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Complexes of alkylaluminum dichlorides with ethers as fully soluble in hydrocarbons catalysts for the synthesis of exo-olefin terminated polyisobutylene at room temperature

Irina V. Vasilenko, Dmitriy I. Shiman, and Sergei V. Kostjuk*

Introduction

Low molecular weight polyisobutylene (PIB) (M\text{MW}=500-5000 g mol\textsuperscript{-1}) with high content of vinylidene (exo-olefin) end groups, that is, so-called highly reactive polyisobutylene (HR PIB), is a key intermediate in the preparation of motor oil and fuel additives. HR PIB is produced commercially by the polymerization of pure isobutylene (IB) or, rarely, C\textsubscript{4} mixture (IB, 1-butene, 2-butenes and hydrocarbons) using complexes of BF\textsubscript{3} with alcohols and/or ethers as co-initiator in hydrocarbons at moderately high temperatures (\textdegree{}C).\textsuperscript{1,2} The main disadvantage of this technique is gaseous state of BF\textsubscript{3} that makes difficulties to handle and is detrimental to equipments. Another advantage of the ether relative to the sulfide are low cost and accessibility towards polymerization of \textsubscript{C}4 mixed feed.\textsuperscript{6}

The cationic polymerization of isobutylene using RAICl\textsubscript{2}-nOPr\textsubscript{2}-based initiating systems (R=Me, Et, 'Bu; n=0.6–1) in non-polar n-hexane at 10 \textdegree{}C and high monomer concentration ([M]=2.8-5.8 M) has been investigated. Among complexes of alkylaluminum dichlorides with diisopropyl ether the best results in terms of exo-olefin content and monomer conversion showed EtAlCl\textsubscript{2}-nOPr\textsubscript{2} and 'BuAlCl\textsubscript{2}-nOPr\textsubscript{2} where n=0.8–0.9. These initiating systems afforded polyisobutylenes with desired low molecular weight (M\text{n}=1,000–1,500 g mol\textsuperscript{-1}) and high content of exo-olefin terminal groups (85–95\%) in a moderate yield (30–60\%). The use of “delayed proton abstraction” approach, i.e. when the polymerization of IB is co-initiated by RAICl\textsubscript{2} and separately added ether, allowed to increase both the reaction rate and the ultimate monomer conversion (70\% in less than 15 min), while the exo-olefin end group content remained high (85\%). Besides, RAICl\textsubscript{2}-OPr\textsubscript{2}-based initiating systems showed high activity and selectivity towards polymerization of \textsubscript{C}4 mixed feed.

One-step method for synthesis of allyl- and isobutenyl-terminated PIB via \textit{in situ} quenching of controlled cationic polymerization of IB with allyltrimethylsilane or isobutenyltrimethylsilane was proposed by the same authors.\textsuperscript{19} However, the former method is quite cumbersome, while the main disadvantage of the last method is the relatively high cost of quenching agents, which are used in excess with respect to the chain ends. As an alternative to these methods, Storey et al. reported the synthesis of mono- and difunctional exo-olefin terminated PIBs with near quantitative functionality via end-quenching of TiCl\textsubscript{4}-co-initiated polymerization of IB with strong hindered bases (2,5-dimethylpyrrole, 1,2,2,6,6-pentamethylpiperidine),\textsuperscript{4} sulfides (di-tert-buty1 sulfide, disopropylsulfide),\textsuperscript{5} and, recently, ethers (disopropyl ether, dioctyl ether).\textsuperscript{6} The use of sulfides and ethers as quenching agents is more efficient as compared to hindered bases since they can be applied at high chain-end (up to 0.1 M) and, consequently, monomer (up to 3.9 M) concentrations. In a meantime, advantages of the ether relative to the sulfide are low cost and absence of odor.\textsuperscript{8} In summary, the great advantage of this approach is the possibility to synthesize mono- and difunctional exo-olefin terminated PIBs (exo\textasciitilde{}100\%) with precisely controlled number-average molecular weight (M\text{\textasciitilde{}n}) and very narrow molecular weight distribution (MWD), but this method suffers from using of low reaction temperatures and chlorinated solvents. In addition, olefinic end groups can be also created via end-quenching of living PIB by 1,1-diphenylethylenec,\textsuperscript{20} but the internal double bond usually showed low reactivity towards further modification by maleic anhydride.\textsuperscript{1,2}

The recent interest to the synthesis of HR PIB by various research groups\textsuperscript{4,5,6,7,8,9,10,11,12,13,14,15,16,17} is driven by the growing demand for HR PIB due to the upcoming changes in the technical standards for lubricating oils/fuel additives.

Currently, three general approaches towards synthesis of HR PIB are intensively developing. The first one is based on the use of controlled cationic polymerization technique and was originally introduced by Kennedy and Ivan as a two-step procedure consisting in the synthesis of tert-chloride terminated PIB followed by successive dehydrochlorination by potassium tert-butoxide.\textsuperscript{18} Then, one-step method for synthesis of allyl- and isobutenyl-terminated PIB via \textit{in situ} quenching of controlled cationic polymerization of IB with allyltrimethylsilane or isobutenyltrimethylsilane was proposed by the same authors.\textsuperscript{19}

The second one consists in the synthesis of HR PIB followed by successive dehydrochlorination by potassium tert-butoxide.\textsuperscript{18} Then, one-step method for synthesis of allyl- and isobutenyl-terminated PIB via \textit{in situ} quenching of controlled cationic polymerization of IB with allyltrimethylsilane or isobutenyltrimethylsilane was proposed by the same authors.\textsuperscript{19} However, the former method is quite cumbersome, while the main disadvantage of the last method is the relatively high cost of quenching agents, which are used in excess with respect to the chain ends. As an alternative to these methods, Storey et al. reported the synthesis of mono- and difunctional exo-olefin terminated PIBs with near quantitative functionality via end-quenching of TiCl\textsubscript{4}-co-initiated polymerization of IB with strong hindered bases (2,5-dimethylpyrrole, 1,2,2,6,6-pentamethylpiperidine),\textsuperscript{4} sulfides (di-tert-buty1 sulfide, disopropylsulfide),\textsuperscript{5} and, recently, ethers (disopropyl ether, dioctyl ether).\textsuperscript{6} The use of sulfides and ethers as quenching agents is more efficient as compared to hindered bases since they can be applied at high chain-end (up to 0.1 M) and, consequently, monomer (up to 3.9 M) concentrations. In a meantime, advantages of the ether relative to the sulfide are low cost and absence of odor.\textsuperscript{8} In summary, the great advantage of this approach is the possibility to synthesize mono- and difunctional exo-olefin terminated PIBs (exo\textasciitilde{}100\%) with precisely controlled number-average molecular weight (M\text{\textasciitilde{}n}) and very narrow molecular weight distribution (MWD), but this method suffers from using of low reaction temperatures and chlorinated solvents. In addition, olefinic end groups can be also created via end-quenching of living PIB by 1,1-diphenylethylenec,\textsuperscript{20} but the internal double bond usually showed low reactivity towards further modification by maleic anhydride.\textsuperscript{1,2}
The second approach developed by Kühn and Voit consists in the use of solvent-ligated complexes with weakly coordinating borate or aluminolate anions ([M(NCCH₂)₃]⁻ (A₃), where M=Mn, Mo, Zn, Fe or Cu) as single-site catalysts for the polymerization of isobutylene. The mechanistic studies showed that polymerization in the presence of above-mentioned complexes proceeds via cationic mechanism and the water acts as an initiator which interacts with vacant coordination site of complex to lead to proton formation. These solvent-ligated complexes were successfully used for the synthesis of HR PIB (exo=60-95%) with relatively narrow MWD (Mₘ/Mₙ=2-5) in dichloromethane or even in non-polar toluene at high reaction temperatures (20-60 °C). Although these complexes can be used in catalytic amounts (~10⁻⁴ M), their high cost probably prevents their current industrial acceptance.

Several years ago we discovered the simple and efficient initiating systems, 2-phenyl-2-propanol (CumOH)/AlCl₃ and H₂O/AlCl₃ for the synthesis of HR PIB. Near at the same time, Wu and co-workers reported independently similar initiating system, i.e. H₂O/AlCl₃·OR₃ (R=Bu or Pr) and, later, H₂O/FeCl₃·OR₂ (R₂O=Et₂O, Bu₂O and Pr₂O). These initiating systems afforded desired low molecular weight PIB (Mₘ=1,000-3,000 g mol⁻¹) with relatively narrow MWD (Mₘ/Mₙ<2.0) in dichloromethane or CH₂Cl₂/n-hexane mixture at temperatures from −40 to 20 °C. In order to avoid the use of toxic chlorinated solvents, we have investigated the cationic polymerization of IB in toluene. It was shown that H₂O/AlCl₃ initiating system allowed to synthesize HR PIB (exo>90%) and that molecular weight of obtained PIBs can be easily controlled by the reaction temperature. The desired low molecular weight polymers with Mₘ=2300 g mol⁻¹ and 1,000 g mol⁻¹ and relatively narrow MWD (Mₘ/Mₙ=2.6 and 1.6) were synthesized in a high yield (>80%) in 10 min at 0 °C and 25 °C, respectively.

Since the commercial process of HR PIB production proceeds in aliphatic hydrocarbon solvents, the cationic polymerization of IB with H₂O/AlCl₃·OR₃ (R₂O=Bu₂O, Pr₂O) initiating systems were then investigated in n-hexane. Although this initiating system afforded HR PIB with acceptable exo-olefin end groups content (75-85%) in n-hexane even at high monomer concentration ([M]=5-8 M), the monomer conversion was relatively low (40-60% in the best conditions) due to low concentration of adventitious water in such non-polar media. In addition, the good functionality was observed only at temperatures below 0 °C (−20 °C) and the molecular weight was higher (Mₘ=3,000–6,000 g mol⁻¹) than required for the application for motor oil/fuel additives (Mₘ=1,000–2,300 g mol⁻¹) while MWD was relatively broad (Mₘ/Mₙ=2–5). In order to overcome above-mentioned limitations of AlCl₃·OR₃-based initiating systems, the complexes of FeCl₃ and GaCl₃ with ethers were recently introduced by Faust et al. as efficient catalysts for the synthesis of HR PIB in n-hexane. The major advantage of these new catalytic complexes in comparison with AlCl₃·OR₃ is the possibility to use them in a combination with alkyl chlorides due to the chlorophilic nature of FeCl₃ and GaCl₃. Therefore, the cationic polymerization of IB with tert-butyl chloride/FeCl₃·OPr₂ (GaCl₃·OPr₂) initiating systems readily proceeded in n-hexane at 0 °C resulting in close to complete monomer conversion (about 80-90%) in 20 min and good functionality (exo=80%). However, the polymerization was investigated only at low monomer concentrations (1 M) and resulting polymer often contained significant amount of tert-chloride terminal groups that is undesirable for the application as oil/fuel additives. Another FeCl₃-based initiating system, H₂O/FeCl₃·PrOH was very recently reported for the synthesis of HR PIB in n-hexane at temperatures well below 0 °C. Although this initiating system allowed to synthesize PIBs with very high content of exo-olefin terminal group (above 90%), the polymerization was relatively slow (70-80% of monomer conversion in 30 min), and the molecular weight was higher than required (Mₘ=3,000–6,000 g mol⁻¹). In addition, for all above-mentioned initiating systems the use of CH₂Cl₂ for the preparation of catalytic complex is required due to the very limited solubility of metal halides/complexes in hydrocarbon solvents that is also detrimental from industrial point of view. Therefore, despite of very encouraging results obtained with MCl₃·OR₂ (M=Al, Fe, Ga) initiating systems during last years, the further improvements are necessary to meet all of the industrial requirements for the synthesis of HR PIB.

The present study describes the polymerization of IB using complexes of alkylaluminium dichlorides with disopropyl ether in n-hexane at room temperature (10 °C) and at high monomer concentrations ([M]=2.5-8.5 M). Under these conditions HR PIB (exo=85-90%) with desired low molecular weight (Mₘ=1,000–2,500 g mol⁻¹) were obtained at high monomer conversion (60-80%) in a short period of time (10 min).

### Experimental

#### Materials

Isobutylene (Aldrich, 99%) was dried in the gaseous state by passing through the column packed with CaCl₂. C₄ mixed feed containing 45.7 wt% of isobutylene, 24.1 wt% of 1-butene, 10.0 wt% of trans-2-butene, 6.7 wt% of cis-2-butene, 10.0 wt% of n-butane, 3.4 wt% of isobutane and traces of 1,3-butadiene and methycyclopropane was purified similarly to isobutylene. n-Hexane (Sigma-Aldrich, >96%) was very recently reported for the synthesis of oils and fuels. The major advantage of this initiating system allowed to synthesize PIBs with very high content of exo-olefin terminal group (above 90%), the polymerization was relatively slow (70-80% of monomer conversion in 30 min), and the molecular weight was higher than required (Mₘ=3,000–6,000 g mol⁻¹). In addition, for all above-mentioned initiating systems the use of CH₂Cl₂ for the preparation of catalytic complex is required due to the very limited solubility of metal halides/complexes in hydrocarbon solvents that is also detrimental from industrial point of view. Therefore, despite of very encouraging results obtained with MCl₃·OR₂ (M=Al, Fe, Ga) initiating systems during last years, the further improvements are necessary to meet all of the industrial requirements for the synthesis of HR PIB.

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and then transferred to the NMR tube, which was previously evacuated and filled by argon.

**Polymerization procedures**

The polymerization reactions were carried out in glass tubes equipped with a cold finger condenser under argon atmosphere at 10 °C unless otherwise stated. Two general approaches to conduct the cationic polymerization of IB were used in this work. In a first approach, the polymerization was induced by the addition of monomer into reaction mixture containing catalytic complex (formed *in situ*) and solvent. As an example of a typical procedure, polymerization was initiated by adding of isobutylene (3.2 g, 5.7×10⁻² mol) to a mixture of a total volume 5.25 mL consisting of solutions of diisopropyl ether (0.2 mL, 1 M) and ³BuAlCl₂ (0.25 mL, 1M) in n-hexane and n-hexane (4.8 mL).

After a predetermined time, ca. 2 mL of ethanol was poured into the glass reactors. In a second approach, the polymerization was initiated by the addition of *free* alkylaluminum dichloride into reaction mixture containing monomer, required amount of ether and solvent. As an example of a typical procedure, polymerization was initiated by adding of solution of EtAlCl₂ in n-hexane (0.22 ml, 1 M) to a mixture of a total volume 10.2 ml containing isobutylene (1.6 g, 2.86×10⁻² mol), solution of diisopropyl ether in n-hexane (0.18 ml, 1 M), and n-hexane (7.6 ml). After a predetermined time, ca. 2 mL of ethanol was poured into the glass reactors. The quenched reaction mixtures were diluted by n-hexane, washed with 0.5 M nitric acid and deionized water to remove the aluminum–containing residues, evaporated to dryness under reduced pressure, and dried in vacuum (60 ºC) to give the product polymers. Monomer conversions were determined gravimetrically.

**Polymer characterization**

Size exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column and one precolumn (PL gel 5 µm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. 35 °C. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). 1H NMR (400 MHz) spectra were recorded in CDCl₃ or C₆D₆ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the residual solvents resonances.

**Table 1**  
Polymerization of isobutylene co-initiated by ³BuAlCl₂/nO₂Pr₂ at different Lewis acid (LA)/O₂Pr₂ ratios in n-hexane at 20 °C

<table>
<thead>
<tr>
<th>Run</th>
<th>LA/O₂Pr₂ (mol/mol)</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
<th>M₄ (SEC) (g mol⁻¹)</th>
<th>M₅ (NMR) (g mol⁻¹)</th>
<th>M₆/M₄</th>
<th>[PIB]⁺ (mM)</th>
<th>End groups distribution (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<tr>
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<td>2.1</td>
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<td>1:1</td>
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<td>520</td>
<td>2.4</td>
<td>10</td>
<td>93</td>
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<td>4</td>
<td>1:0.9</td>
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<td>2.8</td>
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<td>91</td>
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<td>1:0.8</td>
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<td>560</td>
<td>2.0</td>
<td>27</td>
<td>91</td>
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<tr>
<td>6</td>
<td>1:0.6</td>
<td>30</td>
<td>39</td>
<td>2040</td>
<td>3470</td>
<td>2.6</td>
<td>6</td>
<td>53</td>
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</tbody>
</table>

* [IB]=1.0 M; [BuAlCl₂]/[BuAlCl₂/nO₂Pr₂]=22 mM. The polymerization was initiated by the addition of monomer into reaction mixture containing catalytic complex and solvent. ³ Determined by ¹H NMR as M₄(NMR)=56×[(u/2)(b+b+k)/2+d+e+g)]. 4 The content of coupled polymer chains is less than 1 mol%. 5 All values are averaged from several runs.

These preliminary trials showed that alkylaluminum dichloride complexes with diisopropyl ether (optimal molar ratio of Lewis acid to ether is between 1:0.9 and 1:0.8) are very promising catalysts for the synthesis of HR PIB with desired low molecular weight and high content of exo-olefin end groups at room temperature. However, the monomer conversion was very low.

**Results and discussion**

**Preliminary tests**

Complexes of isobutylaluminum dichloride (³BuAlCl₂) and ethylaluminum dichloride (EtAlCl₂) with diisopropyl ether were screened for their potential in the synthesis of HR PIB in n-hexane at room temperature (Table 1). The selection of these Lewis acids is based on our preliminary study of the activity of different organoaluminum compounds (dialkylaluminum chlorides, alkylaluminum sesquichlorides and alkylaluminum dichlorides) and their complexes with various ethers in the cationic polymerization of isobutylene in toluene as a solvent. The choice of diisopropyl ether is based on the previous investigations of our team 11 and others 12,13,15,16 showing that complexes of metal halides (AlCl₃, FeCl₃, GaCl₃) with Pr₂O gave the best results in terms of monomer conversion and exo-olefin end groups content.

As it can be seen from Table 1, free Lewis acid induced fast cationic polymerization of IB (full conversion in 3 min) leading to conventional PIB containing mainly *endo-* and *tri*-substituted double bonds. On the contrary, the use of equimolar complex of ³BuAlCl₂ with diisopropyl ether afforded HR PIB with high content of exo-olefin groups (>90%), but the monomer conversion was very low (<10%) even after 30 min of polymerization (runs 2, 3, Table 1). The use of some excess of Lewis acid over ether (³BuAlCl₂/Pr₂O from 1:0.9 to 1:0.8 mol/mol) allowed to increase the monomer conversion without significant influence on the content of exo-olefin end groups (runs 4, 5 Table 1), while further decrease of ether concentration led to essential diminish of exo-olefin end groups content at the α-end (run 6, Table 1). In addition, the molecular weight of PIBs synthesized with ³BuAlCl₂/Pr₂O ratio of 1:0.6 mol/mol was relatively high indicating the low efficiency of ether towards β-H abstraction at such low its concentration.

This behaviour of alkylaluminum dichloride complexes is completely different from one observed for the complexes of AlCl₃ where the use of even small excess of Lewis acid over ether reduced the exo-olefin terminal groups content significantly. 11

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(about 20-30% in the best cases) and the polymerization was quite slow that is inconsistent with the industrial requirements. The low monomer conversion can be connected either with low concentration of water in non-polar n-hexane (≤0.4 mM) or relatively high probability of ion pair collapse (pathway A in Scheme 1) leading to consumption of initiator (water) with the formation of inactive in the polymerization tert-chloride terminated PIB according to mechanisms proposed by us and Faust et al. Indeed, although the average concentration of PIB chains is by 1 order of magnitude higher than the concentration of initiator (adventitious water) (see Table 1), these values are by 0.5-1 order lower than ones reported for the cationic polymerization of IB with metal halides complexes. Therefore, we assumed that the use of higher monomer concentration would allow to shift the equilibrium between pathways A and B towards ether-assisted chain transfer to monomer (pathway B in Scheme 1).

**Effect of Lewis acid and monomer concentration**

As it can be seen from Table 2, the monomer conversion and the average concentration of PIB chains were gradually increased with increasing monomer concentration that is fully consistent with above mentioned assumption. Importantly, the molecular weight and \(\text{exo}-\text{olefin} \) end groups content almost did not change while MWD became slightly broader with increasing monomer concentration from 1.0 to 5.8 M. The PIBs with desired low molecular weight (\( M_n=1,000-1,500 \) g mol\(^{-1}\)) and high content of \(\text{exo-olefin} \) terminal groups (85–95%) can be obtained even at such high monomer concentration as 5.8 M. Moreover, high functionality and low \( M_n \) retained even in a neat isobutylene, although the polymerization was relatively slow in such conditions (run 4 in Table 2).

**Table 2** Polypropylene of isobutylene co-initiated by RAICl\(_n\)×0.9OPr\(_2\) (R=Me, Et, 'Bu) at different monomer concentrations in n-hexane at 10 °C

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>Run</th>
<th>[IB] (mM)</th>
<th>Conversion (%)</th>
<th>( M_n ) (SEC) (g mol(^{-1}))</th>
<th>( M_n ) (NMR) (g mol(^{-1}))</th>
<th>( M_n/M_w )</th>
<th>[IB] (mM)</th>
<th>End groups distribution (mol%)</th>
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<td>Exo</td>
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<tr>
<td>'BuAlCl(_2)</td>
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<td>24</td>
<td>1520</td>
<td>1070</td>
<td>3.0</td>
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<td>62</td>
<td>1350</td>
<td>930</td>
<td>2.5</td>
<td>194</td>
<td>82</td>
</tr>
<tr>
<td>MeAlCl(_2)</td>
<td>11</td>
<td>5.8</td>
<td>19</td>
<td>3050</td>
<td>2550</td>
<td>3.9</td>
<td>24</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>12'</td>
<td>5.8</td>
<td>37</td>
<td>3090</td>
<td>2715</td>
<td>3.6</td>
<td>44</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>13'</td>
<td>5.8</td>
<td>60</td>
<td>2370</td>
<td>1940</td>
<td>3.1</td>
<td>100</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^{40}\) [LA=0.9OPPr\(_2\)]=22 mM; reaction time: 10 min. The polymerization was initiated by the addition of monomer into reaction mixture containing catalytic complex and solvent.\(^{41}\) Determined by \(^1\)H NMR as \( M_n[M(NR)]=56×(a(12)+(b+b+k)/2+d+e+g))\), see Figure 1 for assignments.\(^{42}\) [IB]/[IB]=56×(conv./\( M_n \))\(^{43}\). All values are averaged from several runs.\(^{44}\) [LA=0.9OPPr\(_2\)]=33 mM;\(^{45}\) Polymerization in a neat isobutylene.\(^{46}\) EtAlCl\(_2≤0.80\)OPr\(_2\) (22 mM) was used as co-initiator.\(^{47}\) Reaction time: 30 min.

The effect of Lewis acid nature on the monomer conversion and \(\text{exo-olefin} \) double bond content has been briefly investigated. The monomer conversion gradually increased in the following series MeAlCl\(_2<\)BuAlCl\(_2<\)EtAlCl\(_2\) (see Table 2) that is fully consistent with the decrease of the strength of corresponding complexes of alkylaluminum dichlorides with ether.\(^{48}\) The molecular weight, the average concentration of PIB chains and the content of \(\text{exo-olefin} \) end groups were quite similar for PIBs synthesized with complexes of \(\text{BuAlCl}_2\) and \(\text{EtAlCl}_2\) (runs 2 and 8 in Table 2). On the contrary, PIBs synthesized with MeAlCl\(_2≤0.90\)OPr\(_2\) as co-initiator were characterized by considerably higher molecular weight, lower concentration of PIB chains and \(\text{exo-olefin} \) end groups content (Table 2). These results indicated that \(\beta\)-H abstraction by disopropyl ether is less
efficient in this case that can be associated with the formation of relatively strong complex between MeAlCl₂ and Pr₂O.

Interestingly, the increase of concentration of the catalytic complex hardly influenced the monomer conversion (with the exception of using MeAlCl₂×0.90OPr₂ as co-initiator) but resulted in significant narrowing of MWD (compare runs 2, 3, runs 9, 10 and runs 12, 13 in Table 2; see Figure S1 for the representative SEC traces) and, in some cases, improving the functionality (runs 2, 3 Table 2). However, the use high concentration of catalytic complex was somewhat detrimental to exo-olefin content during prolonged reaction time (runs 9, 10 and 12, 13 in Table 2) due to faster isomerization/chain coupling at high Lewis acid concentration.

Much stronger effect on the monomer conversion showed the Lewis acid/ether ratio: the use EtAlCl₂×0.80OPr₂ instead of EtAlCl₂×0.90OPr₂ led to the increase of the monomer conversion from 29% to 41% but at the expense of lowering of exo-olefin terminal groups content from 92% to 84% (runs 7 and 8 in Table 2). The further improvement of monomer conversion (up to 55%) can be achieved by the increase of reaction time (runs 8, 9, Table 2). The content of exo-olefin end groups in this case slightly decreased due to the some increase of the fraction of tetra-substituted and coupled polymer chains (Table 2). A typical ¹H NMR spectrum of PIB synthesized at high monomer concentration at room temperature is presented in Figure 1. Interestingly, according to ¹H NMR spectrum (Figure 1), the amount of tert-chloride end groups is very low (<0.2 mol%) for PIBs synthesized with RAICl₂×OPr₂ initiating system in comparison with PIBs obtained with AlCl₃×OPr₂ initiating system (1-2 mol%) probably due to the much slower ion pair collapse (pathway A in Scheme 1) as compared to β-H abstraction (pathway B in Scheme 1).

A brief kinetic investigation of IB polymerization with H₂O/EtAlCl₂×0.80OPr₂ initiating system at [IB]=2.8 M (Figure 2a, curve 1) showed that the reaction was quite fast during the first 8–10 min; after this period of time the monomer conversion increased slowly with increasing reaction time to reach of ultimate conversion of about 50% after 30 min. Therefore, based on data presented in Table 2 and Figure 2, we can conclude that termination of polymerization after 8–10 min allowed keeping functionality (exo-olefin content) at high level due to the suppression of the formation of coupled polymer chains, but at the expense of some decreasing of polymer yield.

![Fig. 1](image1.png)

**Fig. 1** ¹H NMR spectrum of PIB (run 9, Table 2) obtained with H₂O/EtAlCl₂×0.90OPr₂ initiating system at high monomer concentration ([M]=5.8 M) in n-hexane at 10 °C.

The evolution of molecular weight with monomer conversion presented in Figure 2b showed that conventional chain transfer-dominated polymerization took place under investigated conditions: experimental Mₘs were decreased with increasing monomer conversion reaching the value of Mₘ of ca. 1170 g mol⁻¹ after 40% of monomer conversion. The molecular weight distribution slightly broadened throughout the polymerization to reach 3.0 at ultimate monomer conversion.

![Fig. 2](image2.png)

**Fig. 2** (a) Conversion vs. time and (b) Mₘ/NMR, Mₘ/Mₚ vs. conversion plots for the isobutylene polymerization co-initiated by EtAlCl₂×0.80OPr₂ or EtAlCl₂ and separately added diisopropyl ether in n-hexane at 10 °C. [EtAlCl₂]=22 mM; [EtPr₂O]=18 mM; [IB]=2.8 M. The sequence of components addition: (1) complex (EtAlCl₂×0.80OPr₂) was formed in situ and IB was added to system as the last component; (2) EtAlCl₂ was added to the system containing ether and monomer as the last component.

To summarize, PIBs with desired low molecular weight (Mₘ=1,000–1,500 g mol⁻¹) and high content of exo-olefin terminal groups (85–95%) in a moderate yield (30–60%) can be obtained even at such high monomer concentration as 5.8 M. This
is a strong improvement both in terms of molecular weight and exo-olefin content in comparison with \( \text{H}_2\text{O}/\text{AlCl}_3\times\text{OPr}_2 \) initiating system.\(^{1,15}\)

### Polymerization of IB co-initiated by EtAlCl\(_2\) and separately added ether

A way to increase the polymer yield can be the separate addition of Lewis acid and ether. In this approach, called by us “delayed proton abstraction”, the polymerization was initiated by the addition of free alkylaluminum dichloride into reaction mixture containing monomer, ether and solvent (see Experimental Section for details). The idea here is that free Lewis acid would co-initiate the polymerization more efficiently than complexed one, while free ether would still abstract the protons efficiently enough to generate predominantly exo-olefin double bond at polymer termini. This approach was first examined by Faust et al.\(^{5,16}\) in the cationic polymerization of isobutylene with \( \text{H}_2\text{O}/\text{AlCl}_3\times\text{OPr}_2 \) and \( \text{BuCl/GaCl}_3\times\text{OPr}_2 \) initiating systems. However, under such conditions only conventional PIBs containing predominantly tri- and tertia-substituted terminal olefin end groups were invariably obtained even in the presence of excess ether towards Lewis acid,\(^{15,16}\) probably due to the high Lewis acidity and poor solubility of these metal halides in \( n \)-hexane. However, the use of alkylaluminum dichlorides instead of conventional metal halides led to completely different results (Table 3).

As it is shown in Table 3, the use “delayed proton abstraction” approach in the case of \( \text{H}_2\text{O}/\text{EtAlCl}_3\times\text{OPr}_2 \) initiating system allowed to synthesize PIBs with high content of exo-olefin end groups (83%) and relatively high monomer conversion (up to 70%). The investigation of kinetics of the IB polymerization under these conditions showed that saturation conversion was obtained in less than 15 min (Figure 2a, curve 2), i.e. the polymerization is considerably faster that in the case of using of complex of \( \text{RAICl}_2 \) (R=\( \text{Bu}, \text{Et} \)) with disopropyl ether generated in situ (Figure 2a, curve 1). Furthermore, the content of exo-olefin end groups remained constant throughout the polymerization and did not change even after reaching the ultimate monomer conversion (Table 3).

### Table 3: Polymerization of isobutylene co-initiated by EtAlCl\(_2\); in the presence of separately added ether in \( n \)-hexane at 10 °C

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
<th>( M_1 ) (SEC) (g mol(^{-1}))</th>
<th>( M_2 ) (NMR) (g mol(^{-1}))</th>
<th>( \text{M}_i/\text{M}_o )</th>
<th>( [\text{PIB}] ) (mM)</th>
<th>End groups distribution (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>18</td>
<td>3200</td>
<td>2460</td>
<td>3.2</td>
<td>11</td>
<td>Exo 74, Endo 10, Tri 16</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5</td>
<td>20</td>
<td>1710</td>
<td>3.4</td>
<td>25</td>
<td>83, 6, 11</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>15</td>
<td>55</td>
<td>1870</td>
<td>3.7</td>
<td>60</td>
<td>83, 7, 10</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>68</td>
<td>69</td>
<td>2230</td>
<td>3.4</td>
<td>77</td>
<td>83, 6, 11</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>61</td>
<td>20</td>
<td>1770</td>
<td>3.8</td>
<td>136</td>
<td>80, 6, 14</td>
</tr>
</tbody>
</table>

\( [\text{EtAlCl}_2]=22 \text{ mM; } [\text{Pr}_2\text{O}]=18 \text{ mM; } [\text{IB}]=2.8 \text{ M.} \) Determined by \( ^1\text{H} \text{NMR as } M_2(\text{NMR})=56\times[(\text{i}2)/(\text{i}+\text{b}+\text{k}+\text{d}+\text{e}+\text{g})], \) see Figure 1 for assignments.

### Polymerization of \( C_4 \) mixed feed

The \( C_4 \) mixed feed is generally used for the production of conventional PIBs via \( \text{AlCl}_3 \)-co-initiated cationic polymerization at the industrial scale, while HR PIB is usually produced from pure isobutylene. Due to lower price, the use \( C_4 \) mixed feed instead of pure IB for the production of HR PIB is advantageous from economical point of view. To date, only a few reports devoted to the investigation of cationic polymerization of \( C_4 \) mixed feed using \( \text{H}_2\text{O}/\text{AlCl}_3\times\text{OPr}_2 \) or \( \text{H}_2\text{O}/\text{FeCl}_3\times\text{OPTr}_2 \) initiating systems are available in the literature. However, although both of these initiating systems afforded PIBs with high content of exo-olefin end groups (80-95%), the monomer conversion did not exceed 50% and molecular weight was considerably higher (\( M_n=3,000\text{–}10,000\text{ g mol}^{-1} \)) than required for commercial application.\(^{14,25}\) In this work, we briefly examined the efficiency of novel alkylaluminum dichloride-based initiating systems towards synthesis of HR PIB from \( C_4 \) mixed feed in comparison with \( \text{AlCl}_3 \)-based initiating system.

As shown in Table 4, the polymerization of \( C_4 \) mixed feed with \( \text{AlCl}_3\times\text{OPr}_2 \) as co-initiator afforded relatively high molecular weight PIB (\( M_n=1,800\text{ g mol}^{-1} \)) with high content of exo-olefin end groups, but monomer conversion was low (28%) (run 1, Table 4). The addition of small amount of water (initiator) to the system allowed to increase the polymer yield up to 64% and decrease the molecular weight until 6,500 g mol\(^{-1}\) but at the expense of some lowering of exo-olefin content (run 2, Table 4).
An attempt to further decrease the molecular weight by increasing the polymerization temperature led to significant decrease of exo-olefin end groups content. The similar strong dependence of exo-olefin terminal groups content on reaction temperature was observed by us for the cationic polymerization of IB with H2O/AlCl3/O2Pt2 initiating system.21

Table 4 Polymerization of C4 mixed feed co-initiated by AlCl3/O2Pt2 or ‘BuAlCl2 and separately added ether a

<table>
<thead>
<tr>
<th>Run</th>
<th>Co-initiator</th>
<th>Temperature (°C)</th>
<th>Conversion b (%)</th>
<th>Mw (SEC) (g mol–1)</th>
<th>Mn (NMR) c (g mol–1)</th>
<th>Mw/Mn</th>
<th>Mw/Mn e</th>
<th>Exo</th>
<th>Endo</th>
<th>Tetra</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AlCl3/O2Pt2</td>
<td>–20</td>
<td>28</td>
<td>10800</td>
<td>9950</td>
<td>2.9</td>
<td>11</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>AlCl3/O2Pt2</td>
<td>–20</td>
<td>64</td>
<td>6570</td>
<td>6760</td>
<td>2.7</td>
<td>10</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>AlCl3/O2Pt2</td>
<td>0</td>
<td>42</td>
<td>4370</td>
<td>4520</td>
<td>2.4</td>
<td>11</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>‘BuAlCl2</td>
<td>–20</td>
<td>24</td>
<td>2600</td>
<td>2680</td>
<td>4.2</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>‘BuAlCl2</td>
<td>0</td>
<td>63</td>
<td>1470</td>
<td>1470</td>
<td>2.9</td>
<td>8</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a [AlCl3/O2Pt2]= [‘BuAlCl2]= 22 mM; [Pr2]=18 mM. Reaction time: 30 min. b Calculated based on the isobutylene content in C4 mixed feed. c Determined by 1H NMR as Mw(NMR)=56×[(i+j)/[(b+k)/2+3×g–2×e]–2]. d See Figure 1 for assignments. e The content of coupled polymer chains is less than 1 mol%.

The use of H2O/‘BuAlCl3/O2Pt2 initiating system, in contrast to H2O/AlCl3/O2Pt2 system, allowed to synthesize HR PIB from C4 mixed feed with desired low molecular weight (Mw=2,600 g mol–1) and high functionality (exo=86%) (run 4, Table 1). The increase of polymerization temperature from −20 °C to 0 °C led to significant increase of polymer yield and some lowering of molecular weight (up to Mw=1,500 g mol–1) but, in contrast to polymerization with H2O/AlCl3/O2Pt2 initiating system, almost did not influence the exo-olefin content (run 5, Table 4).

Taking into account that C4 mixed feed contained significant amount of other cationically polymerizable olefins such as 1-butene, cis-2-butene and trans-2-butene (see Experimental part for the detailed composition of C4 mixed feed), the possible incorporation of these olefins into polymer chain has been investigated by 1H NMR spectroscopy (Figure 3).

According to Faust et al.,26 only monoaaddition (capping) of 1-butene and cis-2-butene took place, while trans-2-butene did not react with growing polyisobutylene macromations obtained via TiCl3-coinitiated living cationic polymerization. Since the signals of possible terminal βH-Cl groups for PIB–1-butene–Cl at ca. 4 ppm26 and PIB–2-butene–Cl at ca. 4.6 ppm26 were not detected in 1H NMR spectrum (see Figure 3), the following olefinic terminal groups formed due to the β-H abstraction from PIB–1-butene and PIB–2-butene cations can be postulated based on literature data (Scheme 2).26,27

Scheme 2 Possible chain end structures after monoaaddition of 1-butene and 2-butene to PIB+ macrocations following by β-H abstraction by ether.

The signals of the olefinic end groups of PIB capped with 1-butene (structures (IA) and (IB)), a major olefinic component of C4 mixed feed along with isobutylene, should appear near 5.4 ppm.28 However, no signals were observed in this region of 1H NMR spectrum indicating the absence of capping of polyisobutylene with 1-butene under investigated conditions. This observation is consistent with very low reactivity of 1-butene in comparison with isobutylene (isobutylene is ~543 times more reactive than 1-butene).29 The capping of PIB+ macroradical with 2-butene following by β-H abstraction according to Faust et al.26 and Maye et al.27 will result in the structures II–IIC (Scheme 2). The structure II is similar to tri-substituted end...
group (5.17 ppm and 5.36 ppm), while structure IIC is similar to one formed due to the chain coupling (4.81–4.83 ppm) (see Figure 1) and, therefore, these structures can not be distinguished from those formed in the course of isomerization/chain coupling during isobutylene polymerization. On the other hand, the signals of allyl-terminated PIB (structure II-B, 5.1 ppm and 5.6–5.7 ppm) are also absent in the spectrum (Figure 3). Therefore, the reaction of PIB with 2-butenone, which is ~294 times less reactive than isobutylene, is also unlikely under investigated conditions. Probably, the β-H abstraction by disopropyl ether is faster than end capping of PIB by olefins. These results suggest that cationic polymerization of C4 mixed feed with H2O/BuAlCl3/O(Pr)2 initiating system proceeds with high selectivity towards isobutylene polymerization.

To summarize, a great advantage of H2O/BuAlCl3/O(Pr)2 initiating system, in comparison with known systems, is the possibility to synthesize desired low molecular weight polyisobutenes (Mn=1,500–2,500 g mol⁻¹) in a high yield (above 60%) and good functionality (exo=82–86%) via selective cationic polymerization from Ca mixed feed.

Polymerization mechanism

Complex formation

In order to have an insight into polymerization mechanism, the formation of complexes of ethylaluminum dichloride with disopropyl ether as well as the interaction of EtAlCl2 and EtAlCl2-O(Pr)2 with water in non-polar C6D6 has been studied by 1H NMR spectroscopy.

As shown in Figure 4, the formation of complex between EtAlCl2 and Pr2O, similarly to the formation of AlCl3-O(Pr)2 complex, led to significant downfield shift of OCH protons of ether, while CH protons of Pr2O showed upfield shift. For EtAlCl2-O(Pr)2 two types of complexes with downfield shifts of OCH protons of disopropyl ether of 0.83 ppm and 0.93 ppm were observed. A similar observations were recently reported for AlCl3-O(Pr)2 complex in C6D6 at 25 °C. However, the comparison of chemical shifts of OCH protons of disopropyl ether for EtAlCl2-O(Pr)2 and AlCl3-O(Pr)2 in C6D6 revealed much stronger and uniform interaction of Lewis acid with ether for the former catalytic complex (downfield shifts of OCH protons of Pr2O of 0.17 ppm and 0.96 ppm were reported). Interestingly, one resonance of OCH protons at 4.26 ppm in EtAlCl2-O(Pr)2 showed nice splitting of signal, while the second peak at 4.37 ppm had broad line widths (Figure 4c, Figure S2), that indicates the formation of more exchangeable complex in the last case. In addition, the low intensity signal at 4.06 ppm (Figure 4c) can correspond to third type of EtAlCl2-O(Pr)2 complex, but its concentration is very low.

The signals of protons of CH3 and CH2 groups of EtAlCl2-O(Pr)2 also showed downfield shift of 0.46 ppm and 0.19 ppm in comparison with those of EtAlCl2 that confirms the formation of complex (Figure 4b, c, Figure S2, Figure S3). No signals of free Lewis acid or ether were detected in 1H NMR spectrum of EtAlCl2-O(Pr)2 (see Figure 4). Interestingly, only one series of well resolved signals of ethyl group in EtAlCl2 was observed suggesting the formation of presumably one type of complex that is in some contradiction with the conclusions made above. We can not explain this contradiction at present, but, probably, the ethyl group in EtAlCl2 is less sensitive towards complexation and we observed on Figure 4c an average signals for both of complexes. Another explanation can be the formation of dimeric complexes such as (Et2Al2Cl4)O(Pr)2. The generation of similar dimeric complexes was observed during the investigation of Et2AlCl with croton aldehyde.

Initiation

In order to investigate the initiation process, we studied further the interaction of EtAlCl2-O(Pr)2 complex with water. The reaction of water with a 1:1 EtAlCl2-O(Pr)2 complex (EtAlCl2-O(Pr)2·H2O ratio is 1:0.6 mol/mol) is relatively slow that is fully consistent with low activity of equimolar alkylaluminum complexes with disopropyl ether in the cationic polymerization of IB (see Table 1 and discussion therein). Indeed, no significant changes were observed in 1H NMR spectrum of EtAlCl2-O(Pr)2 in 10 min after addition of H2O except of the appearance of ethane peak at 0.8 ppm indicating slow hydrolysis of C–Al bond in EtAlCl2 (see Figure 5a and Figure S5). After 10 h of reaction of EtAlCl2-O(Pr)2 with water, the signals of ethyl group at 0.33 ppm (CH2) and 1.352 ppm (CH3) are almost completely disappeared (Figure 5a). The signals of OCH protons of disopropyl ether at 4.36 ppm and 4.26 ppm become broadened indicating the formation of more exchangeable complexes. In addition, the intensity of signal at 4.06 ppm is increased, while the new signal at 3.65 ppm is appeared (Figure 5a and Figure S6). The signals of methyl proton of disopropyl ether also became broadened (Figure 5, Figure S2 and Figure S6).

These data indicated the formation of several donor-acceptor complexes under investigated conditions. Importantly, no signals of OCH protons of free disopropyl ether at 3.43 ppm are appeared in spectrum (Figure 4a, Figure 5a, Figure S5) as it was reported for the reaction of AlCl3-O(Pr)2 with water15 that can be associated with different mechanism of initiation with H2O/EtAlCl2-O(Pr)2 and H2O/AICl3-O(Pr)2 initiating systems.

Finally, we also investigated briefly the interaction of free EtAlCl2 with water in order to clarify the difference (if any) in the initiation mechanism in the presence of EtAlCl2 and EtAlCl2-O(Pr)2 (Figure 6).
The addition of 0.2 equiv of water into NMR tube containing solution of EtAlCl₂ (0.05 M) in C₆D₆ led to the fast reaction with intensive evolution of ethane resulting in the formation of precipitate. The H NMR analysis of solution revealed the broadening of peaks of ethyl group as well as the appearance of broadening of peaks of ethyl group (Figure 6b and Figure 6c). The reaction of EtAlCl₂ with MgCl₂:H₂O (EtAlCl₂·H₂O=1:0.6 mol/mol) proceeds in more controlled fashion up to complete disappearance of signals of ethyl group of EtAlCl₂ (Figure 6a). Besides, in this case all products formed during the reaction of EtAlCl₂ with MgCl₂·6H₂O are soluble in C₆D₆.

**Mechanism**

The performed in this study ¹H NMR investigation of interaction of EtAlCl₂ with disopropyl ether allowed us to conclude that the formation of complex proceeds efficiently even in non-polar media. It is well known that aluminum alkyls as well as alkylaluminum dichlorides are present in dimeric form in solution. Taking into account the nice splitting of signals of ethyl group in EtAlCl₂ (Figure 4b and Figure S3) as well as literature data, we can postulate the formation of dinuclear chloride-bridged dimers of EtAlCl₂ rather than alkyl-bridged dimers. The addition of ether to these dimers leads to formation of monomeric complex (Scheme 3a) in non-polar C₆D₆ and n-hexane⁻⁻, as it is evidenced by ¹H NMR spectroscopy (Figure 4c).

Based on the ¹H NMR study as well as literature data, the reaction of H₂O with EtAlCl₂·OPr₂ is accompanied by the direct hydrolysis of Al–C bond followed by the formation of etherate of corresponding alumoxane. The similar reaction pathway was also proposed for the interaction of EtAlCl₂ with H₂O, which proceeds through the formation of an aqua-complex EtAlCl₂·H₂O followed by the transformation into alumoxane derivatives such as (Cl₂Al)₂O and (C₂H₅AlCl)₂O. The formation of alumoxane during the interaction of EtAlCl₂ with H₂O was also observed by ¹H NMR spectroscopy (see Figure 6). The initiation of polymerization occurs by H⁺ formed in the reaction of alumoxane with water (Scheme 3b). However, the initiation by H⁺ formed in the course of reaction of EtAlCl₂·OPr₂ with water can not be fully excluded (Scheme 3c).

The formation of alumoxane during the initiation step of polymerization can help to explain the following experimental observations. (i) High content of exo-olefin end groups even under excess of Lewis acid over ether (RAICl₂·OPr₂=1:0.8 mol/mol) is consistent with the consumption of free Lewis acid for the formation of alumoxane (the presence of even traces of free Lewis acid is detrimental for the functionality of PIBs obtained with AlCl₃ and GaCl₃ etherates). (ii) The relatively low monomer conversion and relatively low average concentration of PIB chains obtained with H₂O/RAICl₂·OPr₂ initiating system in comparison with complexes of conventional metal halides can be connected with the consumption of two molecules of water on the formation of one active center. (iii) The high exo-olefin end groups content obtained during IB polymerization co-initiated by RAlCl₂ and separately added ether (PIBs containing mainly tri- and tetra-substituted double bonds were formed in the case of separate addition of AlCl₃ or GaCl₃ and disopropyl ether) can be explained by the retarded initiation due to the formation of alumoxane at the very early stage of reaction. (iv) Relatively broad molecular weight distribution even at the beginning of reaction which almost does not change in the course of polymerization (Figure 2) (significant broadening of MWD with increasing monomer conversion was not change in the course of polymerization (Figure 2)) (significant broadening of MWD with increasing monomer conversion was not change in the course of polymerization (Figure 2)) (significant broadening of MWD with increasing monomer conversion was not change in the course of polymerization (Figure 2)). Finally, we would like to comment on the possible termination during RAICl₂·OPr₂-co-initiated isobutylene polymerization. Despite the relatively low concentration of water in non-polar n-hexane, the continuous β-H abstraction by ether would theoretically lead to slow consumption of.
of all monomer that is not observed in the present conditions (see Figure 2a). Therefore, the consumption of Lewis acid (alumoxane) on the process similar to one presented in Scheme 1 (pathway A) is most probably responsible for the termination of polymerization.

![Scheme 3 Complex formation and possible pathways for initiation of cationic polymerization of isobutylene with H2O/EtAlCl2 initiating system.](image)

**Conclusions**

We report here new efficient initiating systems based on complexes of alkylaluminum dichlorides with disopropyl ether for the synthesis of highly reactive PIB at room temperature and at high monomer concentrations ([IB]=2.8–5.8 M). In contrast to conventional metal halides-based systems 11,16 is they higher activity and at the same time good selectivity towards β-H abstraction at some excess of Lewis acid over ether. Moreover, PIbs with high content of exo-olefin were readily obtained for the first time using “delayed proton abstraction” approach, i.e. when the polymerization of IB is co-initiated by RAICl2 in the presence of separately added ether. Finally, RAICl2×OPr2-based initiating systems showed high activity and selectivity towards polymerization of C4 mixed feed: low molecular weight PIbs (Mn<2,500 g mol⁻¹) in such high yield (above 60%) were synthesized for the first time. Mechanistic studies suggest that reaction of EtAlCl2×OPr2 with water during the initiation stage of reaction is accompanied by the direct hydrolysis of AI–C bond followed by the formation of ethers of corresponding alumoxane (Cl2AlO×nOPr2). From the obtained results it is evident that RAICl2×OPr2-based initiating systems showed great potential for industrial application and can be a good alternative to currently used BF3-based systems. The one disadvantage of RAICl2×OPr2-based initiating systems can be moderate monomer conversion (up to 70%) obtained in this work. However, the addition of external water to the system allowed increasing the monomer conversion up to 90–95% without any deleterious effect on the exo-olefin end groups content. These results will be reported soon in a forthcoming paper.

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**Notes and references**

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† Electronic Supplementary Information (ESI) available: 1H NMR spectra of EtAlCl2, EtAlCl2×OPr2 and products of their reaction with water. See DOI: 10.1039/b000000x/

‡ In some 1H NMR spectra of EtAlCl2×OPr2 at higher concentration (0.1 M), the second series of signals of ethyl group was appeared (see Figure S4), but at relatively low concentration in comparison with a main series of signals.


17 K. J. Bartelson, P. De, R. Kumar, J. Emert and R. Faust, *Polymer* 2013, **54**, 4858.


Graphical Abstract

Complexes of alkylaluminum dichlorides with ethers as fully soluble in hydrocarbons catalysts for the synthesis of exo-olefin terminated polyisobutylene at room temperature

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