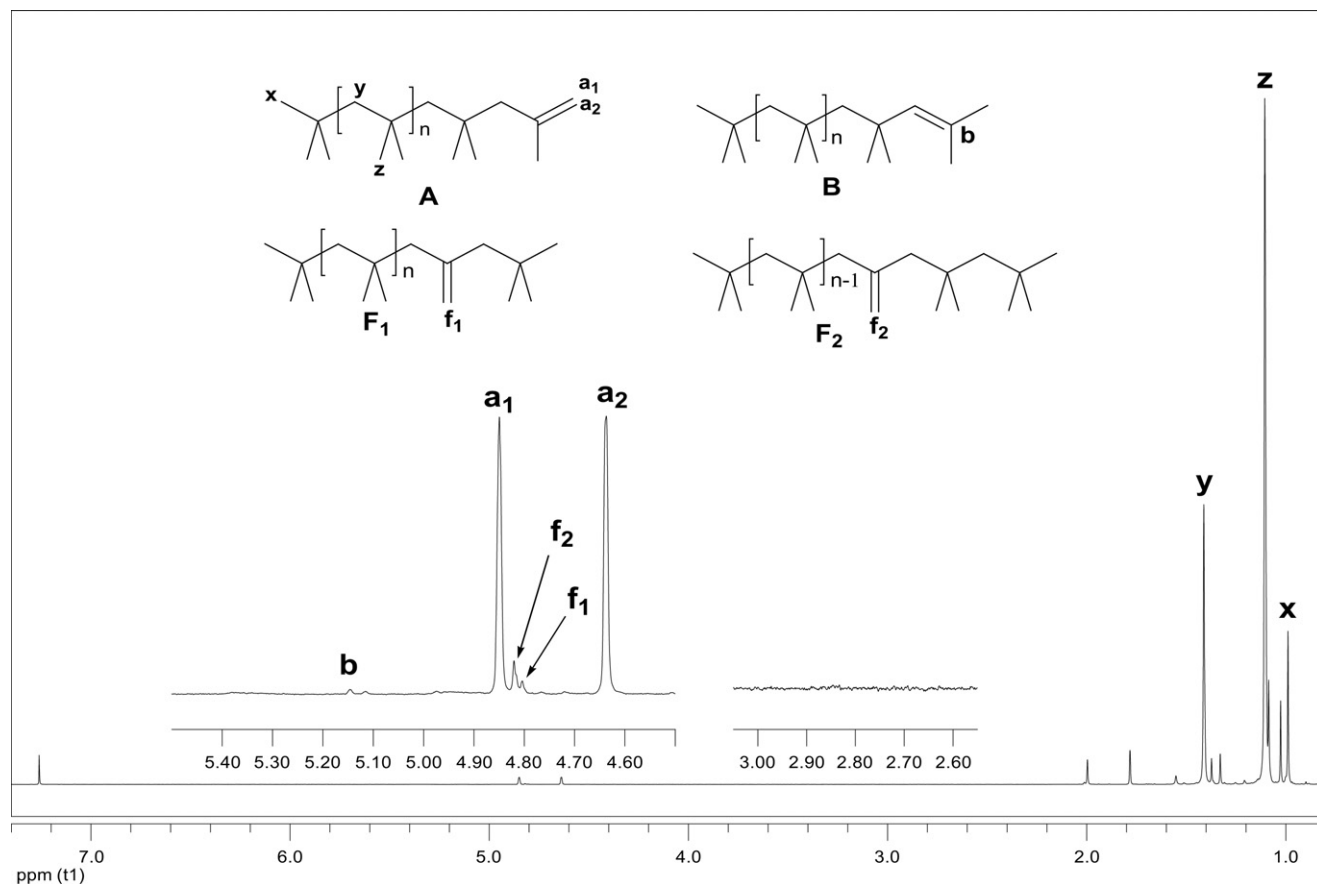


Fig. 5. ^1H NMR spectrum (600 MHz) of HRPIB obtained with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OP}_2$ initiating system ($[\text{OP}_2] = 0.027\text{ mol L}^{-1}$).

Table 1
Effects of AlCl_3 concentration and polymerization time on monomer conversion, M_n , M_w/M_n and unsaturated structures of PIBs.

| No. | $[\text{AlCl}_3]$ (mol L^{-1}) | Time (min) | Conv (%) | Content of various structures in PIB chains (mol%) | | | | M_n (g mol^{-1}) | M_w/M_n |
|-----|--|---------------|----------|--|-----|-------|-------|----------------------------------|-----------|
| | | | | A | B | F_1 | F_2 | | |
| 14 | 0.005 | 20 | 23 | 88.7 | 4.4 | 0.9 | 1.3 | 3300 | 2.4 |
| 21 | 0.01 | 2 | 24 | 93.8 | 4.6 | 0 | 0 | 3100 | 2.3 |
| 22 | 0.01 | 10 | 32 | 88.9 | 4.4 | 0.9 | 2.2 | 3100 | 2.2 |
| 23 | 0.01 | 20 | 40 | 88.2 | 4.4 | 0.9 | 2.6 | 2900 | 2.4 |
| 24 | 0.01 | 40 | 52 | 86.6 | 4.3 | 1.3 | 3.9 | 2700 | 2.3 |
| 25 | 0.01 | 60 | 60 | 86.0 | 4.3 | 2.4 | 3.4 | 2500 | 2.4 |
| 26 | 0.02 | 2 | 34 | 90.0 | 3.7 | 0.9 | 3.2 | 2600 | 1.8 |
| 27 | 0.02 | 10 | 48 | 88.0 | 4.4 | 1.3 | 3.0 | 2300 | 1.8 |
| 28 | 0.02 | 20 | 55 | 87.3 | 4.3 | 1.7 | 4.3 | 2200 | 1.9 |
| 29 | 0.02 | 40 | 61 | 83.1 | 4.2 | 2.1 | 6.2 | 2000 | 1.9 |
| 30 | 0.02 | 60 | 69 | 80.1 | 4.8 | 2.8 | 6.4 | 2200 | 1.9 |
| 15 | 0.03 | 20 | 58 | 84.5 | 4.2 | 2.1 | 5.9 | 1800 | 1.8 |
| 31 | 0.04 | 2 | 49 | 86.5 | 4.3 | 1.3 | 4.3 | 1700 | 1.7 |
| 32 | 0.04 | 10 | 57 | 84.0 | 4.2 | 2.1 | 5.8 | 1600 | 1.9 |
| 33 | 0.04 | 20 | 60 | 80.8 | 4.8 | 2.8 | 7.2 | 1700 | 1.8 |
| 34 | 0.04 | 40 | 72 | 78.6 | 4.6 | 2.7 | 10.0 | 1500 | 1.7 |
| 35 | 0.04 | 60 | 75 | 76.5 | 4.5 | 4.5 | 10.2 | 1500 | 1.8 |

$[\text{OB}_2]/[\text{AlCl}_3] = 1.01$; CH_2Cl_2 ; $[\text{IB}] = 1.82 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}] = 0.0012 \text{ mol L}^{-1}$ $T = 0^\circ\text{C}$ (bath); $t_p = 20 \text{ min}$.

increasing $[\text{AlCl}_3]$ at every set of the same polymerization time. It suggests that the number of initiating species and initiation rate will be increased by increasing $[\text{AlCl}_3]$ and the anionic organometallic species may be involved in promoting the β -proton elimination from $-\text{CH}_3$ group in the normal tertiary carbocations and chain transfer to monomer. The highly reactive PIBs with more than 80% of *exo*-olefin end groups (structure A), having M_n s of 1700–3300 g mol^{-1} and M_w/M_n of around 2.0, could be prepared at different AlCl_3 concentrations for appropriate reaction time. However, the content of *exo*-olefin end groups (structure A) in PIB chains decreased to some extents from 88.7 to 80.8 mol% with increasing AlCl_3 concentration from 0.005 to 0.04 mol L^{-1} due to the increase in total contents of F_1 and F_2 from 2.2 to 10.0 mol% in the case of 20 min. It can be observed from Table 1 and Fig. 6 that both the characteristic resonances at $\delta = 4.80$ and 4.82 for internal vinylenes (F_1 and F_2) were enhanced while the content of *endo*-olefin end groups (B) kept almost unchanged at ~ 4.4 mol% with increasing $[\text{AlCl}_3]$. Furthermore, it can be found that high concentration of AlCl_3 in polymerization system also led to more formation of internal vinylenes (F_1 and F_2) at similar monomer conversions, such as at around 60% conversions (run No. 25, 29, 33 in Table 2). Therefore, transfer reaction to create isomers F_1 and F_2 could be promoted at higher AlCl_3 concentrations. The content of structure F_1 is normally less than that of structure F_2 for each PIB sample in Table 1. The effect of polymerization time at $[\text{AlCl}_3] = 0.01, 0.02$ and 0.04 mol L^{-1} respectively indicates that the cationic polymerization of IB initiated by $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ proceeded with a relatively rapid rate and monomer conversion gradually increased with polymerization

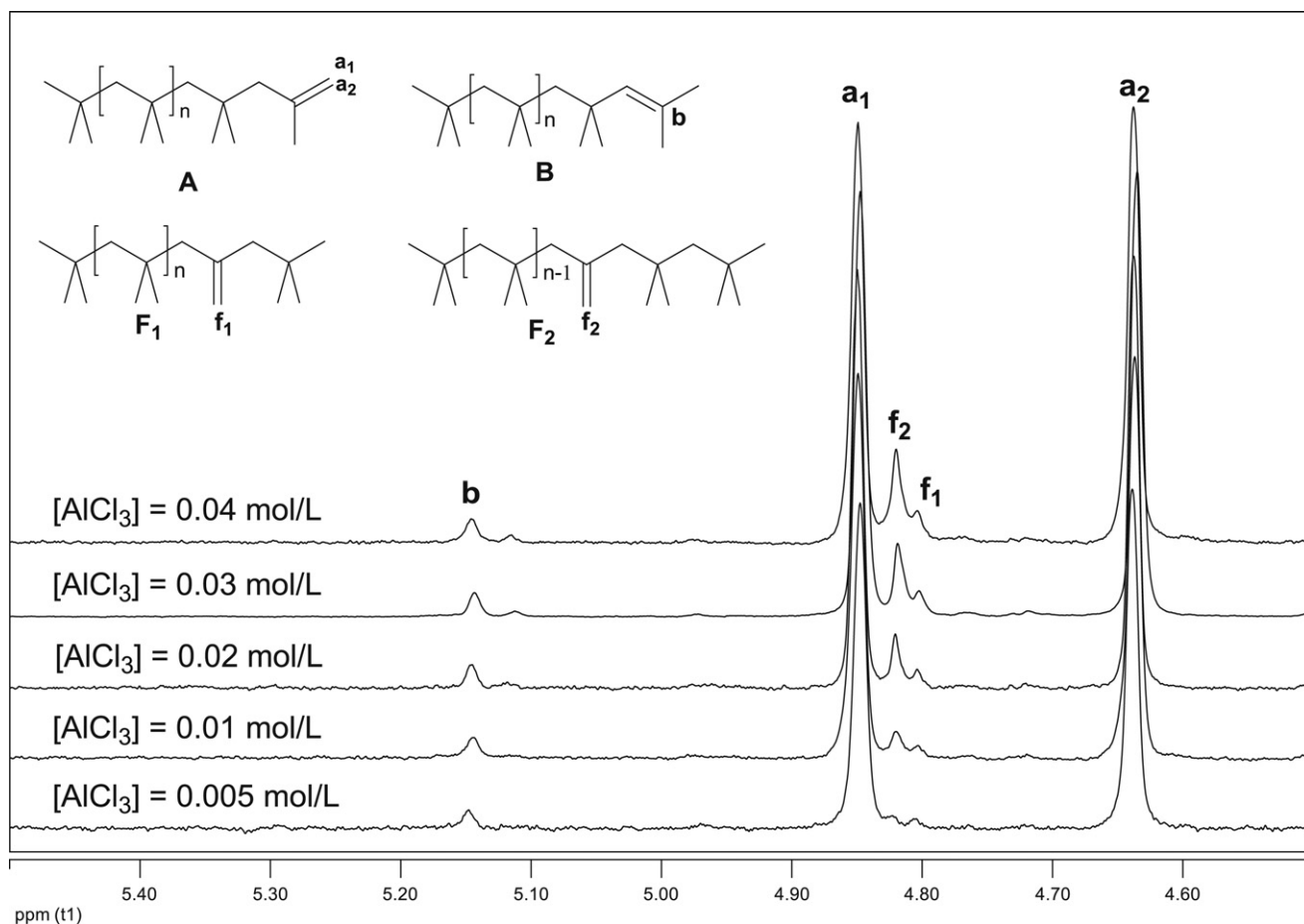


Fig. 6. ^1H NMR spectra in the 4.5–5.3 region (600 MHz) of PIBs obtained with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ initiating system at different AlCl_3 concentrations ($t = 20 \text{ min}$).

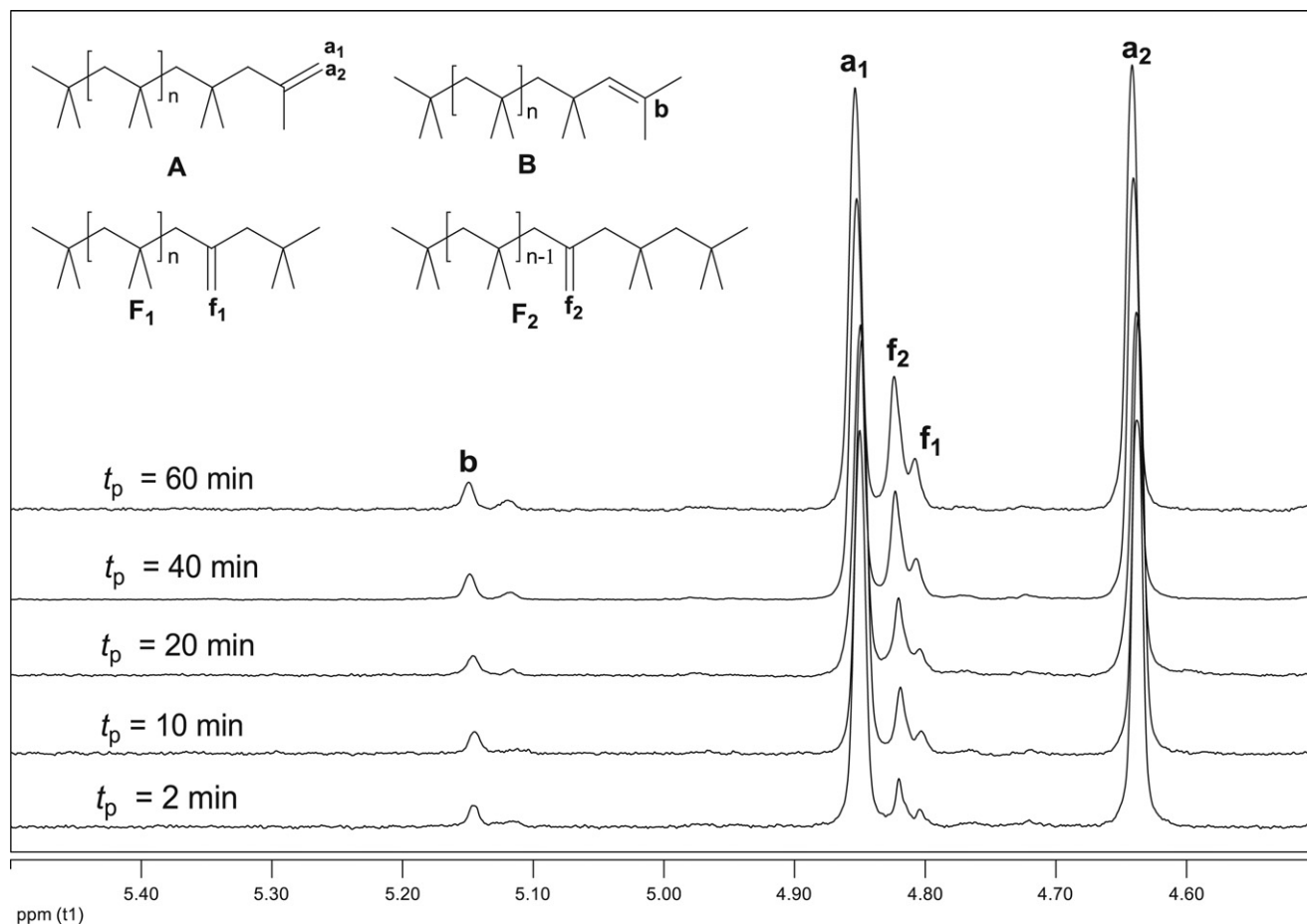


Fig. 7. ^1H NMR spectra (600 MHz) of PIBs obtained with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ initiating system at various reaction times ($[\text{AlCl}_3] = 0.04 \text{ mol L}^{-1}$).

time. When $[\text{AlCl}_3] = 0.01 \text{ mol L}^{-1}$, the content of *exo*-olefin end groups was 93.8 mol% after 2 min of polymerization and then gradually reduced to 86 mol% after 60 min. The nearly similar effect of polymerization time on *exo*-olefin end groups can be observed when $[\text{AlCl}_3] = 0.02$ or 0.04 mol L^{-1} . It can be also observed from Table 1 and Fig. 7 that contents of internal vinylenes of F_1 and F_2 increased definitely with reaction time from 2 to 60 min at different AlCl_3 concentrations. The content of *endo*-olefin end groups (structure B) in PIB chains was hardly affected by prolonging polymerization time from 2 to 60 min. Consequently, it may be suggested that some of the *exo*-olefin end groups (A) formed initially could be further protonated to recreate the normal PIB carbenium ion (I) at high concentration of Lewis acid and/or by prolonging reaction time. And then (I) further underwent carbenium ion rearrangements and resulted in formation of internal vinylenes (F_1 and F_2) ultimately, as shown in Scheme 2.

Table 2

Effect of polymerization temperature on monomer conversion, M_n , M_w/M_n and double bond structures of PIBs.

| Run. | T_p ($^\circ\text{C}$) | Conv (%) | Content of various structures in PIB chains (mol%) | | | | M_n (g mol^{-1}) | M_w/M_n |
|------|----------------------------|----------|--|-----|--------------|--------------|-------------------------------|-----------|
| | | | A | B | F_1 | F_2 | | |
| 41 | 20 | 45 | 82.0 | 6.5 | 1.2 | 4.9 | 1500 | 1.8 |
| 42 | 10 | 43 | 84.0 | 5.0 | 1.3 | 5.5 | 1900 | 2.1 |
| 43 | 0 | 43 | 86.5 | 4.3 | 1.3 | 5.2 | 2200 | 2.1 |
| 44 | -10 | 44 | 86.5 | 4.3 | 1.3 | 4.9 | 2800 | 2.1 |
| 45 | -20 | 43 | 88.4 | 3.5 | 1.3 | 4.9 | 3800 | 2.2 |

$[\text{OB}_2]/[\text{AlCl}_3] = 1.03$; CH_2Cl_2 ; $[\text{IB}] = 1.82 \text{ mol L}^{-1}$; $[\text{H}_2\text{O}] = 0.0008 \text{ mol L}^{-1}$; $t = 20 \text{ min}$.

These results are similar to the observations reported for the isomerization of end groups in PIB chains at high concentration of Lewis acid (BF_3 , TiCl_4 , MeAlBr_2 or Me_2AlBr) and for long polymerization time [1,20,26]. It can be concluded that highly reactive PIBs with large proportion of *exo*-olefin end groups (structure A) could be favorably prepared under the appropriate conditions of low AlCl_3 concentration and/or short polymerization time.

Polymerization temperature is also a critical factor for the propagation and termination in cationic polymerization of IB. Both the β -proton elimination and transfer side reactions (isomerizations) will be increased by increasing reaction temperature, which is a common problem in the conventional cationic polymerization of IB. To examine the effect of polymerization temperature, the cationic polymerizations of IB with $\text{H}_2\text{O}/\text{AlCl}_3/\text{OB}_2$ initiating system were conducted at various temperatures ranging from -20 to 20 $^\circ\text{C}$. The detail information from GPC and ^1H NMR characterization is listed in Table 2. It can be seen that the content of *exo*-olefin end groups (structure A) in PIB chains decreased slightly from 88.4 to 82.0 mol% with increasing temperature from -20 to 20 $^\circ\text{C}$ due to the corresponding 3 mol% of increase in *endo*-olefin end groups (structure B). Higher temperature will accelerate the β -proton elimination but decrease the selectivity from $-\text{CH}_3$, leading to decreases in molecular weight and *exo*-double bonds while increase in *endo*-double bonds. The β -proton elimination from $-\text{CH}_2-$ group to form *endo*-double bond terminal groups slightly increased with polymerization temperature, whereas total β -proton elimination from $-\text{CH}_3$ and $-\text{CH}_2-$ group and isomerization were almost independent on polymerization temperature. The content of structure F_1 or F_2 actually kept almost unchanged with increasing polymerization temperature,

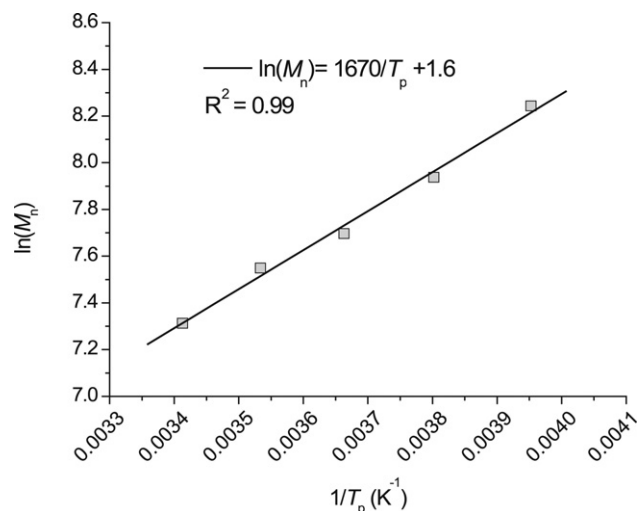


Fig. 8. Arrhenius plot of $\ln(M_n)$ versus $1/T_p$ for cationic polymerization of IB with $H_2O/AlCl_3/OB_2$ initiating system.

as shown in Table 2. Very interestingly, low molecular weight HRPIBs ($M_n = 1500\text{--}1900\text{ g mol}^{-1}$) carrying 82.0–84.0 mol% of *exo*-olefin end groups could be achieved even at room temperatures of 10–20 °C. The inverse effect of polymerization temperature on molecular weights is quantitatively expressed by Arrhenius equation, i.e. $\ln M_n = \ln A - \Delta E/RT$, that is M_n depends on $1/T_p$ [27]. The overall activation energy difference (ΔE or E_{DP}) was calculated to be -13.9 kJ mol^{-1} from the slope of the linear Arrhenius plot of $\ln(M_n)$ vs $1/T_p$ for the temperature interval from -20 to 20 °C, as shown in Fig. 8. The molecular weights of PIBs obtained with this $H_2O/AlCl_3/OB_2$ initiating system are therefore less temperature dependent than for conventional $AlCl_3$ -coinitiating system from -100 to -30 °C ($E_{DP} = -23\text{ kJ mol}^{-1}$) [28]. Furthermore, both the β -protons eliminated from $-CH_3$ and $-CH_2-$ group can reinitiate monomer to form new polymer chains, resulting in little difference in molecular weight distribution in such polymerization system. The polymerization for HRPIBs is thought to be a dominant chain transfer process. Higher temperature will accelerate the β -proton elimination, leading to broad MWD of the obtained polymers. One should expect to obtain polymers with broad MWD at high temperature. However, the PDI of PIBs obtained almost kept constant at ~ 2.1 at polymerization temperature from -20 to 10 °C and PDI was 1.8 for the PIB obtained at 20 °C, as shown in Table 2. It seems that the polymers with low PDIs have been obtained at higher temperature. This result is similar to those reported by Mandal et al. [29], in which the MWDs of the polystyrenes obtained at -25 °C and 0 °C were relatively broader compared to that obtained for polystyrenes prepared at 25 °C.

On the other hand, it has been found that the equilibrium between the dormant species and the active species during the cationic polymerization also affected the MWDs of the obtained polymers and that fast equilibrium was required to prepare the polymers with narrow MWDs [30–32]. Therefore, as mentioned in the cationic polymerization of styrene [29], it is proposed that the unchanged MWDs or even narrow MWD with increasing polymerization temperature is possibly due to the increasing equilibrium rate between the dormant and the activated species [29,30].

4. Conclusions

This initiating system of $H_2O/AlCl_3$ /dialkyl ether was successfully developed for the cationic polymerization of isobutylene to prepare low molecular weight polyisobutylenes ($M_n = 1300\text{--}2200\text{ g mol}^{-1}$; $M_w/M_n = 1.7\text{--}2.0$) with *exo*-olefin end groups (structure A) of more

than 80 mol%, even up to 94 mol% at 0 °C or higher temperatures. These obtained highly reactive polyisobutylenes can be comparable to those produced industrially by the best BF_3 -based initiating system. The more weakly coordinating counter anion mediated by bulky dialkyl ether resulted in more rapid β -proton abstraction from $-CH_3$ group in the tertiary cations (I) of the growing PIB chains and less isomerization through carbenium ion rearrangements, thus to predominantly produce highly reactive PIBs with *exo*-double bond end groups. The carbenium ion rearrangements via 1,2-hydride and 1,2-methide shifts leading to formation of internal double bond isomers (structures C and E) could be suppressed by the introduction of sufficient dialkyl ether. The internal vinylene isomers (structures F_1 and F_2) created via 1,2-hydride and 1,3-methide shifts could also be reduced with decreasing $AlCl_3$ concentration and/or shortening polymerization time. The content of *endo*-olefin end groups (structure B) in PIB chains increased slightly with polymerization temperature by 3% from -20 to 20 °C. It can be found that high content of *exo*-olefin end groups in the resulting polyisobutylenes could be favorably achieved by decreasing $AlCl_3$ concentration, polymerization temperature and time. Further investigation of this system is currently underway in our laboratory.

Acknowledgments

The financial supports from the National Natural Science Foundation of China (Grant No. 20774008 and 20934001) are greatly appreciated.

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