Effects of Ether on the Cationic Polymerization of Isobutylene Catalyzed by AlCl₃

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ABSTRACT: In this work, we prepared different initiator solutions containing ether and AlCl₃ by changing the addition sequence of ingredients, studied the interactions between ether and AlCl₃ from the evolution of the Fourier transform infrared (FTIR) spectra by comparison, and investigated the catalytic performances of AlCl₃ affected by ether for isobutylene polymerization. We observed that different preparation methods of initiator solutions could lead to two kinds of interactions between ether and H₂O/AlCl₃ in hexane. The strong interaction could stabilize carbenium ions and seriously decrease the catalytic performance, whereas the weak interaction could promote isomerization and proton elimination. Moreover, we found that the preparation method of initiator solutions was not a critical factor in CH₂Cl₂. Finally, a universal mechanism based on the AlCl₃-ether interactions in different solvents was proposed to understand the effects of ether on the cationic polymerization catalyzed by AlCl₃ thoroughly.

INTRODUCTION

Polyisobutylenes (PIBs), produced by the cationic polymerization of isobutylene (IB),¹⁻³ have drawn attention from both industry and academia in recent years because of their distinguished properties with respect to thermal stability, flexibility at ambient temperature, impermeability to gases, and so forth.⁴⁻⁷ These excellent properties lead to their wide applications in auto tyres, medical bottle plugs, sealants, ashless dispersants, gasoline additives, and so forth.⁸⁻¹⁰ Different applications of PIBs need different molecular weights (Mₙ). According to Mₙ, commercially available PIBs can be classified into three categories: (i) high-molecular-weight PIBs (Mₙ > 100 000 g mol⁻¹); (ii) medium-molecular-weight PIBs (MPIBs, Mₙ = 10 000–100 000 g mol⁻¹), and (iii) low-molecular-weight PIBs (LPIBs, Mₙ < 5000 g mol⁻¹).¹¹⁻¹³ Recently, many attentions have been paid on the LPIBs with a high content of exo-olefin end groups and narrow molecular weight distribution, denoted as highly reactive PIBs (HRPIBs), because of their high activity in synthesizing lubricants and gasoline additives.¹⁴⁻¹⁹

The initiator solution of H₂O/aluminum chloride (AlCl₃) is widely adopted for IB polymerization because of the low cost and high efficiency,²⁰⁻²³ in which H₂O and AlCl₃ work as the initiator and the coinitiator, respectively. However, the polymerization initiated by H₂O/AlCl₃ involves complicated chain reactions, such as isomerization, chain termination, and so forth. To control the chain reactions, nucleophilic reagents such as ether or ester are usually added in the initiator solution. The basicity and steric hindrance of the nucleophilic reagent as well as the stability of the corresponding complex have great influence on polymerization.²⁴⁻²⁵

Through the regulation of nucleophilic reagents, many functional polymers with different molecular weights were attained, such as the HRPIBs, MPIBs with high content of exo-olefin, and so forth.²⁶⁻³³ The availability of various polymers indicates the complicated effects of nucleophilic reagents on polymerization. Although researchers always gave some explanations on specific experimental results, the interactions of initiators, coinitiator and nucleophilic reagents, are still lack of systematic understanding.³⁴⁻⁴⁰ In this work, we prepared different initiator solutions containing ether and AlCl₃ by changing the addition sequence of ingredients, studied the interactions between ether and AlCl₃ from the evolution of the Fourier transform infrared (FTIR) spectra of ether by comparison, investigated the catalytic performance of AlCl₃ affected by ether on IB polymerization according to conversion determination and product characterization, and proposed a universal mechanism to clarify the effects of ethers on the cationic polymerization catalyzed by AlCl₃. Herein, both normal ether [diethyl ether (Et₂O), pKₐ = -3.59] and branched ether [isopropyl ether (iPr₂O), pKₐ = -4.30] were used to study the influence of basicity and steric hindrance; both the nonpolar solvent (n-hexane) and the polar solvent [dichloromethane (CH₂Cl₂)] were used to introduce the influence of solvent environment; the microflow reactor was exploited as a suitable platform for investigating instantaneous processes including cationic polymerization.⁴¹⁻⁴³ Through the research, the effects of ether on the cationic polymerization catalyzed by AlCl₃ in different solvents are understood thoroughly to provide a rational and effective access to customized functional polymers.

Received: December 28, 2017
Accepted: February 8, 2018
Published: February 20, 2018
RESULTS AND DISCUSSION

For the cationic polymerization of IB, solvents have great influence on the chain reactions because the polarity of solvents could affect the reactivity of active centers distinctly. Herein, we investigated the polymerization processes in a nonpolar solvent (n-hexane) and a polar solvent (CH2Cl2) separately.

Cationic Polymerization of IB in Hexane. Effects of Et2O. The initiator solutions prepared with different preparation methods were determined by attenuated total reflection (ATR)—FTIR to cognize the interaction between Et2O and AlCl3, as shown in Figure 1. For the free Et2O, the characteristic peak appears at 1126 cm⁻¹.

When AlCl3 comes in direct contact with Et2O, denoted as method 1, the absorbance at 1126 cm⁻¹ is much weakened and many new peaks emerge, which indicates the interaction between Et2O and AlCl3. The complex could react with H2O to form an associated ion pair, which would initiate the polymerization, as shown in entries 1–3 of Table 1. PIBs with a relatively high content of exo-olefin, narrow D, and low conversion were obtained with the initiator solution prepared by method 1. A reasonable explanation is that the interaction between Et2O and AlCl3 could catalyze H2O to form a stabilized carbenium ion corresponding to slow chain propagation and isomerization. Besides, it should be noted that (1) extending the residence time from 12 to 600 s could not help to increase the conversion, indicating serious and fast chain termination, and (2) both Mₚ and the content of exo-olefin decrease when the temperature increases from −20 to 20 °C, indicating that high temperature could accelerate the isomerization and proton elimination simultaneously.

The ATR–FTIR spectrum of the initiator solution prepared by modified method 1 is almost the same as that of the initiator solution prepared by method 1, except the absorbance at 1126 cm⁻¹ which becomes quite less because of the removal of free Et2O by vacuuming. The corresponding polymerization performance could be seen in entries 4–5 of Table 1. Compared with entries 1–3, the content of exo-olefin becomes even higher and the conversion increases too, which indicates that the free Et2O may result in the decrease of the polymerization rate and the promotion of isomerization. However, the conversions in entries 4–5 are still relatively low because the carbenium ions are still stabilized by the strong interaction between AlCl3 and ether.

For the initiator solution prepared by method 2, the ATR–FTIR spectrum shows some new peaks, such as 1010, 887, and 770 cm⁻¹, but the characteristic peak of free Et2O at 1126 cm⁻¹ is still obvious. The experimental results of IB polymerization (entries 6–13, Table 1) show that both the conversion and D have great improvement, but the content of exo-olefin decreases seriously. A reasonable explanation on the enhanced conversion is that some AlCl3 combines with H2O in hexane in advance, which provides well-dissociated protons with high reactivity. The narrow D corresponds to enhanced proton elimination or isomerization because of the existence of free (or not strongly interacted) Et2O. In detail, entries 6–8 correspond to the same reaction conditions except for the ratio of Et2O to AlCl3. The increased ratio of Et2O to AlCl3 results in a remarkable decrease of Mₚ and the content of exo-olefin, which indicates that the additive Et2O promotes isomerization superior to proton elimination. Entries 9–13 reflect the effects of polymerization temperature. Within the range from −20 to 30 °C, a maximum conversion was achieved at around 10 °C because of the compromise between chain propagation and chain termination, which are both enhanced with temperature increase. Moreover, the lower Mₚ and narrower D at higher temperature were attributed to the higher proton elimination rate.

In general, the interaction between Et2O, AlCl3, and H2O, as well as the effects of Et2O on the polymerization of IB catalyzed by AlCl3 in a nonpolar solvent hexane, was highly dependent on the preparation method of the initiator solution. It may

![Figure 1. ATR–FTIR spectra for the interaction between AlCl3 and Et2O in hexane.](image)

| Table 1. Polymerization of IB Catalyzed by AlCl3 with the Addition of Et2O in Hexanea |
|---|
| entry | T (°C) | t (s) | AlCl3 (mmol L⁻¹) | [Et2O]/[AlCl3] | conv (%) | Mₚ (GPC) | D | tri + endo (%) | tetra (%) |
| 1a | 0 | 12 | 5.09 | | 1.42 | 6 | 3850 | 2.45 | 76 | 11 | 13 |
| 2b | −20 | 600 | 5.56 | | 1.30 | 8 | 5980 | 2.60 | 82 | 9 | 9 |
| 3c | 20 | 600 | 5.56 | | 1.30 | 6 | 1500 | 2.15 | 65 | 16 | 19 |
| 4d | −20 | 600 | 7.63 | | 1.00 | 14 | 4300 | 2.13 | 91 | 6 | 3 |
| 5e | 20 | 600 | 7.42 | | 1.00 | 8 | 2200 | 2.04 | 83 | 8 | 9 |
| 6f | 20 | 12 | 5.92 | | 1.22 | 52 | 2710 | 2.19 | 14 | 48 | 38 |
| 7g | 20 | 12 | 7.86 | | 1.53 | 61 | 1960 | 2.03 | 9 | 59 | 32 |
| 8h | 20 | 12 | 8.43 | | 2.00 | 88 | 1470 | 1.73 | 3 | 69 | 28 |
| 9i | −20 | 12 | 8.04 | | 1.50 | 11 | 6840 | 2.42 | 25 | 36 | 39 |
| 10j | 0 | 12 | 8.04 | | 1.50 | 24 | 5790 | 2.97 | 15 | 55 | 30 |
| 11k | 10 | 12 | 8.04 | | 1.50 | 75 | 2460 | 2.35 | 11 | 62 | 27 |
| 12l | 20 | 12 | 8.04 | | 1.50 | 67 | 1850 | 2.13 | 5 | 62 | 33 |
| 13m | 30 | 12 | 8.04 | | 1.50 | 49 | 1570 | 1.84 | 8 | 50 | 42 |

a[H2O] = 0.45 mmol L⁻¹; [IB] = 0.75 mol L⁻¹. bGravimetric conversion. cMethod 1 was adopted for initiator solution preparation. dModified method 1 was adopted for initiator solution preparation. eMethod 2 was adopted for initiator solution preparation.
Entries 14–17 in Table 2 correspond to the polymerization process using initiator solutions prepared by method 1. Compared with entries 1–3 in Table 1, the conversion was improved by substituting Et2O with iPr2O. Meanwhile, the content of exo-olefin decreases remarkably. These phenomena were related to the weakened interaction between ether and AlCl3. It allows AlCl3/iPr2O complexes to catalyze the proton dissociation more effectively and weakens the effect of iPr2O on the stability of carbenium ions. We could also observe from entries 14–17 that (1) the conversion has a remarkable increase with the residence time increasing from 60 to 600 s, indicating the delay of chain termination, and (2) the content of exo-olefin increases and the \( M_n \) decreases with the increase of temperature, indicating the enhancement of proton elimination. Compared with Et2O, iPr2O did not show the clear effect of isomerization because the steric hindrance may cause it to have a substantial effect on the end of propagating chains only.

For the initiator solution prepared by method 2, the ATR–FTIR spectrum shows that most of characteristic peaks are accordant with those of free iPr2O. The corresponding polymerization experiments were listed as entries 18–19 in Table 2. The results are similar with those in entries 6–13 of Table 1. High conversion and broad \( D \) were obtained. H2O catalyzed by AlCl3 could provide a well-dissociated proton to start fast initiation, which is affected by the little amount of additive iPr2O as iPr2O does not participate in the interaction between H2O and AlCl3. Meanwhile, iPr2O could promote chain transfer as well as inhibit chain termination to achieve high conversion.

**Cationic Polymerization of IB in CH2Cl2.** According to the above-mentioned experiments, the effects of the addition sequence of solvents on the interaction between AlCl3, ether, and H2O as well as polymerization performance were quite distinct in hexane (the nonpolar solvent). Herein, to recognize whether the addition sequence always needs serious consideration, CH2Cl2 as a typical polar solvent was adopted to carry out similar investigations.

From the ATR–FTIR spectra shown in Figure 3, for the initiator solution containing AlCl3 and Et2O, the addition sequence of CH2Cl2 has a little influence on the composition of the initiator solution. In detail, the characteristic peak of Et2O at 1126 cm\(^{-1}\) disappears and some new peaks emerge, such as the peaks at 990 and 975 cm\(^{-1}\). The spectrum indicates that there exists intensive interaction between Et2O and AlCl3 in CH2Cl2. Table 3 shows the polymerization performances of various initiator solutions. Evidently, the influence of the preparation method on the polymerization could be neglected. The high content of exo-olefin is resulted from the intensive interaction between Et2O and AlCl3, which stabilizes the carbenium ions effectively. On the other hand, the low

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**Table 2. Polymerization of IB Catalyzed by AlCl3 with the Addition of iPr2O in Hexane**

| entry | \( T \) (°C) | \( t \) (s) | AlCl3 (mmol L\(^{-1}\)) | \( [iPr2O]/[AlCl3] \) | conv. (%) | \( M_n \) (GPC) | \( D \) | exo (%) | tri + endo (%) | tetra (%) |
|-------|-------------|-------------|-----------------|-------------------|----------|----------------|------|---------|----------------|---------|
| 14\(^a\) | 20 | 60 | 4.44 | 1.61 | 20 | 2340 | 2.68 | 33 | 33 | 34 |
| 15\(^a\) | 20 | 600 | 4.44 | 1.61 | 40 | 1810 | 2.95 | 41 | 28 | 31 |
| 16\(^a\) | 0 | 60 | 4.44 | 1.61 | 16 | 5270 | 3.09 | 26 | 35 | 39 |
| 17\(^a\) | 0 | 600 | 4.44 | 1.61 | 32 | 4960 | 3.61 | 25 | 29 | 46 |
| 18\(^a\) | 0 | 12 | 4.30 | 1.66 | 70 | 5420 | 4.12 | 8 | 51 | 41 |
| 19\(^a\) | 25 | 12 | 4.69 | 1.52 | 38 | 2230 | 3.16 | 12 | 51 | 37 |

\(^a[H2O] = 0.45\) mmol L\(^{-1}\); \([iPr2O] = 7.14\) mmol L\(^{-1}\); \([IB] = 0.75\) mmol L\(^{-1}\). \(^b\)Gravimetric conversion. \(^*\)Method 1 was adopted for the preparation of the initiator solution. \(^*\)Method 2 was adopted for the preparation of the initiator solution.

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**Figure 2.** ATR–FTIR spectra for the interaction between AlCl3 and iPr2O in hexane.

**Figure 3.** ATR–FTIR spectra for the interaction between AlCl3 and Et2O in CH2Cl2.
conversion is resulted from the poor dissociation of protons from H₂O because the catalytic effect of AlCl₃ is inhibited by Et₂O seriously. Besides, the higher ratio of Et₂O to AlCl₃ corresponds to lower Mₙ and higher conversion, indicating that excessive Et₂O could promote proton elimination.

The initiator solutions containing AlCl₃ and iPr₂O prepared by method 1 and method 2 also presented similar ATR–FTIR spectra (Figure 4), and the polymerization performances shown in Table 4 were quite similar too. Compared with the interaction between Et₂O and AlCl₃, the interaction between iPr₂O and AlCl₃ is weaker. However, it could effectively accelerate proton elimination and chain transfer to obtain the high content of exo-olefin and high conversion.

In general, the effects of ether on the IB polymerization catalyzed by AlCl₃ in CH₂Cl₂ are independent on the interaction with AlCl₃. When the interaction between ether, AlCl₃ and H₂O is easy to control and reproduce in CH₂Cl₂, a typical polar solvent. On the contrary, the interaction has the potential to be regulated facilely toward various requirements in hexane, a typical nonpolar solvent. If we regulate the cationic polymerization catalyzed by AlCl₃ or other Lewis acid in hexane by adding nucleophilic reagents, the addition sequence of reagents should be considered first.

**Investigation of Polymerization Mechanism.** To understand the various effects of ether on IB polymerization catalyzed by AlCl₃, we proposed the evolution of AlCl₃-involved interactions during the preparation of initiator solutions containing AlCl₃ and ether, as shown in Scheme 1.

Scheme 1. Evolution Routes of AlCl₃-Involved Interactions during the Preparation of Initiator Solutions Containing AlCl₃ and Ether

**Table 3. Polymerization of IB Catalyzed by AlCl₃ with the Addition of Et₂O in CH₂Cl₂**

| Entry | T (°C) | AlCl₃ (mmol L⁻¹) | [Et₂O]/[AlCl₃] | conv. (%) | Mₙ (GPC) | D | exo (%) | tri + endo (%) | tetra (%) |
|-------|--------|-----------------|----------------|-----------|-----------|---|---------|---------------|----------|
| 20ᵇ  | 0      | 7.98            | 1.21           | 19        | 1050      | 2.02 | 92      | 6             | 2        |
| 21ᶜ   | 0      | 8.10            | 1.19           | 20        | 1000      | 1.95 | 93      | 6             | 1        |
| 22ᶜ   | 0      | 6.75            | 1.07           | 12        | 1550      | 2.17 | 92      | 6             | 2        |
| 23ᶜ   | 0      | 6.82            | 1.06           | 13        | 1660      | 2.20 | 91      | 6             | 3        |

**Table 4. Polymerization of IB Catalyzed by AlCl₃ with the Addition of iPr₂O in CH₂Cl₂**

| Entry | T (°C) | AlCl₃ (mmol L⁻¹) | [iPr₂O]/[AlCl₃] | conv. (%) | Mₙ (GPC) | D | exo (%) | tri + endo (%) | tetra (%) |
|-------|--------|-----------------|----------------|-----------|-----------|---|---------|---------------|----------|
| 24ᶜ   | 0      | 4.20            | 1.60           | 88        | 3740      | 2.10 | 88      | 6             | 6        |
| 25ᶜ   | 0      | 4.20            | 1.60           | 84        | 3650      | 2.18 | 85      | 8             | 7        |

**Note:** The solid line and the dashed line correspond to strong and weak interactions between pairing groups, respectively.

**Note:** [H₂O] = 1.12 mmol L⁻¹; t = 60 s; [IB] = 0.75 mol L⁻¹. ¹Gravimetric conversion. ²Method 1 was adopted for the preparation of the initiator solution. ³Method 2 was adopted for the preparation of the initiator solution.

**Figure 4. ATR–FTIR spectra for the interaction between AlCl₃ and iPr₂O in CH₂Cl₂.**
contact with AlCl₃ first, denoted as sequence 2. In nonpolar hexane, sequence 1 leads to a strong interaction between AlCl₃ and H₂O, and the interaction between AlCl₃ and ether will be weak. With the electrophilicity of AlCl₃, the proton would be ionized easily to show high reactivity. The additive ether could promote the proton elimination or isomerization (for Et₂O only in this work) greatly and delay chain termination to achieve high conversion or low content of exo-olefin. Sequence 2 leads to a strong interaction between AlCl₃ and ether, which is helpful to stabilize carbenium ions and obtain a high content of exo-olefin. The interaction between AlCl₃ and H₂O will be weak, inhibiting the dissociation of protons to decrease conversion seriously. Compared with Et₂O, sequence 1 allows iPr₂O to have a weaker effect in promoting chain transfer and stronger effect in delaying chain termination, and sequence 2 allows iPr₂O to have a weaker effect in stabilizing carbenium ions.

In CH₂Cl₂ with high polarity, the interaction between AlCl₃ and H₂O and the interaction between AlCl₃ and ether are always of weak interaction. One weak interaction may allow AlCl₃ to have another weak interaction with the other Lewis base. Thus, there will be no difference between sequence 1 and sequence 2. Moreover, the proton is prone to dissociating from H₂O in polar solvents and is loosely bound by the counterion, presenting a relatively high reactivity.

### EXPERIMENTAL SECTION

**Materials.** n-Hexane (C₆H₁₃, 97.5+%, anhydrous), iPr₂O (99.0+%, CH₃Cl₂ (99.9+%, anhydrous), and AlCl₃ (99+%, anhydrous) were purchased from J&K Scientific (China). Et₂O (99.5+%) and ethanol (analytical reagent) were obtained from Sinopharm Chemical Reagent Co. Ltd (China). IB (99.9+%, anhydrous) was obtained from Dalian Special Gases Co., Ltd (China) and used directly as received. n-Hexane and CH₃Cl₂ were dried over Solvent Puri- fication Assembly (VAC, USA), and the content of water was determined by a Coulometric Karl Fischer moisture meter (Mettler Toledo, Switzerland). iPr₂O and Et₂O were distilled to remove stabilizer and then dried over molecular sieve 5Å overnight. iPr₂O, Et₂O, AlCl₃, n-hexane, and CH₃Cl₂ were stored in a glovebox (Mikrouna, China).

**Preparation of Initiator Solutions.** The initiator solution, consisted of AlCl₃, iPr₂O or Et₂O and n-hexane or CH₃Cl₂, was prepared in a glovebox, shortly before experiments. Two methods were taken to prepare the initiator solution. Method 1: ether was added onto the AlCl₃ solid first to form an AlCl₃−ether complex, and then the solvent, n-hexane or CH₃Cl₂, was added and stirred by using a magnetic stirrer (IKA, Germany) to obtain the initiator solution. To remove the ether not combining with AlCl₃ further, modified method 1 was also proposed. In modified method 1, vacuum treatment on the AlCl₃−ether complex was carried out before adding solvents. Method 2: hexane or CH₃Cl₂ was added onto the AlCl₃ solid first, and then ether was added and stirred to obtain the initiator solution. The content of AlCl₃ in the initiator solution was determined by a UV−vis spectrophotometer (UV-2450, Shimadzu).

**Polymerization of IB.** The polymerization of IB was carried out in a microflow system composed of three T-shaped micromixers (M1 for the mixing of IB and diluent (n-hexane or CH₃Cl₂), M2 for the mixing of the IB and initiator solutions, and M3 for the injection of the terminator agent, ethanol), two precoupling (or preheating) coiled tubes (C1 and C2, inner diameter 900 μm), and a microtube reactor (R, inner diameter 900 μm), as shown in Figure 5. The polymerization of IB proceeded throughout R1, and the reaction time could be changed by the flow rate and the length of R1. Four syringe pumps were used to deliver IB, n-hexane, initiator solution, and terminator, respectively. IB was transferred as the liquid from the bottom of the IB cylinder into the syringe and then mixed with n-hexane in the tube as the liquid under the pressure of 3 bar.

**Characterization.** **Size Exclusion Chromatography.** Molecular weight and dispersity value (D) of the polymers were measured by a Waters gel permeation chromatography (GPC) instrument composed of a Waters 2707 autosampler, a 1515 Isocratic HPLC pump, a 2414 refractive index detector, and three Styragel GPC columns, Styragel HT3, HT4, and HT5 (o.d., 7.8 mm; length, 300 mm; particle size, 10 μm; the detection range of molecular weight, 500 to 4 × 10⁶), thermostatted at 38 °C. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated with polystyrene standards. The results were processed by the Breeze 2 software from Waters.

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** Proton NMR (¹H NMR) spectra were recorded on a JNM-ECA 600 MHz spectrometer using CDCl₃ as the solvent. The PIB end-group content was calculated from ¹H NMR spectroscopy. Figure 6 shows a typical ¹H NMR spectrum. As seen, the main
resonance signals observed are located at $\delta = 1.11 (z), 1.41 (y), 0.99 (x), 4.85 (a1), 4.64 (a2), 5.17 (c1), 5.37 (c2), 5.15 (d)$, and 2.83 (e). The two characteristic protons of the exo-olefin end group (structure A, protons a1 and a2) appear as two well-resolved peaks at 4.85 and 4.64 ppm, respectively, while small amounts of the E and Z configurations of the trisubstituted olefin end group (structure C, protons c1 and c2) appear at 5.37 and 5.17 ppm. The one characteristic proton of the endo-olefin end group (structure D, proton d) appears at 5.15 ppm. The signal corresponding to the tetrasubstituted olefin end group (structure E, proton e) is a broad multiplet at 2.85 ppm. The methylene, methyl, and end methyl protons of the PIB chains (structure A, protons y, z, and x, respectively) usually appear at 1.41, 1.11, and 0.99 ppm, respectively.

**ATR−FTIR Spectroscopy.** The ATR−FTIR spectra were recorded in situ by using a Mettler Toledo ReactIR 15 instrument with a DiComp probe coupled to an MCT detector via AgX fiber. Each spectrum was collected every 256 s by accumulating 256 scans with a wavenumber resolution of 4 cm$^{-1}$ over the spectral range of 650−3000 cm$^{-1}$. The ATR−FTIR spectrum of the diluent (n-hexane or CH$_2$Cl$_2$) was chosen as the background. The measurement temperature was 25 °C.

## CONCLUSIONS

For the cationic polymerization of IB in hexane, we exploited different preparation methods to obtain different initiator solutions containing AlCl$_3$ and ether. Through FTIR measurement and reaction evaluation, two kinds of interactions between ether and H$_2$O/AlCl$_3$ and their different influences on chain reactions were revealed, which areas follows: (1) when AlCl$_3$ comes in contact with ether first, a strong interaction can take place to stabilize H$_2$O/AlCl$_3$ and decrease the reactivity of polymerization of IB catalyzed by AlCl$_3$ in hexane and (2) when AlCl$_3$ comes in contact with hexane first to interact with H$_2$O in hexane, only weak interaction between ether and H$_2$O/AlCl$_3$ can exist to promote proton elimination and isomerization. As for the AlCl$_3$-catalyzed polymerization of IB in CH$_2$Cl$_2$, the effects of ether are similar because of the weak interactions of H$_2$O/AlCl$_3$ and ether in polar solvents. Furthermore, the evolution routes of the AlCl$_3$-involved interactions were proposed to analyze the effect of ether on the polymerization when using different preparation methods of initiator solutions. In general, as ether was adopted to regulate the AlCl$_3$-catalyzed polymerization of IB, the reproducible process could be facilely achieved in polar solvents, while various processes with more potential are worth expecting in nonpolar solvents. This work deepens the understanding on the effects of ether on AlCl$_3$-catalyzed cationic polymerization and may provide support to achieve the rational process design for customized polymers.

## ACKNOWLEDGMENTS

The authors are gratefully thankful for the support of the National Natural Science Foundation of China (21176136 and 21422603) and National Science and Technology Support Program of China (2011BAC06B01) on this work.

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