This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Synthesis of Highly Reactive Polyisobutylene by FeCl₃/Ether Complexes in Hexanes; Kinetic and Mechanistic Studies†

Rajeev Kumar, a Priyadarsi De, b Bin Zheng, c Kuo-Wei Huang, c Jack Emert d and Rudolf Faust* a

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The kinetics and mechanism of the polymerization of isobutylene catalyzed by FeCl₃•ether complexes in hexanes at 0 °C was investigated. The polymerization rates increased in the diisopropyl ether < 2-chloroethyl ethyl ether < bis(2-chloroethyl) ether order, attributed to electronic effects. The polymerization rates increased with increasing initiator and catalyst concentration. The first order plots, however, deviated from the linear suggesting that the cation concentration decreases with time. The previously proposed mechanism is inadequate to explain this finding. The decrease in the polymerization rate with time is explained by the low solubility of the H⁺OR‘FeCl₃⁻ complexes that precipitate during polymerization. Based on mechanistic studies the revised mechanism now also includes the equilibrium H⁺OR‘FeCl₃⁻ ⇌ HCl + FeCl₃•OR‘.

Introduction

There is an increasing demand of polyisobutylene (PIB) based ashless dispersants for motor oil and fuel additives.¹ Lubricants or fuel dispersants are low molecular weight (M₆ ~ 500 - 5000 g/mol), oil soluble PIB or polybutenes (copolymers of isobutylene (IB) with C₄ olefins) with polar oligoamine end-groups.² The precursor polybutene or PIB olefins are generally produced by the AlCl₃ (or EtAlCl₃) catalyzed polymerization of a C₄ mixture, or by BF₃ catalyzed IB polymerization.³,⁴ Polybutenes contain an internal double bond, which has low reactivity towards maleic anhydride.³ Therefore, a chlorination/dehydrochlorination procedure to create a diene moiety is required to react efficiently with maleic anhydride. However, the final product may contain up to 5000 ppm residual chlorine. PIB exo-olefin, which is obtained using a BF₃ complex with ether or alcohol as catalyst, readily reacts with maleic anhydride in a thermal “ene” reaction to produce PIB succinic anhydride and subsequently polyisobutenylsuccinimide ashless dispersants.⁶ Because the final product does not contain any chlorine, this highly reactive (HR) PIB is more desirable than polybutenes.

Since BF₃ is detrimental for industrial equipment, and also requires low temperature to produce HR PIB, several methods have been developed in the recent past to obtain HR PIB.⁷,⁸,⁹ Arguably the most promising catalyst system comprises a Lewis acid/Lewis base complex.¹⁰ The latest development in new catalyst development for the synthesis of HR PIB has been reviewed recently.¹¹ The novel univalent gallium salts [Ga(C₅H₅F)]₃[Al(OR)₃]₄ and [Ga(1,3,5-Me₃C₅H₅)₂][Al(OR)₃]₄ (R¹ = C(CF₃)₃) were tested for initiating or catalyzing the synthesis of HR-PIB in several solvents.¹² Kostjuk et al., and Wu et al., reported the use of AlCl₃ and FeCl₃ ether complexes for the polymerization of IB in dichloromethane (DCM) or in DCM/hexanes 80/20 (v/v) mixtures to give HR PIB with more than 90% exo-olefinic content in the molecular weight range of 1100 – 3500 g/mol. The use of chlorinated solvent for the synthesis of HR PIB is a major drawback for this system, since rates and exo-olefin contents decrease with decreasing solvent polarity. In addition, only adventitious water has been shown to initiate the polymerization of IB in conjunction with the AlCl₃•ether complex.¹⁷ We have reported the use of GaCl₃ or FeCl₃ ether complexes for the polymerization of IB in nonpolar solvents in conjunction with conventional cationic initiators such as tert-butylchloride (t-BuCl),³⁸ and studied the steric and electronic effects of the ether structures on the polymerization rates and exo-olefin content.¹⁹ The aim of this work is to probe the proposed polymerization mechanism via kinetic studies, and to find a system that provides fast polymerization and high exo-olefinic end group content.

Experimental section

Materials

Technical grade hexanes (Doe & Ingalls) were refluxed over H₂SO₄ for 48 h, then washed with 10 % KOH aqueous solution and finally washed with distilled water until the aqueous layer was neutral. The hexanes were pre-dried by vigorously mixing with anhydrous Na₂SO₄ for 30 min and then refluxing over CaH₂ for 48 h. Then the hexanes were distilled onto CaH₂, refluxed again for 24 h, and freshly distilled just before the polymerization reactions. Dichloromethane (DCM, 99.8%, Aldrich) was washed with 5% KOH aqueous solution and washed with distilled water until the aqueous layer was neutral. It was stored over Na₂SO₄ overnight and then refluxed for 12 h with CaH₂ and distilled onto phosphorus pentoxide (P₂O₅). It was refluxed again for 24 h and...
freshly distilled just before polymerization. Isobutylene (IB, Matheson Tri Gas) was dried by passing it through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at -30 °C before use. 2-Methyl-1,3-propene-3,3,3-d (IB-d3) from C/D/N Isotopes Inc., Canada, 98.3 atom % D, iron trichloride (FeCl3, Aldrich 97%), t-BuCl (98%, TCI America) and P2O5 (98%, Alfa Aesar) were used as received. The IB-d3 was condensed in a receiver flask at -50 °C before use. Diisopropyl ether (i-Pr2O, anhydrous 99%), 2-chloroethyl ethyl ether (CEEE, 99%) and 2-chloroethyl ether (CEE, 99%), were purchased from Aldrich and used without any further purification. Cumyl chloride was prepared from cumyl alcohol (Aldrich, 97%) as reported elsewhere.

Preparation of FeCl3•dialkyl ether complexes in DCM

The FeCl3•dialkyl ether complexes were prepared just before the polymerization of IB. In the glove box, DCM was added to FeCl3, which had been previously weighed and sealed in a 20 mL vial with a Teflon septum. Next, an equimolar amount of the appropriate ether was added slowly via a syringe to the sealed vial containing the Lewis acid while stirring to form a 1.0 M Lewis acid/ether complex solution.

Polymerization of IB

Polymerization reactions were performed under a dry N2 atmosphere in an MBraun glovebox (MBraun, Inc., Stratham, NH). IB was condensed and distributed to the polymerization reactors, screw top culture tubes (75 mL), at 30 °C. The polymerizations, which were co-initiated with FeCl3•ether complexes at a monomer concentration of [IB] = 1.0 M, were performed in hexanes at 0 °C and terminated with methanol (MeOH). Monomer conversion was determined gravimetrically.

Characterizations

Number average molecular weights (Mn,GPC) and polydispersity index (PDI) values were obtained from size exclusion chromatography (SEC) with universal calibration using a Waters 717 Plus auto-sampler, a 515 HPLC pump, a 2410 differential refractometer, a MiniDawn multi angle viscosity detector from Wyatt, and five styragelHR GPC columns connected in the following order: 500, 105, 104 and 100 Å. The refractive index (RI) was the concentration detector. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min at room temperature. The results were processed using the Astra 5.4 software from Wyatt Technology Inc. The attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) was performed using a Mettler Toledo ReactIR 4000 instrument equipped with a DiComp probe connected to an MCT detector with a K6 conduit. Sampling wavenumbers were from 4000 to 650 cm⁻¹ at a resolution of 2 cm⁻¹.

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker 500 MHz spectrometer using CDCl3 or CD2Cl2 as solvents (Cambridge Isotope Laboratories, Inc.). A typical ¹H NMR spectrum of HR PIB obtained in this study is shown in Fig. 1. The two protons characteristic of the exo-olefin end group (Structure I, protons a1 and a2) appear at 4.85 and 4.64 ppm, while the endo-olefin end group (Structure II, proton d) shows a peak at 5.15 ppm. Small amounts of the E and Z configurations of another tri-substituted olefin end group (Structure III, protons e1 and e2) could be noticed at 5.37 and 5.17 ppm. The tetra-substituted olefin end group (Structure IV, proton f) appears as a broad multiplet at 2.85 ppm. Resonances for coupled PIB chains (Structure V, protons g) are normally found at 4.82 ppm. The methylene protons in the PIBCl end group (Structure VI, protons h) at 1.96 ppm were used to calculate the content of PIBCl. The methylene and methyl protons of the IB repeat unit (Structure I, protons b and c, respectively) were observed at 1.42 and 1.11 ppm, respectively. The number average molecular weights were determined from NMR (Mn,NMR) by using the formula: \( M_{n,NMR} = 56.11 \times ((h/2)/(a_1 + a_2) + d + e_1 + e_2 + f + (g/2) + (h/2)), \) where 56.11 is the molecular weight of IB, and a1, a2, b, c, d, e1, e2, f, g, h, etc. represents the area corresponding to those protons (Fig. 1).

Fig. 1 Typical ¹H NMR spectrum of HR PIB obtained in this study using FeCl3•dialkyl ether complexes.

Density functional calculations

Density functional theory (DFT) calculations were conducted employing the Gaussian 09 package at the B3LYP23,24 level of theory with Pople’s basis set 6-31G(d,p) for all atoms in the gas phase. Solvent effects of hexane were examined by geometries optimization using the polarizable continuum model with the integral equation formalism variant (IEFPCM)25 with the UAKS model. Different rotamers and spin multiplicities were all calculated and compared, and frequency calculations were performed to locate and confirm those structures as global minima for the binding energy calculation.

Results and discussion

Recently, we reported the polymerization of IB to yield HR PIB initiated by t-BuCl and coinitiated by FeCl3•ether complexes in hexanes at 0 °C.19 We have now carried out a more detailed kinetic and mechanistic study. A series of experiments were performed with different complex concentrations and representative data are shown in Tables 1-3. Additional
polymerization data can be found in the supplementary information in Tables S1-S3. The highest exo-olefin content of up to ~ 80% was achieved with the FeCl$_3$·i-Pr$_2$O complex. Furthermore the exo-olefin content remained relatively constant with time up to 60 min. The FeCl$_3$·CEE complex gave slightly lower ~65H75 % exo-olefin content that decreased after 20 min especially at the highest complex concentration due to an increase in coupled product. The FeCl$_3$·CEE complex resulted in the lowest exo-olefin content ~ 60 %. These results may be attributed to the decreasing basicity of the ethers with i-Pr$_2$O > CEEE > 10.

Table 1 Polymerization of [IB] = 1.0 M by FeCl$_3$·i-Pr$_2$O and [t-BuCl] = 0.02 M in hexanes at 0 °C. Polymerization time 60 min.

<table>
<thead>
<tr>
<th>#</th>
<th>[FeCl$_3$·iPr$_2$O] (M)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n$ NMR (g/mol)</th>
<th>$M_n$ GPC (g/mol)</th>
<th>PDF</th>
<th>exo$^d$ (%)</th>
<th>tri+endo$^d$ (%)</th>
<th>tetra$^d$ (%)</th>
<th>PIB-Cl$^d$ (%)</th>
<th>Coupled-PIB$^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>100</td>
<td>800</td>
<td>900</td>
<td>2.1</td>
<td>80</td>
<td>9</td>
<td>9</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>92</td>
<td>700</td>
<td>1100</td>
<td>2.3</td>
<td>77</td>
<td>9</td>
<td>11</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>44</td>
<td>1000</td>
<td>1200</td>
<td>3.0</td>
<td>70</td>
<td>9</td>
<td>12</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$Determined gravimetrically based on monomer feed. $^b$Determined from NMR analysis. $^c$Obtained from SEC measurements. $^d$Calculated from NMR spectroscopic study.

Fig. 2 Polymerization of IB (1.0 M) in the presence of FeCl$_3$·i-Pr$_2$O and t-BuCl (0.02 M) in hexanes at 0 °C: (A) conversion vs time plots at different FeCl$_3$·i-Pr$_2$O concentrations (■: 0.02 M, ●: 0.01 M and ▲: 0.005 M), and (B) corresponding first-order kinetics plots.

Table 2 Polymerization of [IB] = 1.0 M by [FeCl$_3$·CEE] and [t-BuCl] = 0.02 M in hexanes at 0 °C. Polymerization time 60 min.

<table>
<thead>
<tr>
<th>#</th>
<th>[FeCl$_3$·CEE] (M)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n$ NMR (g/mol)</th>
<th>$M_n$ GPC (g/mol)</th>
<th>PDF</th>
<th>exo$^d$ (%)</th>
<th>tri+endo$^d$ (%)</th>
<th>tetra$^d$ (%)</th>
<th>PIB-Cl$^d$ (%)</th>
<th>Coupled-PIB$^d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>90</td>
<td>300</td>
<td>500</td>
<td>2.3</td>
<td>60</td>
<td>16</td>
<td>9</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>100</td>
<td>300</td>
<td>400</td>
<td>2.9</td>
<td>63</td>
<td>14</td>
<td>13</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>99</td>
<td>500</td>
<td>600</td>
<td>2.6</td>
<td>64</td>
<td>13</td>
<td>15</td>
<td>0</td>
<td>7</td>
</tr>
</tbody>
</table>

$^a$Determined gravimetrically based on monomer feed. $^b$Determined from NMR analysis. $^c$Obtained from SEC measurements. $^d$Calculated from NMR spectroscopic study.

Fig. 3 Polymerization of IB (1.0 M) in the presence of FeCl$_3$·CEE and t-BuCl (0.02 M) in hexanes at 0 °C: (A) conversion vs time with different FeCl$_3$·CEE concentrations (■: 0.02 M, ●: 0.01 M and ▲: 0.005 M), and (B) corresponding first-order kinetics plots.
CEEE < CEE order. These findings are in complete agreement with this by determining the binding energies of ethers to FeCl₃. The lower binding energy of i-Pr₂O relative to Et₂O can be explained by steric effects, while the lower binding energies of chloro substituted ethyl ethers are due to electronic effects.

Experimentation was also carried out at different [r-BuCl] while [FeCl₃•i-Pr₂O] was kept constant at 0.01 M. The results are shown in Table 5 and Figure 5. At all initiator concentrations, a fast polymerization was observed at the initial stage of polymerization and the initial slope of the first order plots were approximately proportional to [r-BuCl]. However, all first order plots show a downward curvature.

Although the initial polymerization rates increase with increasing FeCl₃•ether and r-BuCl concentration as expected, all first order plots are curved suggesting that the PIB⁺ concentration decreases during polymerization. The previously proposed mechanism is shown in Scheme 1. The first step is initiation: the ionization of r-BuCl in the presence of FeCl₃•ether and cationation of IB. The propagating macro-cationic species PIB⁺ undergoes β-proton elimination to produce PIB exo-olefin and protonated ether FeCl₄⁻ complex is formed. This protonated ether further transfers the proton to the monomer and polymerization continues.

---

**Table 3** Polymerization of [IB] = 1.0 M by [FeCl₃•CEE] and [r-BuCl] = 0.02 M in hexanes at 0 °C. Polymerization time 60 min.

<table>
<thead>
<tr>
<th>#</th>
<th>[FeCl₃•CEE] (M)</th>
<th>Conv. (%)</th>
<th>M₀,NMR</th>
<th>M₀,GPC</th>
<th>PDF</th>
<th>exo</th>
<th>tri+endo</th>
<th>tetra</th>
<th>PIB-Cl</th>
<th>Coupled-PIB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>95</td>
<td>500</td>
<td>500</td>
<td>2.4</td>
<td>62</td>
<td>20</td>
<td>16</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>100</td>
<td>600</td>
<td>700</td>
<td>2.3</td>
<td>55</td>
<td>23</td>
<td>22</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>100</td>
<td>900</td>
<td>1000</td>
<td>2.4</td>
<td>50</td>
<td>22</td>
<td>26</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

* Determined gravimetrically based on monomer feed. 1 Determined from NMR analysis. 2 Obtained from SEC measurements. 3 Calculated from NMR spectroscopic study.

---

**Table 4** Calculated binding energies of ethers with FeCl₃ (kcal/mol).

<table>
<thead>
<tr>
<th>Ether</th>
<th>Binding energy in gas phase</th>
<th>Binding energy in hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₂O</td>
<td>-16.6</td>
<td>-14.3</td>
</tr>
<tr>
<td>i-Pr₂O</td>
<td>-15.8</td>
<td>-12.6</td>
</tr>
<tr>
<td>CEEE</td>
<td>-13.4</td>
<td>-10.3</td>
</tr>
<tr>
<td>CEE</td>
<td>-12.4</td>
<td>-8.1</td>
</tr>
</tbody>
</table>

---

**Table 5** Polymerization of [IB] = 1.0 M by [FeCl₃•r-Pr₂O] = 0.01 M in hexanes at 0 °C at different [r-BuCl]. Polymerization time 60 min.

<table>
<thead>
<tr>
<th>#</th>
<th>[r-BuCl] (M)</th>
<th>Conv. (%)</th>
<th>M₀,NMR</th>
<th>M₀,GPC</th>
<th>PDF</th>
<th>exo</th>
<th>tri+endo</th>
<th>tetra</th>
<th>PIB-Cl</th>
<th>Coupled-PIB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>45</td>
<td>1400</td>
<td>1300</td>
<td>2.3</td>
<td>70</td>
<td>13</td>
<td>16</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>60</td>
<td>1300</td>
<td>1200</td>
<td>2.7</td>
<td>68</td>
<td>14</td>
<td>15</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>80</td>
<td>1100</td>
<td>1000</td>
<td>2.9</td>
<td>73</td>
<td>11</td>
<td>15</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

* Determined gravimetrically based on monomer feed. 1 Determined from NMR analysis. 2 Obtained from SEC measurements. 3 Calculated from NMR spectroscopic study.

---

The conversion versus time and the first order plots are shown on Figures 2-4. The substantially higher rates of polymerization for both CEEE and CEE versus that of i-Pr₂O, is attributed to the reduced nucleophilicity of these ethers, which increases in the order CEE < CEEE < i-Pr₂O. We previously postulated that the less nucleophilic ether is more easily displaced from the complex, allowing for faster ionization of r-BuCl. We have now confirmed this by determining the binding energies of ethers to FeCl₃ by DFT calculations (Table 4).

We have previously reported that the polymerization of IB was absent with the FeCl₃•Et₂O complex. This is consistent with the high binding energy of this unhindered complex. According to Figures 2-4 the rate of polymerization increases in the i-Pr₂O < CEEE < CEE order. These findings are in complete agreement with the trend in the calculated binding energies of these ethers to FeCl₃.
Fig. 5 Polymerization of IB (1.0 M) in the presence of FeCl₃•i-Pr₂O (0.01 M) and t-BuCl in hexanes at 0 °C: (A) conversion vs time plots at different t-BuCl concentrations (■: 0.01 M, ●: 0.02 M and ▲: 0.04 M), and (B) corresponding first-order kinetics plots.

Scheme 1 Proposed mechanism of IB polymerization in the presence of FeCl₃•dialkyl ether complexes.

According to Scheme 1 the polymerization is first order in monomer and the initial polymerization rate is proportional to [t-BuCl] and [FeCl₃•ROR’]. After all the t-BuCl has reacted, the polymerization rate will depend on the rate of chain transfer to IB since the propagation rate constant of IB is close to the diffusion limit and [PIB] << [t-BuCl]. Thus, in this second stage of the polymerization the concentration of protonated ether should be close to the original [t-BuCl] when the starting concentration of the Lewis acid complex and initiator are the same. In order to clarify the mechanism of initiation, polymerization of IB-d₆ was carried out in the presence of [FeCl₃•i-Pr₂O] = 0.01 M and [t-BuCl] = 0.01 M at 0 °C in hexanes. After 30 min, 53% conversion was obtained. ¹H NMR spectroscopy was used to confirm initiation from t-BuCl (Figure 6), where we observed t-butyl, main chain –CH₂– and chain end –CH₂ protons at 0.99 (9H), 1.39 (n × 2H; n = number average degrees of polymerization) and 1.99 (2H) ppm, respectively.

From the ratio of peak areas at 1.39 and 0.99 ppm, an Mₙ,NMR = 740 g/mol was obtained, which is in excellent agreement with the Mₙ,GPC = 730 g/mol (PDI = 2.6), indicating near-quantitative initiator efficiency with t-BuCl.

However, when the complex concentration is lower than the concentration of the initiator (i.e. [FeCl₃•ROR’] = 0.01 M and [t-BuCl] = 0.02 M), half of the initiator would remain unreacted after all of the complex is protonated. Therefore, in the next stage, an experiment with cumyl chloride as initiator was performed to measure the efficiency of initiation. Cumyl chloride was chosen because the cumyl moiety gives a distinct peak in the ¹H NMR spectrum in the range of 7.0-8.0 ppm. We observed 53 and 94 % monomer conversions at 0.01 and 0.04 M cumyl chloride concentrations, respectively. According to the ¹H NMR
spectra (Figure 7) initiation from cumyl chloride is complete in both cases, because one cumyl group (7.1-7.5 ppm, 5H) is obtained per PIB chain. Also, $M_n$GPC = 1300 (PDI = 2.7) and 800 (PDI = 2.4) g/mol match nicely with the $M_n$NMR = 1300 and 900 g/mol, respectively at 0.01 and 0.04 M cumyl chloride concentrations. These results suggest the existence of the following equilibrium, whereby ionization of the cumyl chloride can proceed and the Lewis base can be regenerated:

$$i-Pr_2OH\cdot FeCl_3^- \rightleftharpoons HCl + FeCl_3\cdot i-Pr_2O$$

This was directly confirmed by ATR FTIR spectroscopy.

Figure 7 shows the ATR FTIR spectra of FeCl$_3$•i-Pr$_2$O complex in DCM, and the spectrum observed after purging with dry HCl (The solubility of the complex in hexanes is too low for ATR FTIR spectroscopy.). Upon purging with HCl two new peaks at 912 and 1060 cm$^{-1}$ appeared that are attributed to the protonated FeCl$_3$•i-Pr$_2$O complex, however, the characteristic C-O-C stretch of the complex ether at 1100 cm$^{-1}$ did not disappear completely. It is anticipated that in hexanes the ratio of protonated/unprotonated complex would be lower. It is also anticipated that the protonated ether salt would have a lower solubility in hexanes compared to that of the FeCl$_3$•i-Pr$_2$O complex.

Thus a 0.02 M FeCl$_3$•i-Pr$_2$O complex solution in hexanes was purged with HCl. During this process a precipitate was observed. The reaction mixture was transferred to a centrifuge tube and allowed to equilibrate at 0 °C. Then it was spun at 3750 rotation per minute for 10 min, an aliquot of the clear solution was transferred to a round bottom flask, the solvent and any excess ether was removed, and the residue was weighed. Based on the mass the concentration of hexanes soluble protonated and unprotonated complex is 0.0037 M. This is substantially lower than the soluble complex concentration.

According to these findings the proposed mechanism shown on Scheme 1 requires a revision. We now propose a revised mechanism shown in Scheme 2, in which the Lewis acid/ether complex is regenerated from protonated ether by loss of HCl, thereby providing a pathway for ionization of excess initiator. This revised scheme also contains an oxonium ion (dormant species) – carbenium ion (active species) equilibrium postulated in our earlier paper. Ummadisetty and Storey$^{10}$ directly observed the oxonium ion formed from the reaction of 2-chloro-2,4,4-trimethylpentane and diisopropyl ether in the presence of excess TiCl$_4$ at -70 °C by $^1$H NMR spectroscopy. At low temperature oxonium ion formation is complete and polymerization is absent. The carbenium ion - oxonium ion equilibrium constant is, however, strongly affected by temperature and the stability of the oxonium ion.$^{31}$ Although the equilibrium constant for the oxonium ion - carbenium ion equilibrium in Scheme 2 has not yet been determined, the polymerization of IB suggests that oxonium ion (transient species) formation is less than complete.

**Scheme 2** Revised mechanism of IB polymerization in the presence of FeCl$_3$•dialkyl ether complexes.

![Scheme 2](image-url)
Conclusion

The rate of the polymerization of IB initiated by t-BuCl and coinitiated by FeCl₃•ether complexes to yield HR PIB can be increased by decreasing the FeCl₃•ether binding energies in the i-Pr₂O > CEE > CEE order. The cation concentration, however, decreases with time for all three complexes due to precipitation of the protonated complex salt H⁺ROR′FeCl₃, which has a much lower solubility than that of FeCl₃•ether complex. The revised mechanism takes this into account in addition to H⁺ROR′FeCl₃ → HCl + FeCl₃•ether equilibrium. Thus for the efficient synthesis of HR PIB by Lewis acid•ether complexes both the complex and the protonated complex salt needs to be reasonably soluble. The recently discovered alkylaluminum dichloride•CEE complex and the protonated complex salt needs to be reasonably soluble. The recently discovered alkylaluminum dichloride•CEE complex and the protonated complex salt needs to be reasonably soluble. The recently discovered alkylaluminum dichloride•CEE complex and the protonated complex salt needs to be reasonably soluble.

Acknowledgement

Financial support from Infineum USA is greatly acknowledged.

Notes and references

(21) After quenching the polymerization, ~0.2 mL ammonium hydroxide solution was added to the polymerization tube at room temperature. Decomposed complex precipitated in the bottom of the tube and the solution was decanted to a 20 mL glass vial. Solvents were removed under the hood, and then the vial was dried at 40 °C under high vacuum for 6 h. Conversions were determined from the initial and final weights of the vial and the IB used during the polymerization.
For “Table of contents entry”

Synthesis of Highly Reactive Polyisobutylene by FeCl₃/Ether Complexes in Hexanes; Kinetic and Mechanistic Studies

Rajeev Kumar, Priyadarsi De, Bin Zheng, Kuo-Wei Huang, Jack Emert and Rudolf Faust*

In this study, the kinetics and mechanism of the polymerization of isobutylene catalyzed by FeCl₃•ether complexes in hexanes at 0 °C was investigated.