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Polyisobutylene with High *exo*-Olefin Content via *β*-H Elimination in the Cationic Polymerization of Isobutylene with $H_2O/FeCl_3$/Dialkyl Ether Initiating System

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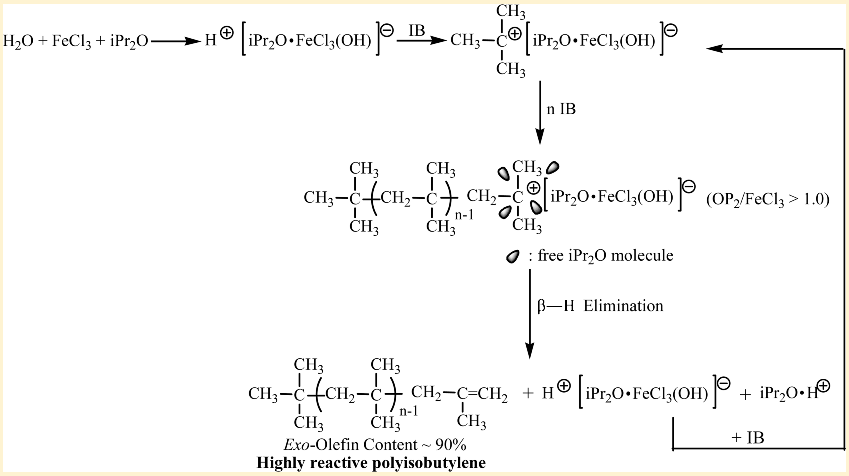
ABSTRACT:



The cationic polymerizations of isobutylene (IB) with $H_2O/FeCl_3$/dialkyl ether initiating system were conducted in dichloromethane (CH_2Cl_2) at temperatures from −20 to +20 °C, in which the dialkyl ether includes diethyl ether (Et_2O), dibutyl ether (Bu_2O) or diisopropyl ether (iPr_2O). The highly reactive polyisobutylenes (HRPIBs) with high content of *exo*-olefin end groups ($-CH_2-C(CH_3){=}CH_2$) 82−91 mol % and acceptable monomodal molecular weight distribution ($M_w/M_n = 1.7-2.3$) could be successfully synthesized at low concentration of $FeCl_3$ at 0.005 $mol \cdot L^{-1}$ at 0 or even 10 °C. These results are comparable to those of commercial HRPIBs produced industrially at far below 0 °C. The directly rapid *β*-proton elimination from $-CH_3$ of the growing chain ends and chain transfer reaction to monomer were dependent on concentration of $iPr_2O \cdot FeCl_3$ complex (1:1), concentration of free iPr_2O ($[\text{free } iPr_2O] = [iPr_2O] - [FeCl_3]$) if ($iPr_2O \cdot FeCl_3 > 1$) and polymerization time. The much higher concentration of PIB chains formed in the polymerization system (C_{PIB}) than that of components in initiating system indicates a chain-transfer dominated caionic polymerization process. To the best of our knowledge, this is the first example to achieve HRPIBs with such high *exo*-olefin end groups by $FeCl_3$-based initiating system.

■ INTRODUCTION

The *β*-proton elimination from the growing chain ends in cationic polymerization of vinyl monomers is one of the most important chain-breaking reactions to decrease molecular weight and to form *exo*- and/or *endo*-double bonds at the end groups. The *β*-proton elimination and chain transfer reaction to monomer should be suppressed in the living cationic polymerization of isobutylene (IB), however, it can be beneficially used to prepare polyisobutylenes (PIBs) with desired reactive *exo*-olefin end groups.[1] The polyisobutylenes (PIBs) with more than 60 mol % of *exo*-olefin terminals, preferably more than 75 mol %, are normally referred to as "highly reactive" PIBs (HRPIBs) since only terminal *exo*-olefin terminal has a sufficiently high reactivity.[2−4] HRPIBs differ from those conventional PIBs and have found applications as intermediates in the preparation of additives for fuels and lubricants since only terminal *exo*-olefin has a sufficiently high reactivity. 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 co-initiator, which having low reactivity for further functionalization reactions.[4−8] The high content of *exo*-olefin end groups is one of the most important quality criteria for HRPIBs. HRPIBs can react with maleic anhydride by direct addition reaction to synthesize PIB/maleic anhydride adducts and have found applications as intermediates in the preparation of additives for fuels and lubricants.[2−4]

Received: November 26, 2010
Revised: February 11, 2011
Published: March 11, 2011

Commercial HRPIBs with low molecular weight HRPIBs (M_ns ≈ 800−2300 g·mol^{-1}) and more than 80 mol % *exo*-olefin end groups can be produced by a single-step process via cationic polymerization of IB in hexane with the complexes of BF_3 with secondary aliphatic alcohol and/or ether as initiating systems at temperatures from −60 to 0 °C.[2] Heteropolyacids were used to produce highly reactive polyisobutylene with quite broad molecular weight distributions.[4] Recently, the initiating systems consisting of solvent-ligated $[M(NCMe)_6]^{2+}$ (M^{II} = Mn, Cu, Mo, Fe, or Zn) complexes with the bulky, noncoordinating counterions such as $[C_3H_3N_2\{B(C_6F_5)_3\}_2]^-$ have been reported for preparing HRPIBs with M_ns of 600−7000 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.[9−12] 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_ns of 10000−29000 g·mol^{-1} and M_w/M_n of 1.9−2.5 at room temperature.[13] Very recently, a simple and efficient $H_2O/AlCl_3$/dibutylether or diisopropylether initiating system has been developed in our lab to prepare HRPIBs carrying high contents of *exo*-olefin end groups even up to 93 mol % and having low M_n of 1300 - 3800 g·mol^{-1} at −20 to +20 °C in CH_2Cl_2.[14] It was also reported that 2-phenyl-2-propanol (CumOH) in combination with $AlCl_3$ OBu_2 complex was used to synthesize HRPIBs (M_n = 1000−5000 g·mol^{-1}) containing 86−95% of *exo*-olefin end groups at rather lower reaction temperatures (−60 to −20 °C).[15] However, the relatively high $AlCl_3$ concentration of around 0.02 mol·L^{-1} was needed to co-initiate the cationic polymerization of IB.[14,15] On the other hand, HRPIBs could also be prepared by specific termination reaction after completion of cationic polymerization or modification from *tert*-chloro-terminated functional PIB chains.[16−19] The inifer technique provided the first reliable route for the preparation of well-defined *tert*-chloride-terminated PIBs, which represents a milestone for the macromolecular engineering of cationic polymerization.[20] The cationic polymerization of IB co-initiated by $FeCl_3$ normally led to conventional PIBs with very broad molecular weight.[21,22]

According to the mechanism in cationic polymerization of isobutylene, the β-H elimination from $-CH_3$ or $-CH_2-$ in polymer chain ends leads to the possible formation of expected *exo*-olefin and unexpected *endo*-olefin end groups, respectively. In this paper, we continue our serial research on the direct synthesis of HRPIBs with large proportions (even up to 91%) of *exo*-olefin terminal groups by developing $H_2O/FeCl_3$/dialkyl ether initiating system to increase the selectivity for β-H elimination from $-CH_3$. The effects of polymerization conditions on monomer conversion, number-average molecular weight (M_n), molecular weight distribution (MWD) and double bond structures of the resulting PIBs were investigated. The possible mechanistic for the synthesis of HRPIBs via cationic polymerization of IB with $H_2O/FeCl_3$/dialkyl ether initiating system was proposed.

EXPERIMENTAL SECTION

Materials. Dichloromethane (CH_2Cl_2; AR.; Beijing Yili Fine Chemical Co.) and *n*-hexane (n-Hex; AR.; Beijing Yili Fine Chemical Co.) were purified as described previously.[14,23] Tetrahydrofuran (THF; AR.; Beijing Yili Fine Chemical Co.), diethyl ether (Et_2O; 99%; Tianjin Fuchen Chemical Co.; packaging under nitrogen), dibutylether (Bu_2O; 99%; Tianjin Fuchen Chemical Co.; packaging under nitrogen) and diisopropylether (iPr_2O; 99%; Tianjin Guangfu Chemical Co.; packaging under nitrogen) were distilled from CaH_2 before use. Anhydrous $FeCl_3$ (99%, Alfa Chem. Co.; packaging under nitrogen), isobutylene (IB; 99.9%; Beijing Yanshan Petroleum Chemical Co.) and ethanol (Analytical Reagent) were used as received.

Procedures. All the manipulation, reactions and cationic polymerizations were carried out under a dry nitrogen (N_2) atmosphere. General procedures of reagents were as described as our previous work.[14,23] Specific reaction conditions are listed in the captions of figures and tables. Isobutylene polymerizations were conducted under dry N_2 atmosphere in a tube reactor (~120 mL). The monomer solution in CH_2Cl_2 ($[IB]_0$ = 2 mol·L^{-1}) was prepared in a chilled 1000 mL round-bottom flask at −40 °C. Then, 20 mL of the monomer solution was air-tightly transferred to every test tube (~120 mL) via a 20 mL volumetric pipet and cooled at the desired reaction temperature for about 38 min. The cationic polymerization was started by addition of the mixed solution of $FeCl_3$ and dialkyl ether in CH_2Cl_2 with syringe. The reaction system was quenched and neutralized at predetermined times by injection of 4 mL ethanol containing 1% NaOH. After evaporation of the volatiles, the polymer was rewashed with *n*-hexane and ethanol. The polymer products were dried in a vacuum oven at 40 °C to a constant weight overnight. The monomer conversion was determined gravimetrically.

Instrumentation. The H_2O concentration in the components and in the polymerization system was monitored electrochemically with a SF-6 water determination apparatus (Shandong Zibo Water Analytical Co.) in conjunction with a Karl−Fischer reagent for coulometric titration according to the method described.[14,23] The molecular weight and molecular weight distribution (MWD; i.e., M_w/M_n) of the polymers were determined with a Waters 515−2410 gel permeation chromatography (GPC) system equipped with four Waters styragel columns connected in the following series: 500, 10^3, 10^4, and 10^5 at 30 °C. THF was 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}. The calibration of molecular weight was based on polystyrene standards. NMR spectroscopy of the polymers was performed on a Bruker AV600 MHz spectrometer using $CDCl_3$ as a solvent at 25 °C. ^{1}H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H = 0.00). The FTIR spectra were recorded by a Nicolet 6700 spectrophotometer with a diamond tipped attenuated total reflection (ATR) immersion probe (Axiom DMD-270X-LT), as described as our previous work.[24] The interaction of diisopropylether (iPr_2O) with $FeCl_3$ in CH_2Cl_2 was monitored by immersing the attenuated total reflection (ATR) probe into the glass reactor at 0 °C. FTIR data collection and processing were performed with Nicolet's OMNIC Series software. The FTIR spectrum of CH_2Cl_2 was chosen as the background for spectrum record. Each spectrum was collected every 32s by accumulating 32 scans with an instrument resolution of 4 cm^{-1} over the spectral range of 800 to1200 cm^{-1}.

RESULTS AND DISCUSSION

Cationic Polymerization of IB with $H_2O/FeCl_3$ Initiating System. The control experiment of the cationic polymerization of IB initiated by $H_2O/FeCl_3$ was carried out for comparison in the absence of dialkyl ether at 0 °C and the resulting polyisobutylene (PIB) was subjected to GPC and ^{1}H NMR analyses. This conventional cationic polymerization of IB was an uncontrolled process, resulting in a nearly complete conversion within 10 min and PIB with M_n of 3300 g·mol^{-1} and a quite broad MWD (M_w/M_n = 3.48), which is similar to the results reported by Plesch, Kennedy, and their co-workers in a series of papers and books.[25−27] The ^{1}H NMR spectrum in Figure 1 shows that this PIB product carried several complicated isomerized end groups. The strong resonance signals at δ = 1.11 (z) and 1.42 (y) are assigned to the $-CH_3$ and $-CH_2$ protons of the structural units along the main chain of PIB respectively. The resonance at δ = 0.99 (x) for the protons in headgroup of $-C(CH_3)_3$ confirmed that the initiating active center H^+ ($FeCl_3OH^-$) induced the cationic polymerization of IB.[25,26,28] The β-proton abstraction from the

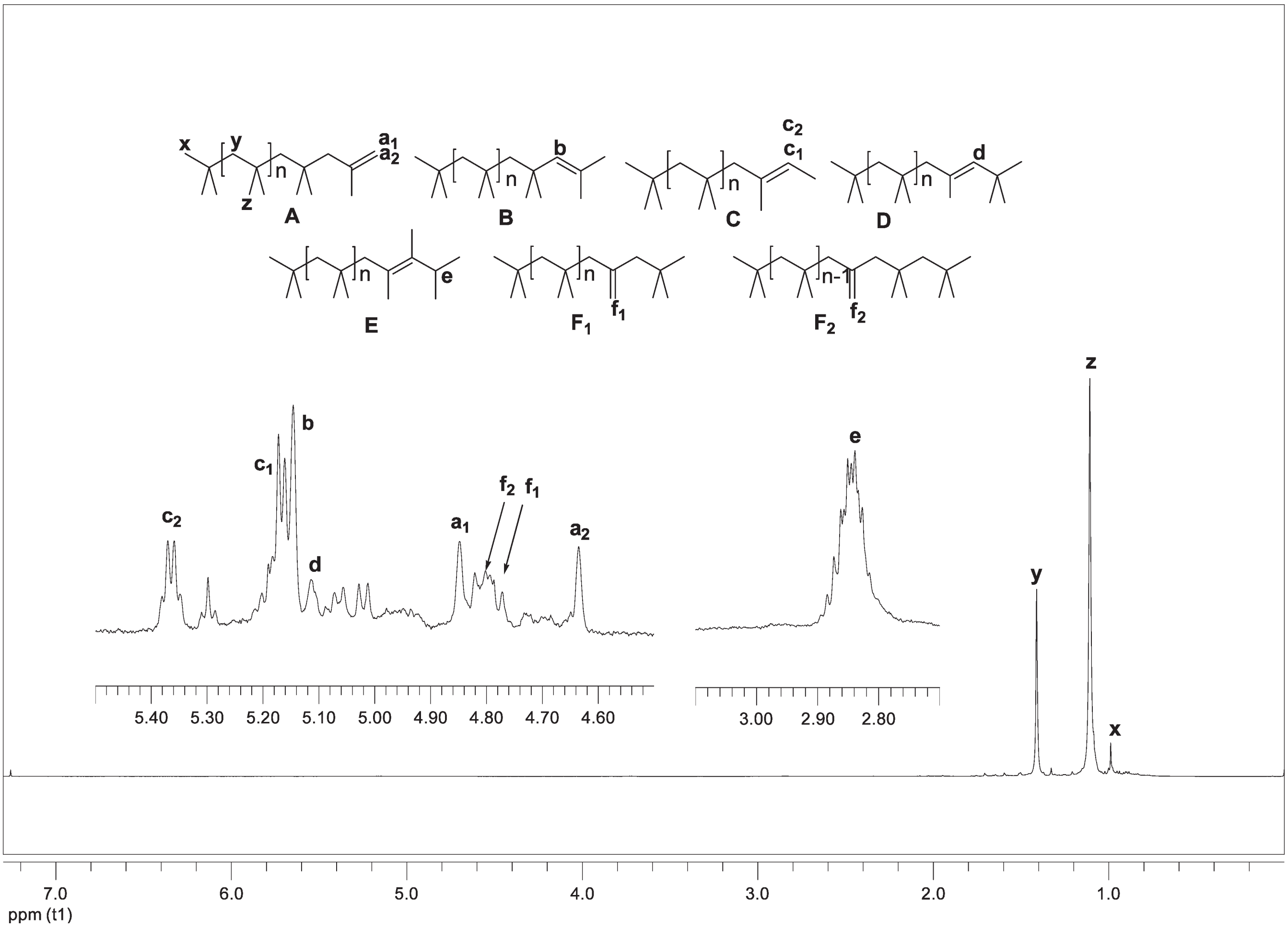


Figure 1. ^1H NMR spectrum of PIB obtained with $H_2O/FeCl_3$ initiating system in the absence of dialkyl ether. $[H_2O] = 1.1\ mmol \cdot L^{-1}$; $[FeCl_3] = 5\ mmol \cdot L^{-1}$; $[IB] = 1.82\ mol \cdot L^{-1}$; polymerization temperature $(T) = 0\ °C$; polymerization time $(t_p) = 10$ min; in CH_2Cl_2.

growing tertiary carbocation normally leads to *exo*- or *endo*-double bond end groups, i.e., $-CH_2-C(CH_3){=}C\boldsymbol{H}_2$ (structure A) or $-CH_2-C\boldsymbol{H} = C(CH_3)_2$ (structure B). The expansion of the olefin region (inset in Figure 1) at $\delta = 4.64$, 4.85 (a_1, a_2) and $\delta = 5.15$ indicates very low content of structure A but high fraction of structure B in the PIB chains.[5,7,29] A variety of internal unsaturated bonds can also be formed by transfer side reactions or isomerization from the normal growing tertiary carbocation via carbenium ion rearrangements by hydride and/or methide shifts.[5,7,29] The two strong quartet resonances at =5.17, 5.37 (c_1, c_2) and the intensive multiple resonances at $\delta = 2.85$ (e) are definitely attributed to $-C(CH_3){=}C\boldsymbol{H}(CH_3)$ (structure C for *Z*- and *E*- configuration) and $-CH_2C(CH_3){=}C(CH_3)-C\boldsymbol{H}(CH_3)_2$ (structure E) in PIB chains, respectively.[29] These two internal unsaturated structures (C and E) have also been obviously observed in commercial conventional low molecular weight PIBs co-initiated by $AlCl_3$.[6,7,14] The resonances at $\delta = 4.80$ and 4.82 were assigned to internal vinylene isomers F_1 and F_2 respectively.[29] These two structures of F_1 and F_2 are very similar and differ only by a shift of the double bond of one monomer unit inside the polymer chain. A weak singlet peak at $\delta = 5.12$ was attributed to the proton in $-C(CH_3){=}C\boldsymbol{H}C(CH_3)_2$ (sructure D).[29] In addition, there still are many minor undefined resonances, such as single resonances at $\delta = 4.77$, doublet resonances at $\delta = 5.01$, 5.03 and $\delta = 5.06$, 5.08, triplet resonances at $\delta = 5.30$ for unknown reasons. These undefined resonances still exist in the ^1H NMR spectrum even after purification for the polymer product for extra 4 times by *n*-hexane and ethanol. Therefore, the expected vinylidene route to produce highly reactive PIBs (structure A) is the minor one while the isomerizations via carbenium ion rearrangement are serious for the conventional cationic polymerization with $H_2O/FeCl_3$ initiating system.

Cationic Polymerization of IB with $H_2O/FeCl_3$/Dialkyl Ether Initiating System. The cationic polymerizations of isobutylene (IB) initiated by $H_2O/FeCl_3$ were carried out by introducing diethyl ether (Et_2O), dibutyl ether (Bu_2O) or diisopropyl ether (iPr_2O) into the polymerization system in CH_2Cl_2 at 0 °C. A summary of GPC and ^1H NMR results of the resultant PIBs are listed in Table 1. It can be obviously seen from Table 1 that the polymers with low molecular weights (M_n = 1500−1600 $g \cdot mol^{-1}$) and monomodal molecular weight distributions (MWD, $M_w/M_n = 1.7-2.2$) could be obtained in the presence of the above 3 kinds of dialkyl ethers.

Figure 2 shows a representative ^1H NMR spectrum of PIB obtained at $iPr_2O/FeCl_3 = 1.0$ (molar ratio). Compared to the expansion of the olefin region shown in Figure 1, it can be clearly observed that the strong characteristic resonance signals at δ = 4.64 and 4.84 are for *exo*-olefin end groups (structure A) and all the contents of structure A reached more than 87% in the presence of different dialkyl ethers. The selectivity of β-proton from $-CH_3$ has been greatly improved and the content of

Table 1. Cationic Polymerization of IB Initiated with $H_2O/FeCl_3$ in the Presence of Different Dialkyl Ethers[a]

		contents of various end groups, mol %										
dialkyl ether	convn %	A	B	D	E	F_1	F_2	G	M_n, $g\cdot mol^{-1}$ by ^1H NMR	M_n, $g\cdot mol^{-1}$ by GPC	M_w/M_n by GPC	C_{PIB} $mmol\cdot L^{-1}$
Et_2O	34	89.3	4.4	0.9	0.9	1.3	2.7	0.4	1400	1500	1.75	24.8
Bu_2O	58	87.1	3.4	0.9	2.6	1.3	4.3	0.4	1500	1300	1.91	39.4
iPr_2O	73	87.5	2.6	0.9	3.5	1.3	3.9	0.3	1700	1600	2.21	43.8

[a] $[FeCl_3] = 5\ mmol\cdot L^{-1}$, $[IB] = 1.82\ mol\cdot L^{-1}$, $T = 0$ °C, $t_p = 10$ min, $[H_2O] = 0.8\ mmol\cdot L^{-1}$, CH_2Cl_2, dialkyl ether/$FeCl_3$ = 1.0. The average concentration of PIB macromolecular chains in polymerization system, $C_{PIB} = [IB]\times 56\times Conv./M_{n,NMR}$.

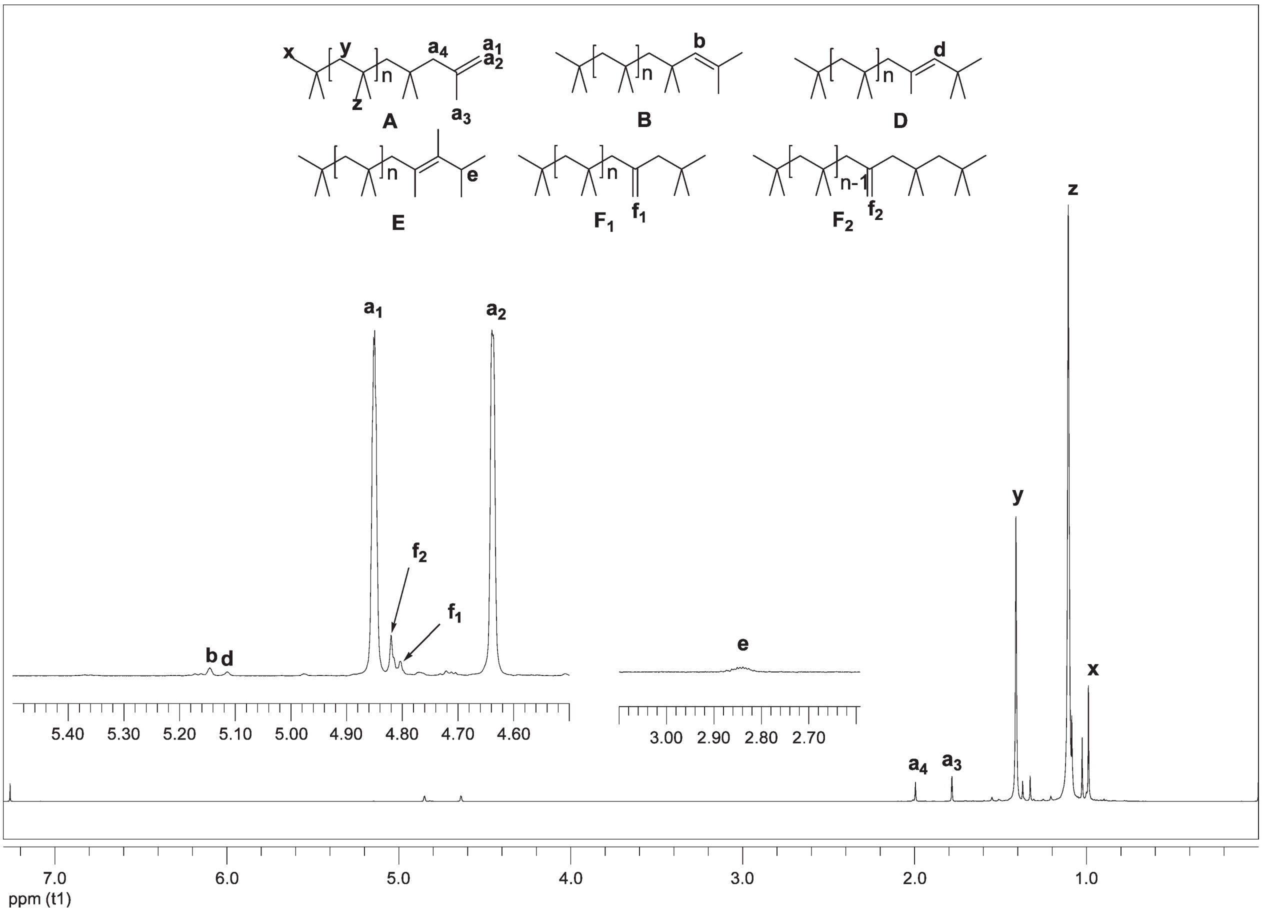


Figure 2. ^1H NMR spectrum of PIB obtained with $H_2O/FeCl_3/iPr_2O$ initiating system. The polymerization conditions are shown in Table 1.

structure B decreased to 2.6 - 4.4%. As shown in Table 1, all the isomerized structures of C (~0%), D (<1%), E (0.9−3.5%), F_1 (~1.3%) and F_2 (2.7−4.3%) were decreased to a very low level. The very low content (<0.5%) of structure G ($-CH_2-C(CH_3)_2$-Cl, δ = 1.68 and 1.96) indicates that the resulting PIB chains were almost free of *tert*-Cl terminal groups and the termination via chlorine transfer from counteranion did not take place during polymerization.[19] Moreover, the average concentration of PIB macromolecular chains in polymerization system (C_{PIB}) is by 2 orders of magnitude higher than the concentration of initiator ($[H_2O] = 0.8\ mmol\cdot L^{-1}$), indicating that this reaction is a chain transfer dominated cationic polymerization process. Therefore, it can be concluded that these dialkyl ethers played crucial roles in accelerating the β-proton elimination from $-CH_3$ in the growing PIB chain ends and effectively suppressing side transfer reactions via carbenium ion rearrangements. The complexation of $FeCl_3$ with dialkyl ethers decreased the Lewis acidity of $FeCl_3$ and thus side reactions, such as carbenium ion rearrangement and isomerizations, due to the strongly acidic free $FeCl_3$ are suppressed and thus generated high content of *exo*-olefin terminal groups. A similar phenomenon could be also observed in IB polymerizations with H_2O or CimOH/$AlCl_3$/dialkyl ethers initiating system.[14,15]

As shown in Table 1, the chemical structure and sterical hindrance of the alkyl groups in dialkyl ether molecules obviously influenced the monomer conversion, molecular weight, molecular weight distribution, contents of the end groups and the average concentration of PIB chains formed in the polymerization system (C_{PIB}). The basicity order of the above three dialkyl ethers is Et_2O ($pK_a = -3.59$) > iPr_2O ($pK_a = -4.30$) > Bu_2O ($pK_a = -5.40$) and the sterical hindrance of alkyl group increases as Et_2O < Bu_2O < iPr_2O.[30] Therefore, Et_2O should have the most efficiency among the

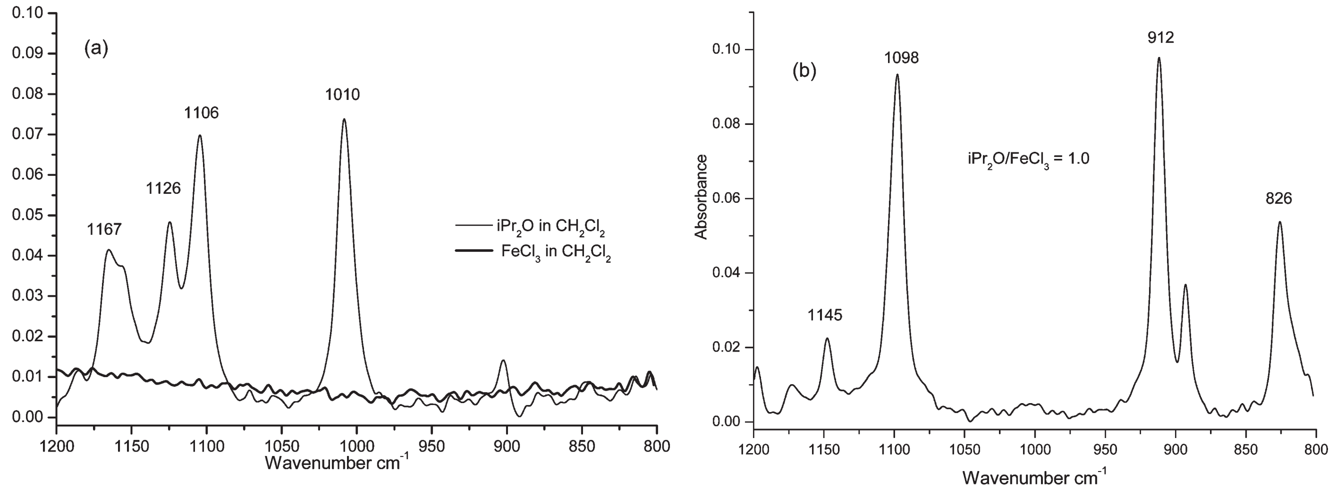


Figure 3. ATR-FTIR spectra of iPr$_2$O, FeCl$_3$ and complex of iPr$_2$O with FeCl$_3$ in CH$_2$Cl$_2$: (a) iPr$_2$O in CH$_2$Cl$_2$ with 0.34 mol·L^{-1}, FeCl$_3$ in CH$_2$Cl$_2$; (b) complex of iPr$_2$O with FeCl$_3$, iPr$_2$O/FeCl$_3$ = 1.0, [FeCl$_3$] = 0.44 mol·L^{-1} in CH$_2$Cl$_2$. The FTIR spectrum of CH$_2$Cl$_2$ was taken as the background.

three ethers on monomer conversion and molecular weight distribution under the same other conditions. The experimental data in Table 1 prove this point. However, monomer conversion (73%) obtained for the iPr$_2$O system is higher than that (58%) for the Bu$_2$O system, and the polymer obtained with H$_2$O/FeCl$_3$/iPr$_2$O system has slightly broad molecular weight distribution (M_w/M_n = 2.21). That more efficiency of Bu$_2$O on monomer conversion and molecular weight distribution than that of iPr$_2$O may be mainly due to the limited steric accessibility of the oxygen in iPr$_2$O molecule and thus formation of relatively weak complex of iPr$_2$O with FeCl$_3$. It has also been reported that the proton scavenging by BC1$_3$·ED (ED = ethyl acetate, tetrahydrofuran, diethyl ether, etc.) complexes may be responsible for the narrow molecular weight distribution (MWD) products obtained in BC1$_3$-*co*-initiated living polymerization of IB.[31] The coordination strength between dialkyl ether and Lewis acid should be ascribed to the basicity and sterical hindrance of dialkyl ether, which are consistent with those in literatures.[32] Moreover, the efficiency of ethers on suppressing the side reactions via carbenium ion rearrangement decreased as Et$_2$O > Bu$_2$O > iPr$_2$O, which is supported by the sum value of the contents of structure D, E, F$_1$, and F$_2$ from 5.8% for Et$_2$O to 9.6% for iPr$_2$O. The higher content of *exo*-olefin terminals for the Et$_2$O system in Table 1 also indicates stronger proton scavenging by Et$_2$O·FeCl$_3$ complex. The average concentration of the polymer chains (C_{PIB}) in the polymerization system with H$_2$O/iPr$_2$O·FeCl$_3$ is higher than those in the other two systems, suggesting that higher tendency of chain transfer reaction to monomer occurred in the presence of iPr$_2$O·FeCl$_3$.

It has been reported that Lewis acid, such as BCl$_3$, TiCl$_4$, AlCl$_3$, or EtAlCl$_2$, can form well-defined complexes with O-containing EDs, leading to a decrease in Lewis acidity.[31,33−35] The acidity of FeCl$_3$ could be moderated by its interaction with dialkyl ether, leading to a decrease in the cationicity of the resulting PIB growing species, as reported previously in the IB polymerization co-initiated by AlCl$_3$.[14,15,23c,33] The complex reaction of iPr$_2$O with FeCl$_3$ were investigated with the assistance of ATR FTIR spectroscopy. ATR FTIR spectroscopy has been exploited in the investigation of kinetics and mechanism in the cationic polymerization of IB.[36] Herein, ATR FTIR spectroscopy was applied to investigate *in situ* the interaction of iPr$_2$O with FeCl$_3$ in CH$_2$Cl$_2$ by monitoring the spectra on real-time during the formation of complex. The ATR FTIR spectrum of iPr$_2$O solution in CH$_2$Cl$_2$ ([iPr$_2$O] = 0.34 mol·L^{-1}) was collected by an ATR probe and the descriptions are given in Figure 3a. All the signal bands at 1010, 1206, 1106, and 1167 cm^{-1} are assigned to C—O—C stretch in iPr$_2$O. No signal appeared at 800 to 1200 cm^{-1} for FeCl$_3$ solution in CH$_2$Cl$_2$. Figure 3b shows the ATR FTIR scans for the complex of iPr$_2$O with FeCl$_3$. When mixing equivalent molecules of iPr$_2$O and FeCl$_3$ in CH$_2$Cl$_2$, all the FTIR bands at 1010, 1206, 1106, and 1167 cm^{-1} assigned to the C—O—C stretch disappeared and the new FTIR bands generated correspondingly at 826, 912, and 1098 cm^{-1}. The disappearance of all the characteristic bands of C—O—C stretch indicates the formation of complex between iPr$_2$O and FeCl$_3$ with 1:1 molar ratio.

In order to identify the formation of 1:1 complex of iPr$_2$O·FeCl$_3$, we further investigate the interaction between iPr$_2$O and FeCl$_3$ by setting iPr$_2$O/FeCl$_3$ molar ratios at 1.5, 2.0, 2.5, and 3.0, and the corresponding FTIR spectra obtained at various iPr$_2$O/FeCl$_3$ molar ratios are presented in Figure 4. It can be observed that the addition of excess iPr$_2$O has almost no effect on the signal height of iPr$_2$O·FeCl$_3$ complex (1:1) at 826 and 912 cm^{-1}. In contrast, the signal intensity of characteristic bands of C—O—C stretch for iPr$_2$O at 1010, 1206, and 1167 cm^{-1} enhanced progressively with an increase in iPr$_2$O/FeCl$_3$ molar ratio, suggesting that free iPr$_2$O molecules existed in the initiating system when iPr$_2$O/FeCl$_3$ molar ratios >1. In order to quantify the concentration of free iPr$_2$O molecules in the systems, the quantitative determination of iPr$_2$O in CH$_2$Cl$_2$ was investigated by collecting the characteristic absorbance at 1010 cm^{-1} at different iPr$_2$O concentrations. The experimental results are given in Figure 5. The proportional linearity between the signal intensity at 1010 cm^{-1} and iPr$_2$O concentration in the range of 0.09−2.1 mol·L^{-1} indicates that the absorbance at 1010 cm^{-1} was able to quantify the concentration of free iPr$_2$O molecules in the systems when iPr$_2$O/FeCl$_3$ molar ratios >1. The concentration of free iPr$_2$O molecules ([free iPr$_2$O]) can be defined as the difference between the concentration of iPr$_2$O and FeCl$_3$ assumed the formation of 1:1 complex, i.e. [free iPr$_2$O] = [iPr$_2$O] − [FeCl$_3$]. The absorbance intensity at 1010 cm^{-1} (●) at different [free iPr$_2$O] in CH$_2$Cl$_2$ was actually on the straight line presented in Figure 5. It is consequently verified that iPr$_2$O with FeCl$_3$ formed

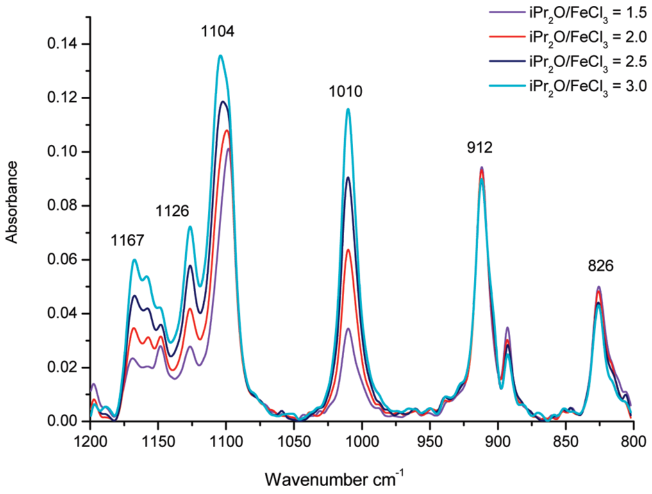


Figure 4. ATR FTIR monitoring of the complex reaction of iPr_2O and $FeCl_3$ with different $iPr_2O/FeCl_3$ molar ratios ($[FeCl_3] = 0.44\ mol \cdot L^{-1}$). The FTIR spectrum of CH_2Cl_2 was taken as the background.

the 1:1 complex and the excess iPr_2O existed as free molecules in the initiating system when $iPr_2O/FeCl_3$ molar ratios >1.

Effect of $iPr_2O/FeCl_3$ Molar Ratios. In order to get deep insight of polymerization mechanism, the effect of $iPr_2O/FeCl_3$ molar ratios on the cationic polymerization of IB with $H_2O/FeCl_3/iPr_2O$ initiating system and β-proton elimination at the PIB chain ends was further investigated. Table 2 presents the monomer conversion, molecular weight, molecular weight distribution and the contents of double bonds in PIB chains synthesized at different molar ratios of $iPr_2O/FeCl_3$. It can be seen that monomer conversion decreased obviously from 73% to 29% with increasing $iPr_2O/FeCl_3$ ratio from 1.0 to 1.6 and no polymerization did occur at $iPr_2O/FeCl_3 = 1.8$. On the other hand, the M_n of the resulting PIB polymer decreased and MWD narrowed with increasing $iPr_2O/FeCl_3$ ratio. The content of *exo*-olefin end groups (structure A) could also be further increased up to more than 90 mol % by increasing iPr_2O concentrations. The highly reactive polyisobutylenes (HRPIBs) with high content (~90 mol %) of *exo*-olefin terminals and polydispersity of around 2.0 could be synthesized at $iPr_2O/FeCl_3 = 1.2$, 1.4, or 1.6, which can be comparable with the commercial HRPIB product.

As we known, the living cationic polymerization of IB has been achieved with a *tert*-alkyl ester, alcohol, ether or chloride as an initiator and with $TiCl_4$ or BCl_3 as a co-initiator in the presence of external electron pair donors (EDs) and proton traps since 1986.[1,37] The key species responsible for mediating living cationic polymerization of IB are FCA-ED complexes, formed by Lewis acid-Lewis base interaction, where FCA = BCl_3, and $TiCl_4$, and ED = ethyl acetate, tetrahydrofuran, etc.[31,38] Several theories have been advanced to describe the mechanistic roles of EDs in quasiliving cationic polymerization: (1) carbocation stabilization.[1,37c,39] EDs and/or their complexes with Lewis acid co-initiators interact with the growing chain end to reduce its cationicity and thus to convert highly reactive species into less reactive species; (2) proton scavenging.[38,40] External EDs and 2,6-di-*tert*-butylpyridine bring about living polymerization by trapping protons; (3) apparent stabilization of the growing chain ends.[41,42] Living cationic polymerizations are the result of the control of the reaction kinetics but not of the change of the mechanism, due to a reduction in the instantaneous carbocation concentration; (4) common ions effect and scavenging of protic impurities.[43] The basic additives (or EDs) suppress the concentration of unpaired chain carriers through the in situ production of common ions via the scavenging of protic impurities. It has also been proposed that EDs could retard the propagation and presented a minus reaction kinetic order on IB polymerization rate in $TiCl_4$ and $AlCl_3$ co-initiating systems and free EDs in the polymerization system are inhibitors of IB polymerization.[23c,31,38,44]

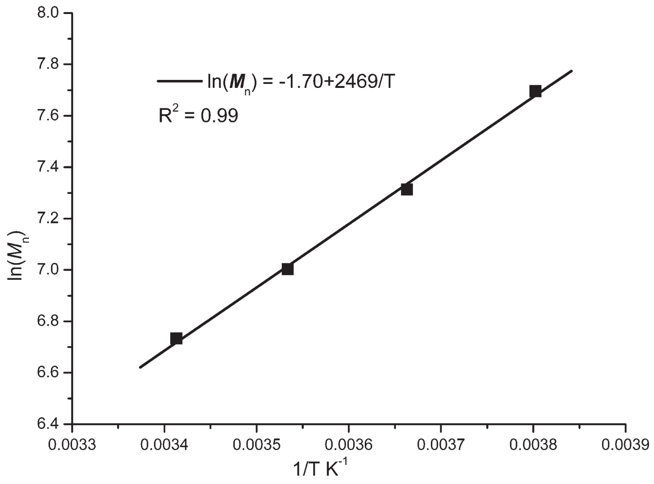


Figure 5. Plots of signal intensity at 1010 cm^{-1} at different concentrations of iPr_2O and of free iPr_2O.

Here, according to the above experimental results, a possible mechanism for the synthesis of HRPIB via the cationic polymerization of isobutylene with $H_2O/FeCl_3/iPr_2O$ initiating system was proposed, as shown in Scheme 1. Since well-defined complexe (1:1) of $FeCl_3$ with ether formed rapidly, free molecules of $FeCl_3$ and iPr_2O should be absent in the polymerization system when $iPr_2O/FeCl_3 = 1$. The complex of $iPr_2O \cdot FeCl_3$ (1:1) with lower Lewis acidity than $FeCl_3$ was used as co-initiator, in conjunction with initiator (H_2O) to create the protic initiation, leading to the formation of *tert*-butyl headgroup $(CH_3)_3C-$ in polymer chain. The counteranion $[iPr_2O \cdot FeCl_3(OH)]^-$, formed by the combination of $iPr_2O \cdot FeCl_3$ with the anionic part (OH^-) from initiator, associates with the growing carbocation and thus affected the cationicity of the growing ends and selective β-proton elimination from $-CH_3$. The proton scavenging from $-CH_3$ in the growing carbocation by $iPr_2O \cdot FeCl_3$ in counteranion could form H^+-$[iPr_2O \cdot FeCl_3(OH)]^-$,and subsequently reinitiate the IB polymerization. It is postulated that the polymerization process took place by chain-breaking via predominant β-proton elimination from $-CH_3$ in the growing carbocation and then by protic reinitiation to create a new polymer chain, resulting in the formation of many short polymer chains with low molecular weight ($M_n \sim 1500$) and high content (~90%) of *exo*-olefin terminals.

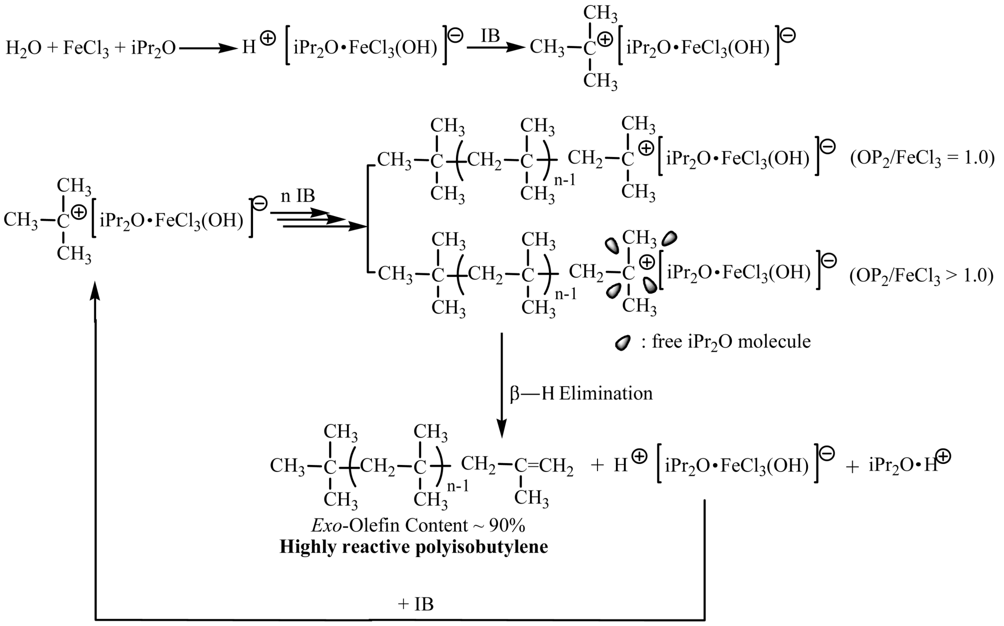
When $iPr_2O/FeCl_3 > 1$, free iPr_2O molecules existed while free $FeCl_3$ molecules were still absent in the polymerization systems. The free iPr_2O molecules could interact with the growing carbocations and affected the microsurroundings around the propagating centers, leading to decreases in polymerization rate and monomer conversion due to the higher nucleophilicity of iPr_2O than that of isobutylene. On the other hand, free iPr_2O molecules could also abstract β-proton from growing carbocation to form $iPr_2O \cdot H^+$, resulting in increasing content of *exo*-olefin end groups and decreasing the possibility of protic reinitiation to form a new polymer chain. The average concentration of PIB macromolecular chains (C_{PIB}) in the polymerization system

Table 2. Cationic Polymerizations of IB at Various $iPr_2O/FeCl_3$ Molar Ratios[a]

		contents of various end groups %										
$iPr_2O/FeCl_3$ molar ratio	convn %	A	B	D	E	F_1	F_2	G	M_n, $g \cdot mol^{-1}$ by ^1H NMR	M_n, $g \cdot mol^{-1}$ by GPC	M_w/M_n by GPC	C_{PIB} $mmol \cdot L^{-1}$
1.0	73	87.5	2.6	0.9	3.5	1.3	3.9	0.3	1800	1600	2.21	41.3
1.2	58	89.8	1.8	0.9	2.7	1.3	3.1	0.3	1700	1600	2.18	34.8
1.4	47	90.1	1.8	0.9	1.8	1.4	3.6	0.5	1300	1400	2.00	36.8
1.6	29	90.5	1.8	0.9	1.8	1.4	3.2	0.5	1300	1300	1.90	22.7
1.8	0	/	/	/	/	/	/	/	/	/	/	

[a] $[FeCl_3] = 5\ mmol \cdot L^{-1}$, $[IB] = 1.82\ mol \cdot L^{-1}$, $T = 0$ °C, $t_p = 10$ min, $[H_2O] = 0.8\ mmol \cdot L^{-1}$, CH_2Cl_2. The average concentration of PIB macromolecular chains in polymerization system, $C_{PIB} = [IB] \times 56 \times convn/M_{n,NMR}$.

Scheme 1. Possible Mechanism for the Synthesis of Highly Reactive Polyisobutylene via Cationic Polymerization of Isobutylene with $H_2O/FeCl_3/iPr_2O$ Initiating System



decreased from 41.3 to 22.7 $mmol \cdot L^{-1}$ with increasing $iPr_2O/FeCl_3$ molar ratio from 1.0 to 1.6.

Therefore, the counteranion with less Lewis acidity, the absence of free $FeCl_3$ molecules and the presence of free iPr_2O molecules ($iPr_2O/FeCl_3 > 1$) should be responsible for the highly selective elimination of β-proton from $-CH_3$ in growing PIB chain ends and thus the achievement of high content of *exo*-olefin end groups. The absence of free $FeCl_3$ also reduces the serious isomerizations to different isomers shown the Figure 1.

With $H_2O/FeCl_3/iPr_2O$ initiating system, a reasonable $iPr_2O/FeCl_3$ molar ratios = 1.1 was selected to obtain a moderate polymerization rate and high *exo*-olefin content in the further investigation with a special focus on the influences of $FeCl_3$ concentration, polymerization time and temperature on monomer conversion, M_n, M_w/M_n, and unsaturated structures in PIB chains.

Effect of $FeCl_3$ Concentration and Polymerization Time. $FeCl_3$ concentration ($[FeCl_3]$) is one of the most important variables in controlling degree of polymerization and different unsaturated structures. The influence of $[FeCl_3]$ was investigated and the experimental results are summarized in Table 3. The monomer conversion increased from 20% to 86% while M_n decreased from 1800 to 1100 $g \cdot mol^{-1}$ with increasing $[FeCl_3]$ from 0.003 to 0.010 $mol \cdot L^{-1}$. The average concentration of PIB macromolecular chains (C_{PIB}) in polymerization system greatly increased from 13.6 to 87.6 $mmol \cdot L^{-1}$ with increasing $[FeCl_3]$ from 0.003 to 0.010 $mol \cdot L^{-1}$. The increase tendency of C_{PIB} is much higher than that of $[FeCl_3]$, indicating the serious proton scavenging by $iPr_2O \cdot FeCl_3$ and chain transfer reaction to monomer by the reinitiation from $H^+[iPr_2O \cdot FeCl_3(OH)]^-$. On the other hand, the content of *exo*-olefin end groups (structure A) in PIB chains decreased to some extents from 90.3 to 82.3 mol % with increasing $FeCl_3$ concentration from 0.003 to 0.010 $mol \cdot L^{-1}$ for the increase in contents of isomers of D, E, F_1, and F_2, especially isomer F_2. Highly reactive PIBs with large proportion of *exo*-olefin end groups could be favorably prepared under the appropriate conditions of low $FeCl_3$ concentration.

It can be also seen from Table 3 that the cationic polymerization of IB could proceed moderately to 20% of monomer conversion within 10 min even at a very low $[FeCl_3]$ of 0.003 $mol \cdot L^{-1}$ and got 90.3 mol % of *exo*-olefin terminals in polymer chains. The $[FeCl_3]$ used in this research is far less than the concentration of $AlCl_3$ (e.g., 0.02 $mol \cdot L^{-1}$) in the

Table 3. Effects of $[FeCl_3]$ and t_p on Conversion, M_n, M_w/M_n, and Unsaturated Structures of PIBs[a]

			content of various end groups										
$[FeCl_3]$ mmol·L^{-1}	$t_p$min	convn %	A	B	D	E	F_1	F_2	G	M_n, g·mol^{-1} by ^{1}H NMR	M_n, g·mol^{-1} by GPC	M_w/M_n by GPC	C_{PIB} mmol·L^{-1}
3	10	20	90.3	5.4	0.0	0.9	0.4	1.3	1.6	1500	1800	2.32	13.6
4	10	55	90.6	2.7	0.9	1.8	0.9	2.3	0.8	1400	1500	2.41	40.0
5	10	69	88.0	2.6	0.9	2.6	1.3	3.9	0.6	1500	1500	2.15	46.9
7.5	10	74	86.3	2.6	0.9	2.6	1.7	5.2	0.9	1100	1200	2.14	68.6
10	10	86	82.3	2.5	1.7	2.5	2.9	7.0	1.1	1000	1100	2.07	87.6
5	2	26	91.9	2.8	0.0	2.8	0.5	1.4	0.6	1900	2200	2.16	13.9
5	5	46	90.0	2.7	0.9	2.7	1.3	1.8	0.6	1600	1700	2.25	29.3
5	20	76	85.8	2.6	0.9	2.6	2.1	5.6	0.4	1400	1400	2.38	55.3
5	30	82	82.2	2.5	1.6	2.5	3.3	7.4	0.5	1400	1200	2.34	59.7

[a] $iPr_2O/FeCl_3 = 1.1$; Solvent = CH_2Cl_2; $[IB] = 1.82$ mol·L^{-1}; $T = 0$ °C; $[H_2O] = 1.1$ mmol·L^{-1}. The average concentration of PIB macromolecular chains in polymerization system, $C_{PIB} = [IB] \times 56 \times \text{convn}/M_{n,NMR}$.

Table 4. Effect of Reaction Temperature on Conversion, M_n, M_w/M_n, and Unsaturated Structures of PIBs[a]

		content of various end groups										
T, °C	convn %	A	B	D	E	F_1	F_2	G	M_n, g·mol^{-1} by ^{1}H NMR	M_n, g·mol^{-1} by GPC	M_w/M_n by GPC	C_{PIB} mmol·L^{-1}
20	66	78.4	4.7	2.3	5.5	3.1	5.5	0.5	900	840	1.72	74.7
10	68	86.1	3.4	0.9	3.4	1.7	3.9	0.6	1000	1100	1.93	69.3
0	69	88.0	2.6	0.9	2.6	1.3	3.9	0.6	1500	1500	2.15	46.9
−10	65	90.3	2.7	0.9	1.8	0.9	2.7	0.7	2000	2200	2.78	27.2

[a] $[FeCl_3] = 5$ mmol·L^{-1}, $[IB] = 1.82$ mol·L^{-1}, $T = 0$ °C, $t_p = 10$ min, $[H_2O] = 0.8$ mmol·L^{-1}, CH_2Cl_2, $iPr_2O/FeCl_3 = 1.1$. The average concentration of PIB macromolecular chains in polymerization system, $C_{PIB} = [IB] \times 56 \times \text{convn}/M_{n,NMR}$.

polymerization of IB with $H_2O/AlCl_3/iPr_2O$ or Bu_2O initiating system.[14,15] Compared to our previous research on IB polymerization with $H_2O/AlCl_3/Bu_2O$ initiating system,[14] it can be also observed that near 3 times higher in monomer conversion and 1/3 times lower in molecular weight of PIB could be obtained with $H_2O/FeCl_3/iPr_2O$ initiating system under concentration of Lewis acid at 0.010 mol·L^{-1} and the same other reaction conditions. The probable causes for the difference in the concentration of Lewis acid are the differences in hardness of the two Lewis acids and in radium of metal ions (Al^{3+}, Fe^{3+}).

The effect of polymerization time (t_p) at $[FeCl_3] = 0.005$ mol·L^{-1} is listed in Table 3. The cationic polymerization of IB initiated by $H_2O/FeCl_3/iPr_2O$ system proceeded with a relatively rapid rate at $[FeCl_3] = 0.005$ mol·L^{-1} and monomer conversion gradually increased up to 82% with t_p in 30 min. The content of *exo*-olefin end groups was 91.9 mol % after 2 min of polymerization and then gradually reduced to 82 mol % after 30 min and the contents of internal vinylenes (F_1 and F_2) increased correspondingly.

According to the above observations, this is an indication of a chain-transfer dominated polymerization process implicating serious β-proton elimination from $-CH_3$ group in the normal growing tertiary carbocations scavenged by $iPr_2O\cdot FeCl_3$ complex and free iPr_2O molecule, as shown in Scheme 1. The highly reactive PIBs with 88 mol % of *exo*-olefin end groups (structure A), having monomer conversion of 69%, M_ns of 1500 g·mol^{-1} and M_w/M_n of around 2.1 could be prepared under relatively low $[FeCl_3]$ of 0.005 mol·L^{-1}. These increasing isomerization with $[FeCl_3]$ and t_p are similar to those results reported for the isomerization of end groups in PIB chains at high concentration of Lewis acid (BF_3, $TiCl_4$, $AlCl_3$, $MeAlBr_2$, and Me_2AlBr) and for long polymerization time.[5,14,45,46]

Effect of polymerization temperature. Polymerization temperature (T) is also a critical factor for the elementary reactions in the cationic polymerization of IB. An increase in polymerization temperature leads to the promotion in the β-proton elimination from the normal growing species and in the isomerizations via carbenium ion rearrangement mechanism. In order to examine the effect of polymerization temperature, the cationic polymerizations of IB with $H_2O/FeCl_3/iPr_2O$ initiating system ($iPr_2O/FeCl_3 = 1.1$) were conducted at various temperatures ranging from −10 to +20 °C and the experimental results are given in Table 4. It can be seen that the content of *exo*-olefin end groups (structure A) in PIB chains decreased slightly from 90.3 to 86.1 mol % with increasing temperature from −10 to 10 °C and further greatly decreased to 78.4 mol % at 20 °C due to the increase in isomerizations for D, E, F_1, and F_2. Higher temperature will accelerate both β-proton elimination and isomerizations while decrease the selectivity of β-proton abstraction from $-CH_3$, leading to decreases in molecular weight and content of *exo*-olefin terminals and increases in the contents of *endo*-double bond (structure B) and other isomers. Very interestingly, low molecular weight HRPIBs ($M_n = 1100$ g·mol^{-1}) carrying 86.1 mol % of *exo*-olefin end groups could be achieved even at 10 °C.

The inverse effect of polymerization temperature on molecular weights has been quantitatively expressed by Arrhenius equation, i.e. $\ln M_n = \ln A - \Delta E/RT$, that is M_n depends on $1/T_p$.[27,47] The overall activation energy difference (ΔE or E_{DP}) was calculated to be −20.5 kJ·mol^{-1} from the slope of the linear

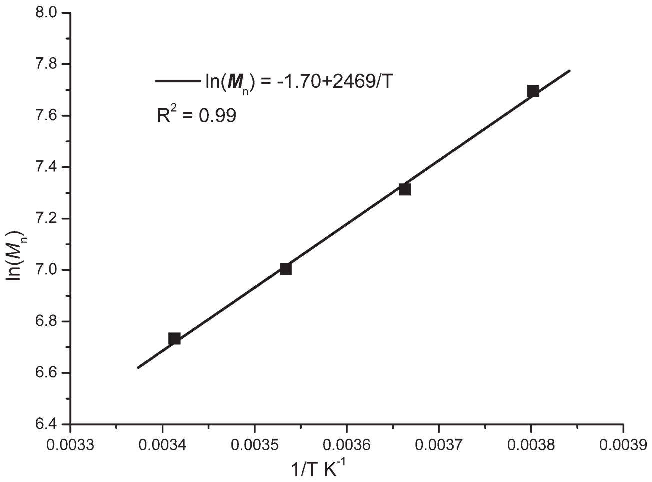


Figure 6. Arrhenius plot of ln(M_n) versus $1/T$ for IB polymerization with $H_2O/FeCl_3/iPr_2O$ initiating system.

Arrhenius plot of ln(M_n) vs $1/T_p$ for the temperature interval from −10 to +20 °C, shown in Figure 6. This value of ΔE is similar to the results (~ −23 kJ·mol^{-1}) for the classical polymerization systems of IB co-initiated with BF_3, $AlCl_3$ or $EtAlCl_2$ over the temperature range of −100 to −30 °C.[27,48] The M_n decreased and average concentration of PIB macromolecular chains in polymerization system (C_{PIB}) increased with polymerization temperature, suggesting that the rate of chain transfer reaction was improved by increasing temperature. The MWD of PIBs became narrower with increasing polymerization temperature and M_w/M_n reached 1.72 for PIB obtained at 20 °C, shown in Table 4. This result is similar to those in cationic polymerization of styrene or IB co-initiated by $AlCl_3$.[14,15,49] The decrease in polydispersity index of polymers is probably due to the increasing chain transfer rate or the increasing equilibrium rate between the dormant and the activated species with increasing temperature since fast equilibrium was required to prepare the polymers with narrow MWDs.[49−52]

CONCLUSIONS

The initiating system of $H_2O/FeCl_3$/dialkyl ether has been successfully developed for the cationic polymerization of isobutylene to prepare highly reactive polyisobutylenes with low molecular weight of M_ns = 840−2200 g·mol^{-1} and carrying high content of *exo*-olefin end groups even up to 91% at 0 °C or higher temperatures. The cationic polymerization of isobutylene with this $FeCl_3$−based initiating system shows high selectivity for the β-proton elimination from $-C\boldsymbol{H}_3$ in growing PIB chain ends and high tendency of chain transfer reaction to monomers. The dialkyl ether, diethyl ether (Et_2O), dibutyl ether (Bu_2O), or diisopropyl ether (iPr_2O) decreased the Lewis acidity of $FeCl_3$ through formation of 1:1 complex and moderated the high cationity of propagating carcocationic species. When $iPr_2O/FeCl_3$ molar ratios >1, free iPr_2O molecules existed in the polymerization system. Both the $iPr_2O\cdot FeCl_3$ complex and free iPr_2O molecule should be responsible for the β-proton scavenging and thus for the formation of high content of *exo*-olefin end groups. The caionic polymerization of IB was considered to be a chain-transfer dominated process, and the rates of β-proton elimination and chain transfer reaction to monomer were dependent on the concentrations of $iPr_2O\cdot FeCl_3$ complex and free iPr_2O molecule and polymerization temperature. The isomerizations via carbenium ion rearrangement increased with [$FeCl_3$], polymerization temperature and time.

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ACKNOWLEDGMENT

The financial support from National Natural Science Foundation of China (Grant 20934001) from IRT 0706 is greatly appreciated.

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