

**Cationic Polymerization of Isobutylene and C<sub>4</sub> Mixed Feed Using Complexes of Lewis Acids with Ethers: A Comparative Study**

Shiman Dmitriy I., Bereziianko Ivan A., Vasilenko Irina V., Kostjuk Sergei V.

Cite this article as:

Shiman Dmitriy I., Bereziianko Ivan A., Vasilenko Irina V., Kostjuk Sergei V.. Cationic Polymerization of Isobutylene and C<sub>4</sub> Mixed Feed Using Complexes of Lewis Acids with Ethers: A Comparative Study[J]. *Chinese J. Polym. Sci.*, 2019, 37(9): 891-897. doi: 10.1007/s10118-019-2290-4

View online: <https://doi.org/10.1007/s10118-019-2290-4>

---

**Articles you may be interested in**

[A User-friendly Living Cationic Polymerization: Degenerative Chain-transfer Polymerization of Vinyl Ethers by Simply Using Mixtures of Weak and Superstrong Protonic Acids](#)

Chinese J. Polym. Sci. 2019, 37(9): 851 <https://doi.org/10.1007/s10118-019-2233-0>

[CATIONIC POLYMERIZATION OF ISOBUTYLENE COINITIATED BY AlCl<sub>3</sub> IN THE PRESENCE OF ETHYL BENZOATE](#)

Chinese J. Polym. Sci. 2010, 28(1): 55

[Synthesis of Highly Reactive Polyisobutylenes with BF<sub>3</sub>Cyclohexanol Initiating System](#)

Chinese J. Polym. Sci. 2011, 29(3): 360 <https://doi.org/10.1007/s10118-011-1042-x>

[TiCl<sub>4</sub>共引发异丁烯正离子聚合合成反应活性聚异丁烯](#)

SYNTHESIS OF REACTIVE POLYISOBUTYLENE BY TiCl<sub>4</sub>COINITIATED CATIONIC POLYMERIZATION OF ISOBUTYLENE

高分子学报. 2008(2): 129 <https://doi.org/10.3724/SP.J.1105.2008.00129>

[HES/TiCl<sub>4</sub>体系引发异丁烯可控正离子聚合](#)

CONTROLLED CATIONIC POLYMERIZATION OF ISOBUTYLENE WITH HES/TiCl<sub>4</sub> INITIATING SYSTEM

高分子学报. 2008(12): 1166 <https://doi.org/10.3724/SP.J.1105.2008.01166>

[活性正离子聚合制备聚\(异丁烯-b-α-甲基苯乙烯\)嵌段共聚物](#)

SYNTHESIS OF POLY(ISOBUTYLENE-b-α-METHYLSTYRENE) COPOLYMERS BY LIVING CATIONIC POLYMERIZATION

高分子学报. 2008(6): 574 <https://doi.org/10.3724/SP.J.1105.2008.00574>

# Cationic Polymerization of Isobutylene and C<sub>4</sub> Mixed Feed Using Complexes of Lewis Acids with Ethers: A Comparative Study

Dmitriy I. Shiman<sup>a</sup>, Ivan A. Bereziianko<sup>a,b</sup>, Irina V. Vasilenko<sup>a</sup>, and Sergei V. Kostjuk<sup>a,b,c\*</sup>

<sup>a</sup> Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya St., Minsk 220006, Belarus

<sup>b</sup> Department of Chemistry, Belarusian State University, 14 Leningradskaya st., Minsk 220006, Belarus

<sup>c</sup> Sechenov First Moscow State Medical University, Institute for Regenerative Medicine, 8-2 Trubetskaya st., Moscow 119991, Russia

**Abstract** The cationic polymerization of C<sub>4</sub> mixed feed and isobutylene co-initiated by AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub>, <sup>t</sup>BuAlCl<sub>2</sub>×*n*O<sup>i</sup>Pr<sub>2</sub>, and [emim]Cl-FeCl<sub>3</sub>×*n*O<sup>i</sup>Pr<sub>2</sub> ([emim]Cl: 1-ethyl-3-methylimidazolium chloride) has been investigated. AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> co-initiated cationic polymerization of C<sub>4</sub> mixed feed proceeds at a lower rate than polymerization of isobutylene affording polymers with higher molecular weight. Complexes of <sup>t</sup>BuAlCl<sub>2</sub> with diisopropyl ether of different compositions are more suitable co-initiators than AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> for the synthesis of highly reactive polyisobutylene (HR PIB) from C<sub>4</sub> mixed feed due to their higher activity in the polymerization as well as possibility to prepare polyisobutylenes with lower molecular weight and higher content of *exo*-olefin end groups. However, <sup>t</sup>BuAlCl<sub>2</sub> needs activating *via* addition of external water (initiator) and/or interaction with salts hydrates in order to increase the reaction rate and the saturated monomer conversion. [Emim]Cl-FeCl<sub>3</sub>/<sup>i</sup>Pr<sub>2</sub>O is a quite promising catalyst for the preparation of HR PIB with high *exo*-olefin end group content (> 80%) and relatively low polydispersity ( $M_w/M_n < 2.8$ ) *via* cationic polymerization of C<sub>4</sub> mixed feed. The sonication of reaction mixture in case of using [emim]Cl-FeCl<sub>3</sub> allowed increasing the reaction rate and decreasing the molecular weight.

**Keywords** Cationic polymerization; Isobutylene; C<sub>4</sub> mixed feed; Highly reactive polyisobutylene

**Citation:** Shiman, D. I.; Bereziianko, I. A.; Vasilenko, I. V.; Kostjuk, S. V. Cationic polymerization of isobutylene and C<sub>4</sub> mixed feed using complexes of Lewis acids with ethers: A comparative study. *Chinese J. Polym. Sci.* 2019, 37, 891–897.

## INTRODUCTION

Highly reactive polyisobutylene (HR PIB), a low molecular weight polyisobutylene bearing mainly *exo*-olefin terminal group, is used as a precursor in the preparation of ashless dispersants for fuel and motor oil.<sup>[1]</sup> Among different catalytic systems for the synthesis of HR PIB discovered during the last decade,<sup>[2–8]</sup> the use of complexes of AlCl<sub>3</sub> with ethers, which was independently reported in 2010 by Kostjuk *et al.*<sup>[9]</sup> and Wu *et al.*<sup>[10]</sup>, is more promising due to their low cost as well as high activity and regioselectivity at ambient conditions. Since this discovery, the complexes of other metal halides such as FeCl<sub>3</sub>,<sup>[11–15]</sup> GaCl<sub>3</sub>,<sup>[13]</sup> TiCl<sub>4</sub>,<sup>[16,17]</sup> HfCl<sub>4</sub>,<sup>[18]</sup> and WCl<sub>4</sub><sup>[18]</sup> with ethers/alcohols were shown to be suitable for the synthesis of HR PIB. Although these complexes displayed high activity towards cationic polymerization of isobutylene (IB) in polar solvents<sup>[2,3,9–11]</sup> or toluene,<sup>[19,20]</sup> their activity and regioselectivity significantly reduced in non-polar hydrocarbons due to their poor solubility.<sup>[13,18,21]</sup> The solubility issue was addressed by using complexes of alkylaluminum dichlorides with ethers, which are fully soluble in *n*-hexane and other non-polar sol-

vents.<sup>[22–30]</sup> These new initiating systems, under optimized conditions, induced fast cationic polymerization of isobutylene at high temperature (0–20 °C) and monomer concentration (up to 5 mol·L<sup>-1</sup>) to afford HR PIB with desired low molecular weight ( $M_n < 2500$  g·mol<sup>-1</sup>) and high content of *exo*-olefin end groups (> 80%).<sup>[22–30]</sup> However, the polydispersity of obtained PIBs was typically high ( $M_w/M_n = 3–5$ ), which is detrimental for the application.<sup>[1]</sup> The polydispersity can be improved ( $M_w/M_n = 2.3–3.5$ ) by using the mixture of two ethers of different basicities and steric structures (diethyl and diisopropyl ethers) instead of <sup>i</sup>Pr<sub>2</sub>O<sup>[31]</sup> or micromixing conditions.<sup>[32]</sup> Very recently, we demonstrated that chlorometallate acidic ionic liquids in the presence of ethers initiated the cationic polymerization of IB affording HR PIB with relatively low polydispersity ( $M_w/M_n = 2.0–3.0$ ).<sup>[33,34]</sup> This was made possible due to the heterogeneous nature of polymerization process, which proceeds at the particle interface.<sup>[33,34]</sup>

Cationic polymerization of C<sub>4</sub> mixed feed is used at the industrial scale for production of conventional polyisobutylene, *i.e.* low molecular weight polyisobutylene with internal tri- and tetra-substituted olefinic end groups.<sup>[1,2,3]</sup> Therefore, the polymerization of C<sub>4</sub> mixed feed to yield polyisobutylene with high content of *exo*-olefin end groups is challenging. Despite the huge progress achieved in the synthesis of HR PIB from neat isobutylene using complexes

\* Corresponding author: E-mail [kostjuks@bsu.by](mailto:kostjuks@bsu.by) or [kostjuks@rambler.ru](mailto:kostjuks@rambler.ru)

Invited article for special issue of "Ionic Polymerization"

Received January 15, 2019; Accepted May 9, 2019; Published online June 25, 2019

of Lewis acids with ethers as catalysts,<sup>[2,3,22–34]</sup> considerably less attention has been paid to polymerization of C<sub>4</sub> mixed feed.<sup>[16,28,35,36]</sup> Most of examples reporting the cationic polymerization of C<sub>4</sub> mixed feed deal with application of the first generation of catalysts, namely complexes of metal halides with ethers.<sup>[16,28,35,36]</sup> On the other hand, only limited information is available in the literature regarding to the polymerization of C<sub>4</sub> mixed feed co-initiated by complexes of alkylaluminum dichlorides<sup>[28,37]</sup> and little data was about the activity of acidic ionic liquids/ethers systems towards polymerization of C<sub>4</sub> mixed feed.

Industrial C<sub>4</sub> mixed feed used in this work along with isobutylene (45.7 wt%) contains significant amount of 1-butene (24.1 wt%) and 2-butenes (16.7 wt% *cis* and *trans* isomers) (see experimental section for precise composition of C<sub>4</sub> mixed feed). Since these olefins may act as chain transfer agents or even terminate the polymerization,<sup>[37,38]</sup> detailed study of the cationic polymerization of C<sub>4</sub> mixed feed is required. The aim of this study is to estimate the activity and regioselectivity of above-mentioned three generations of catalysts for the synthesis of HR PIB, *i.e.* complexes with ethers of metal halides, alkylaluminum dichlorides, and acidic ionic liquids, in the cationic polymerization of C<sub>4</sub> mixed feed. The similarities and differences in the polymerization behavior of C<sub>4</sub> mixed feed and neat isobutylene will be discussed and the optimum catalytic system for the polymerization of C<sub>4</sub> mixed feed will be finally selected.

## EXPERIMENTAL

### Materials

Isobutylene (Aldrich, 99%) was dried in the gaseous state by passing through a column packed with drierite. C<sub>4</sub> mixed feed containing 45.7 wt% isobutylene, 24.1 wt% 1-butene, 10.0 wt% *trans*-2-butene, 6.7 wt% *cis*-2-butene, 10.0 wt% *n*-butane, 3.4 wt% isobutane, and traces of 1,3-butadiene and methylcyclopropane was purified similarly to isobutylene. *n*-Hexane (Sigma-Aldrich, > 95%) and CH<sub>2</sub>Cl<sub>2</sub> (Sigma-Aldrich, > 99.5%) were treated with sulphuric acid, washed with aqueous sodium bicarbonate, dried over CaCl<sub>2</sub>, and distilled twice from CaH<sub>2</sub> under an inert atmosphere. Diisopropyl ether (<sup>i</sup>Pr<sub>2</sub>O, Fluka, ≥ 98.5%) and diethyl ether (Sigma-Aldrich, 99%) were distilled over CaH<sub>2</sub> under argon. 1-Ethyl-3-methylimidazolium chloride ([emim]Cl, Sigma-Aldrich, ≥ 95%) was dried in vacuum for 5 h before use. AlCl<sub>3</sub> (Sigma-Aldrich, 99.999%), <sup>i</sup>Bu<sub>3</sub>Al (1 mol·L<sup>-1</sup> solution in hexanes, Sigma-Aldrich), FeCl<sub>3</sub> (Sigma-Aldrich, > 97%), CDCl<sub>3</sub> (Euriso-top<sup>®</sup>), ethanol (Sigma-Aldrich, > 96%), and tetrahydrofuran (anhydrous, Sigma-Aldrich, ≥ 99.9%) were used as received. Complex of AlCl<sub>3</sub> with <sup>i</sup>Pr<sub>2</sub>O (as 1 mol·L<sup>-1</sup> solution in CH<sub>2</sub>Cl<sub>2</sub>) was synthesized following the recipe described in Ref. [21]. Isobutylaluminum dichloride (<sup>i</sup>BuAlCl<sub>2</sub>) was obtained by mixing AlCl<sub>3</sub> and Bu<sub>3</sub>AlCl solutions in a 2:1 molar ratio at room temperature according procedure described in Ref. [28]. The pre-activation of <sup>i</sup>BuAlCl<sub>2</sub> was performed in the presence of required amounts of MgSO<sub>4</sub>·7H<sub>2</sub>O (15 mol% of H<sub>2</sub>O to <sup>i</sup>BuAlCl<sub>2</sub>) as described in Ref. [31]. [Emim]Cl-FeCl<sub>3</sub> was obtained by simple mixing of required amounts of [emim]Cl and FeCl<sub>3</sub> under argon atmo-

sphere according to a procedure described in the literature.<sup>[34]</sup>

### Instrumentation

Size exclusion chromatography (SEC) was performed on a Ultimate 3000 Thermo Scientific apparatus with Agilent PLgel 5 μm MIXED-C column (300 × 7.5 mm) and one precolumn (PL gel 5 μm guard 50 × 7.5 mm) thermostated at 30 °C. The detection was achieved by differential refractometer (thermostated at 35 °C). Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL·min<sup>-1</sup>. The calculation of molar mass and polydispersity was carried out using polystyrene standards (Polymer Labs, Germany). <sup>1</sup>H-NMR (500 MHz) spectra were recorded in CDCl<sub>3</sub> at 25 °C on a Bruker AC-500 spectrometer calibrated relative to the residual solvent resonance. The sonication was performed using Elmasonic S30H ultrasonic bath (ultrasonic power: 80 W; ultrasound frequency: 37 kHz).

### Polymerization Procedures

The polymerization reactions were carried out in glass tubes equipped with a cold finger condenser under argon atmosphere at temperatures from -20 °C to 10 °C. As an example of a typical procedure, polymerization of C<sub>4</sub> mixed feed was initiated by adding 9.6 mL of C<sub>4</sub> mixed feed to a mixture (total volume 0.58 mL) consisting of solutions of diisopropyl ether (0.15 mL, 1 mol·L<sup>-1</sup> in hexane), 6 μL (3.3 × 10<sup>-4</sup> mol) of deionized H<sub>2</sub>O, and pre-activated <sup>i</sup>BuAlCl<sub>2</sub> (0.38 mL, 1 mol·L<sup>-1</sup>). After a predetermined time, *ca.* 2 mL of aqueous ammonia (25%) was poured into the glass reactor to terminate the polymerization. The quenched reaction mixtures were diluted by *n*-hexane and filtered, evaporated to dryness under reduced pressure, and dried in vacuum (≤ 60 °C) to give the product polymers. Monomer conversions were determined gravimetrically.

## RESULTS AND DISCUSSION

### AlCl<sub>3</sub> × O<sup>i</sup>Pr<sub>2</sub> as Catalyst

Equimolar complex of AlCl<sub>3</sub> with diisopropyl ether was selected for the comparative study of cationic polymerization of IB and C<sub>4</sub> mixed feed as one of the most active representatives of the first generation catalysts (complexes of metal halides with ethers) for the synthesis of HR PIB.<sup>[2,3,9–21]</sup> The cationic polymerization of C<sub>4</sub> mixed feed co-initiated by AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> proceeded at a considerably lower rate in comparison with the polymerization of IB affording polymers with higher molecular weight and *exo*-olefin end group content (runs 1 and 2 in Table 1). Since adventitious water acts as the initiator in these experiments and the solubility of H<sub>2</sub>O in IB/*n*-hexane mixture and C<sub>4</sub> mixed feed may be different, we then investigated the effect of adding external H<sub>2</sub>O on the cationic polymerization of these two monomers. The addition of H<sub>2</sub>O allowed to increase the monomer conversion for the polymerization of C<sub>4</sub> mixed feed, although the reaction rate was still lower than that of IB polymerization (runs 3 and 4 in Table 1). However, cationic polymerization of C<sub>4</sub> mixed feed using H<sub>2</sub>O/AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> initiating system resulted in polymers with considerably higher molecular weight than it is required for practical application (*M*<sub>n</sub> ≤ 2300 g·mol<sup>-1</sup>).<sup>[1]</sup> As we showed

**Table 1** Cationic polymerization of C<sub>4</sub> mixed feed and isobutylene in the presence of AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> as co-initiator<sup>a</sup>

Run	M	Time (min)	Initiator (mmol·L <sup>-1</sup> )	T (°C)	Conv. <sup>b</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)		
								<i>exo</i>	<i>endo</i> + <i>tri</i>	<i>tetra</i>
1	IB	10	– <sup>c</sup>	–20	70	5950	3.8	71	12	17
2	C <sub>4</sub>	30	– <sup>c</sup>	–20	28	10800	2.9	82	11	7
3	IB	10	H <sub>2</sub> O	–20	77	2280	4.4	68	13	19
4	C <sub>4</sub>	30	H <sub>2</sub> O	–20	64	6570	2.7	75	10	16
5	IB	10	– <sup>c</sup>	0	57	2950	2.7	71	12	17
6	C <sub>4</sub>	30	– <sup>c</sup>	0	42	4370	2.4	73	11	16

<sup>a</sup> [AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub>] = 22 mmol·L<sup>-1</sup>; [IB] = [C<sub>4</sub>] = 5.2 mol·L<sup>-1</sup>; [H<sub>2</sub>O] = 30 mmol·L<sup>-1</sup>; <sup>b</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization; <sup>c</sup> Adventitious water acted as initiator

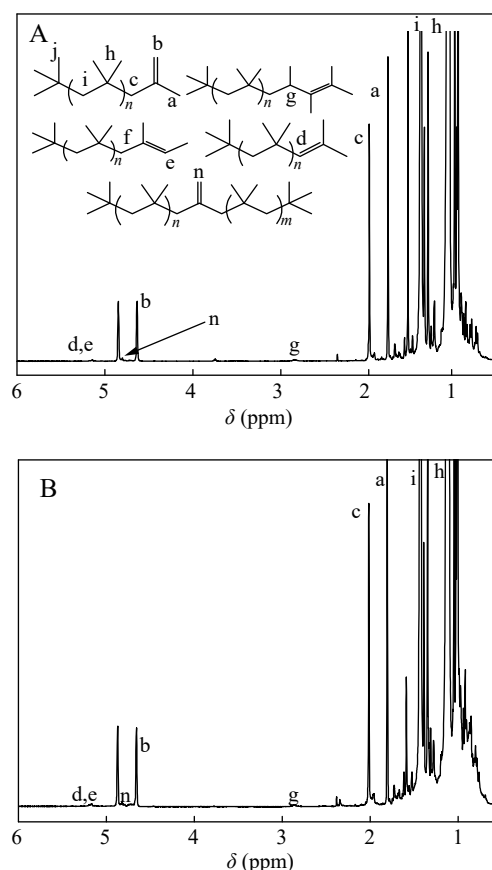
earlier,<sup>[19–21]</sup> the reaction temperature is a powerful tool in controlling the molecular weight during AlCl<sub>3</sub>×ether co-initiated isobutylene polymerization. Indeed, the increase of temperature from –20 °C to 0 °C resulted in some lowering of M<sub>n</sub> of polymers obtained from C<sub>4</sub> mixed feed up to 4370 g·mol<sup>-1</sup>, which is about two times higher than that of the polyisobutylene synthesized from neat IB (Table 1).

In summary, AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> co-initiated cationic polymerization of C<sub>4</sub> mixed feed proceeded at a lower rate than polymerization of isobutylene and afforded polymers with higher molecular weight and *exo*-olefin end group content as well as lower polydispersity. The systematically observed lower conversion and higher M<sub>n</sub> in the case of C<sub>4</sub> mixed feed polymerization can be explained by end-capping of the growing polyisobutylene chains by 1-butene that can lead to slow-down or termination of polymerization.<sup>[37]</sup> <sup>1</sup>H-NMR spectra of the HR PIB synthesized from neat IB and C<sub>4</sub> mixed feed are similar and independent of the catalyst used for polymerization (Fig. 1) indicating very low or no incorporation of 1-butene or other olefins into polymer chain. The similar conclusion was made by Wu *et al.* through the comparison between <sup>13</sup>C-NMR spectra of commercial HR PIB (Glissopal® 1000) and HR PIB prepared from C<sub>4</sub> mixed feed.<sup>[35,36]</sup> On the other hand, a very weak signal was observed in an olefinic part of spectrum at 5.39 ppm (Fig. 2a), which corresponds to the olefinic end group formed after 1-butene addition to polyisobutylene macrocation followed by proton elimination.<sup>[37]</sup> Therefore, 1-butene may copolymerize with IB, but its content in a polymer chain is rather low to be detected by NMR.

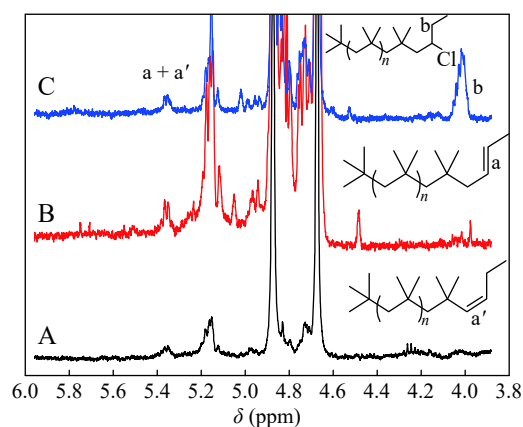
#### <sup>i</sup>BuAlCl<sub>2</sub> × *n*O<sup>i</sup>Pr<sub>2</sub> as Catalyst

The cationic polymerization of both C<sub>4</sub> mixed feed and IB co-initiated by <sup>i</sup>BuAlCl<sub>2</sub>×0.8O<sup>i</sup>Pr<sub>2</sub> terminated at low monomer conversions (runs 1 and 2 in Table 2) due to low concentration of adventitious H<sub>2</sub>O in the system as well as consumption of two molecules of H<sub>2</sub>O for the generation of one proton in the initiation stage.<sup>[28]</sup> On the other hand, the molecular weight of polyisobutylenes synthesized from both C<sub>4</sub> mixed feed and IB in the presence of <sup>i</sup>BuAlCl<sub>2</sub>×0.8O<sup>i</sup>Pr<sub>2</sub> was much lower than those obtained with AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> (see Tables 1 and 2). The addition of external H<sub>2</sub>O (33 mmol·L<sup>-1</sup>) led to the significant increase of monomer conversion and lowering of M<sub>n</sub> for the polymerization of C<sub>4</sub> mixed feed (Table 2).

It should be noted here that the mode of H<sub>2</sub>O addition into to the system hardly affected the monomer conversion but



**Fig. 1** Typical <sup>1</sup>H-NMR spectra of HR PIB synthesized from (A) IB (run 1, Table 2) and (B) C<sub>4</sub> mixed feed (run 8, Table 2)



**Fig. 2** Olefinic part of <sup>1</sup>H-NMR spectra of HR PIB synthesized from C<sub>4</sub> mixed feed using (A) AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub>, (B) <sup>i</sup>BuAlCl<sub>2</sub>×0.8O<sup>i</sup>Pr<sub>2</sub>, and (C) [emim]Cl-FeCl<sub>3</sub>/0.5 <sup>i</sup>O<sup>i</sup>Pr<sub>2</sub> as co-initiators

**Table 2** Cationic polymerization of C<sub>4</sub> mixed feed and isobutylene in the presence of <sup>t</sup>BuAlCl<sub>2</sub>×0.80<sup>i</sup>Pr<sub>2</sub> as co-initiator <sup>a</sup>

Run	M	Time (min)	Conv. <sup>b</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)			
						<i>exo</i>	<i>endo</i> + tri	tetra	coupled
1 <sup>c</sup>	IB	10	36	1470	3.9	91	3	4	2
2 <sup>c</sup>	C <sub>4</sub>	30	24	2600	4.2	86	7	6	1
3 <sup>d</sup>	IB	30	78	1900	3.7	80	9	11	< 1
4 <sup>d</sup>	C <sub>4</sub>	30	70	1450	4.4	79	10	9	2
5 <sup>e,f</sup>	IB	20	74	1230	3.4	88	4	3	5
6 <sup>e,f</sup>	C <sub>4</sub>	30	30	930	6.9	91	3	0	6
7 <sup>e,g</sup>	IB	20	64	1260	3.4	90	4	3	3
8 <sup>e,g</sup>	C <sub>4</sub>	30	64	1280	5.3	81	11	8	< 1

<sup>a</sup> [<sup>t</sup>BuAlCl<sub>2</sub>] = 22 mmol·L<sup>-1</sup>; [<sup>i</sup>Pr<sub>2</sub>O] = 18 mmol·L<sup>-1</sup>; [IB] = [C<sub>4</sub>] = 5.2 mol·L<sup>-1</sup>; [H<sub>2</sub>O]<sub>added</sub> = 33 mmol·L<sup>-1</sup>; T = 10 °C; <sup>b</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization; <sup>c</sup> Adventitious water acted as initiator; <sup>d</sup> Polymerization was initiated by the addition of <sup>t</sup>BuAlCl<sub>2</sub> to the reaction mixture; <sup>e</sup> The sequence for components addition: C<sub>4</sub>, <sup>i</sup>Pr<sub>2</sub>O, <sup>t</sup>BuAlCl<sub>2</sub>, H<sub>2</sub>O, and *n*-hexane; <sup>f</sup> <sup>i</sup>Pr<sub>2</sub>O, <sup>t</sup>BuAlCl<sub>2</sub>, IB, H<sub>2</sub>O for the polymerization of C<sub>4</sub> mixed feed and IB, respectively; <sup>g</sup> H<sub>2</sub>O added after 3 min since the beginning of the polymerization; <sup>h</sup> H<sub>2</sub>O added after 10 min since the beginning of the polymerization

influenced significantly the *exo*-olefin end group content. Indeed, when water was introduced into system after some time since the addition of co-initiator (<sup>t</sup>BuAlCl<sub>2</sub>), the higher amount of *exo*-olefin end group could be obtained (runs 5–8 in Table 2). In contrast, the addition of H<sub>2</sub>O before the co-initiator resulted in polyisobutylenes with lower content of *exo*-olefin terminal group (runs 3 and 4, Table 2). Importantly, the optimal time of H<sub>2</sub>O addition into the system was 3 and 10 min after the beginning of reaction for the polymerization of IB and C<sub>4</sub> mixed feed, respectively (Table 2). This observation is consistent with the lower reaction rate (lower rate of consumption of H<sub>2</sub>O for the initiation) for the cationic polymerization of C<sub>4</sub> mixed feed in comparison with IB. Therefore, the delayed addition of H<sub>2</sub>O is required because excess H<sub>2</sub>O could deactivate the catalyst.

Despite the significant increase of monomer conversion after the addition of external H<sub>2</sub>O as initiator into the system, the conversion was below 80% and 70% for the <sup>t</sup>BuAlCl<sub>2</sub>×0.80<sup>i</sup>Pr<sub>2</sub>-co-initiated cationic polymerization of IB and C<sub>4</sub> mixed feed, respectively. Therefore, in order to increase the polymer yield, it was proposed to add the initiator (H<sub>2</sub>O) with several shots in the course of polymerization. Indeed, the addition of H<sub>2</sub>O into two shots (after 3 and 7 min for IB and after 3 and 15 min for C<sub>4</sub> mixed feed) afforded desired low molecular weight HR PIB (M<sub>n</sub> < 2800 g·mol<sup>-1</sup>) with high *exo*-olefin end group content (> 80%) in high yield (≥ 89%) (Table 3). The observed higher molecular weight of HR PIB prepared from C<sub>4</sub> mixed feed than the one synthesized from IB can be explained by lower polymerization temperature in the former case (see Table 3).

Another approach to increase the activity of <sup>t</sup>BuAlCl<sub>2</sub> in the synthesis of HR PIB, which was developed by us,<sup>[31]</sup> in-

volves the pre-activation of co-initiator by its interaction with salts hydrates. As shown in Table 4 and in our earlier report,<sup>[31]</sup> the pre-activated catalyst required lower amount of ether in comparison with non-pre-activated one (Tables 2 and 3) to retain high functionality at the chain end. However, for the cationic polymerization of isobutylene, the optimal ratio of <sup>i</sup>Pr<sub>2</sub>O to <sup>t</sup>BuAlCl<sub>2</sub> was 0.4, while for the polymerization of C<sub>4</sub> mixed feed, high *exo*-olefin end group content could be observed only at <sup>i</sup>Pr<sub>2</sub>O/<sup>t</sup>BuAlCl<sub>2</sub> = 0.5 (Table 4). At this ratio, HR PIB with desired low molecular weight (M<sub>n</sub> ≤ 2000 g·mol<sup>-1</sup>) but with relatively high polydispersity (M<sub>w</sub>/M<sub>n</sub> ~ 4) can be obtained in a high yield (≥ 90%) in 10 min by the cationic polymerization of C<sub>4</sub> mixed feed with H<sub>2</sub>O/<sup>t</sup>BuAlCl<sub>2</sub>×0.50<sup>i</sup>Pr<sub>2</sub> initiating system (run 4, Table 4).

The polydispersity of HR PIB prepared from C<sub>4</sub> mixed, similarly to that of polyisobutylene synthesized from neat IB, can be improved by using the mixture of two ethers of different steric structures and basicities instead of diisopropyl ether (see runs 5 and 6 in Table 4).

To summarize, complexes of <sup>t</sup>BuAlCl<sub>2</sub> with diisopropyl ether were more suitable co-initiators than AlCl<sub>3</sub>×O<sup>i</sup>Pr<sub>2</sub> for the synthesis of HR PIB from C<sub>4</sub> mixed feed due to their higher activity in polymerization as well as possibility to prepare polyisobutylenes with lower molecular weight and higher content of *exo*-olefin end groups (see Tables 1–4). However, <sup>t</sup>BuAlCl<sub>2</sub> required activation in order to increase the reaction rate and the saturated monomer conversion. Among different ways of catalyst activation (addition of external water (initiator) in one or two shots, reaction of <sup>t</sup>BuAlCl<sub>2</sub> with salts hydrates), the pre-activation of <sup>t</sup>BuAlCl<sub>2</sub> by salts hydrate is the most promising approach due to its efficiency (≥ 90% of monomer conversion in 10 min) and simplicity. In

**Table 3** Effect of H<sub>2</sub>O addition on cationic polymerization of C<sub>4</sub> mixed feed and isobutylene in the presence of <sup>t</sup>BuAlCl<sub>2</sub>×0.60<sup>i</sup>Pr<sub>2</sub> as co-initiator <sup>a</sup>

Run	M	H <sub>2</sub> O addition <sup>b</sup> (min)	Time (min)	T (°C)	Conv. <sup>c</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)			
								<i>exo</i>	<i>endo</i> + tri	tetra	coupled
1	IB	3 + 3	10	10	89	1900	3.6	80	9	11	< 1
2	IB	3 + 7	30	10	93	1380	4.1	83	9	8	< 1
3	C <sub>4</sub>	3 + 3	10	0	50	2680	3.9	89	8	0	3
4	C <sub>4</sub>	3 + 15	30	0	89	2790	4.3	81	11	7	1

<sup>a</sup> [<sup>t</sup>BuAlCl<sub>2</sub>] = 38 mmol·L<sup>-1</sup>; [<sup>i</sup>Pr<sub>2</sub>O] = 23 mmol·L<sup>-1</sup>; [IB] = [C<sub>4</sub>] = 5.2 mol·L<sup>-1</sup>; [H<sub>2</sub>O]<sub>1</sub> = [H<sub>2</sub>O]<sub>2</sub> = 15 mmol·L<sup>-1</sup>. The sequence for components addition: C<sub>4</sub>, <sup>i</sup>Pr<sub>2</sub>O, <sup>t</sup>BuAlCl<sub>2</sub>, H<sub>2</sub>O, and *n*-hexane; <sup>b</sup> Time of H<sub>2</sub>O introduction since the beginning of polymerization; <sup>c</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization

**Table 4** Effect of <sup>t</sup>BuAlCl<sub>2</sub> pre-activation on cationic polymerization of C<sub>4</sub> mixed feed and isobutylene in the presence of <sup>t</sup>BuAlCl<sub>2</sub> as co-initiator<sup>a</sup>

Run	M	O <sup>t</sup> Pr <sub>2</sub> / <sup>t</sup> BuAlCl <sub>2</sub> (mol/mol)	T (°C)	Conv. <sup>b</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)			
							<i>exo</i>	<i>endo</i> + tri	tetra	coupled
1	IB	0.4	10	94	1210	3.7	80	9	9	1
2	C <sub>4</sub>	0.4	0	96	5230	3.6	66	18	16	0
3	IB	0.5	10	86	1420	3.7	81	7	8	4
4	C <sub>4</sub>	0.5	0	90	2050	4.2	72	15	11	2
5 <sup>c,d</sup>	IB	0.5	10	94	1190	2.6	82	6	10	2
6 <sup>c,d</sup>	C <sub>4</sub>	0.5	0	96	1180	3.3	80	10	8	2

<sup>a</sup> [<sup>t</sup>BuAlCl<sub>2</sub>] = 38 mmol·L<sup>-1</sup>; [IB] = [C<sub>4</sub>] = 5.2 mol·L<sup>-1</sup>; [H<sub>2</sub>O]<sub>added</sub> = 33 mmol·L<sup>-1</sup>; time: 10 min. Co-initiator was pre-activated by MgSO<sub>4</sub>·7H<sub>2</sub>O (15 mol% of H<sub>2</sub>O to <sup>t</sup>BuAlCl<sub>2</sub>). The sequence for components addition: H<sub>2</sub>O, <sup>t</sup>Pr<sub>2</sub>O, <sup>t</sup>BuAlCl<sub>2</sub>, C<sub>4</sub>, and *n*-hexane, <sup>t</sup>Pr<sub>2</sub>O, H<sub>2</sub>O, <sup>t</sup>BuAlCl<sub>2</sub>, IB for the polymerization of C<sub>4</sub> mixed feed and IB, respectively; <sup>b</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization; <sup>c</sup> Equimolar mixture of <sup>t</sup>Pr<sub>2</sub>O and Et<sub>2</sub>O was used instead of <sup>t</sup>Pr<sub>2</sub>O; <sup>d</sup> Reaction time: 30 min

addition, pre-activated catalyst can be stored up to 1 month without any loss in activity. It should be noted that HR PIBs prepared from C<sub>4</sub> mixed feed using <sup>t</sup>BuAlCl<sub>2</sub> as a co-initiator were typically characterized by higher polydispersity than those synthesized from IB (Tables 2–4). Finally, HR PIBs synthesized from C<sub>4</sub> mixed feed using H<sub>2</sub>O/<sup>t</sup>BuAlCl<sub>2</sub> × 0.5O<sup>t</sup>Pr<sub>2</sub> initiating system did not contain any significant amount of other olefin in a main chain, while very weak signal at 5.39 ppm (Fig. 2b) indicates that end-capping of polyisobutylene macrocations by 1-butene occurred (Fig. 2b).

#### Ionic Liquids as Catalysts

It was recently demonstrated that acidic imidazole-based ionic liquids (ILs), especially [emim]Cl-FeCl<sub>3</sub> ([emim]Cl: 1-ethyl-3-methylimidazolium chloride), in the presence of diisopropyl ether are very efficient catalysts for the preparation of HR PIB with relatively low polydispersity (*M<sub>w</sub>/M<sub>n</sub>* < 3.0) from neat IB.<sup>[33,34]</sup> This catalytic system was tested for the first time in the cationic polymerization of C<sub>4</sub> mixed feed (Table 5). Note that in all experiments the ionic liquid was dispersed in *n*-hexane before C<sub>4</sub> mixed feed addition; therefore, the concentration of monomer was 3.8 mol·L<sup>-1</sup>.

According to Table 5, [emim]Cl-FeCl<sub>3</sub> either in the presence or in the absence of <sup>t</sup>Pr<sub>2</sub>O showed approximately two times lower activity in the cationic polymerization of C<sub>4</sub> mixed feed as compared to polymerization of isobutylene. Interestingly, [emim]Cl-FeCl<sub>3</sub> allowed to synthesize PIB with quite high *exo*-olefin end group content from C<sub>4</sub> mixed feed even without the addition of ether into the system (runs 1 and 2, Table 5). Several key differences in the polymeri-

zation behavior of IB and C<sub>4</sub> mixed feed can be seen in Table 5. Firstly, the high monomer conversion was obtained for IB polymerization at [IL] = 33 mmol·L<sup>-1</sup>, while in the case of C<sub>4</sub> mixed feed polymerization, the higher concentration of ionic liquid was required (compare run 5 with run 6 in Table 5). Secondly, the relatively high molecular weight polymers were formed during [emim]Cl-FeCl<sub>3</sub>-co-initiated cationic polymerization of C<sub>4</sub> mixed feed at high co-initiator concentrations as compared to the polymerization of IB (runs 5–9 in Table 5). On the other hand, independently of the nature of monomer used (IB or C<sub>4</sub> mixed feed), all synthesized polymers were characterized by relatively low polydispersity (*M<sub>w</sub>/M<sub>n</sub>* < 2.8) due to the heterogeneous nature of the polymerization process.<sup>[33,34]</sup>

Taking into account the heterogeneous nature of the polymerization and poor dispersion of [emim]Cl-FeCl<sub>3</sub> in non-polar *n*-hexane or *n*-hexane/monomer mixture, sonication of reaction mixture before monomer addition was applied. According to the data presented in Table 6, sonication resulted in significant increases of monomer conversion, especially in the case of C<sub>4</sub> mixed feed cationic polymerization. Another positive effect of sonication is the reduction of molecular weight of HR PIB prepared from C<sub>4</sub> mixed feed (see runs 3–5 in Table 6). On the other hand, the sonication did not influence the polydispersity of HR PIB but led to some decrease of *exo*-olefin end group content.

The comparison between the olefinic part of <sup>1</sup>H-NMR spectrum of HR PIB prepared from C<sub>4</sub> mixed feed using [emim]Cl-FeCl<sub>3</sub> as catalyst (Fig. 2c) and the spectra of HR PIB synthesized with AlCl<sub>3</sub> × O<sup>t</sup>Pr<sub>2</sub> (Fig. 2a) and <sup>t</sup>BuAlCl<sub>2</sub> ×

**Table 5** Cationic polymerization of C<sub>4</sub> mixed feed and isobutylene using [emim]Cl-FeCl<sub>3</sub> as co-initiator at 0 °C<sup>a</sup>

Run	M	IL (mmol·L <sup>-1</sup> )	Conv. <sup>b</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)				
						<i>exo</i>	<i>endo</i> + tri	tetra	PIBCl	coupled
1 <sup>c</sup>	IB	22	27	5400	3.8	53	20	19	7	1
2 <sup>c</sup>	C <sub>4</sub>	22	18	5800	3.5	74	16	7	3	0
3	IB	22	18	1700	2.2	84	7	3	4	2
4	C <sub>4</sub>	22	19	1700	2.7	82	8	5	2	3
5	IB	33	71	1630	2.6	84	8	6	1	1
6	C <sub>4</sub>	33	24	2200	2.8	86	5	4	4	1
7	IB	44	95	1800	2.5	87	8	3	1	1
8	C <sub>4</sub>	44	68	3900	2.6	81	9	7	3	0
9 <sup>d</sup>	C <sub>4</sub>	44	88	3700	2.6	75	10	9	4	2

<sup>a</sup> [IB] = 5.2 mol·L<sup>-1</sup>; [C<sub>4</sub>] = 3.8 mol·L<sup>-1</sup>; [<sup>t</sup>Pr<sub>2</sub>O] = 11 mmol·L<sup>-1</sup>; time: 30 min; <sup>b</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization; <sup>c</sup> Without the addition of <sup>t</sup>Pr<sub>2</sub>O; <sup>d</sup> Reaction time: 60 min

**Table 6** Effect of sonication of the reaction mixture on the cationic polymerization of C<sub>4</sub> mixed feed and isobutylene using [emim]Cl-FeCl<sub>3</sub> as co-initiator at 0 °C<sup>a</sup>

Run	M	Sonication <sup>b</sup>	Conv. <sup>c</sup> (%)	M <sub>n</sub> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>	End group distribution (mol%)				
						<i>exo</i>	<i>endo</i> + tri	tetra	PIBCl	coupled
1	IB	NO	71	1630	2.6	84	8	6	1	1
2	IB	YES	93	1830	2.4	81	10	8	1	0
3	C <sub>4</sub>	NO	24	2200	2.8	86	5	4	3	2
4	C <sub>4</sub>	YES	51	2200	2.8	82	6	5	4	3
5 <sup>d</sup>	C <sub>4</sub>	YES	78	2500	2.5	81	7	7	3	2

<sup>a</sup> [IB] = 5.2 mol·L<sup>-1</sup>; [C<sub>4</sub>] = 3.8 mol·L<sup>-1</sup>; [emimCl-FeCl<sub>3</sub>] = 33 mmol·L<sup>-1</sup>; [Pr<sub>2</sub>O] = 11 mmol·L<sup>-1</sup>; time: 30 min; <sup>b</sup> *n*-hexane/1L mixture sonicated for 3 min; <sup>c</sup> With respect to isobutylene content in the case of C<sub>4</sub> mixed feed polymerization; <sup>d</sup> Reaction time: 60 min

0.8O<sup>+</sup>Pr<sub>2</sub> (Fig. 2b) reveals the appearance of a new signal at 3.9 ppm in addition to the signal at 5.39 ppm. This new signal corresponds to the methine proton of CH–Cl group, which was formed after PIB<sup>+</sup> capping with 1-butene followed by irreversible termination *via* ion pair collapse.<sup>[37]</sup> It should be noted that this signal is much more intensive than the signal at 5.39 ppm, which corresponds to olefinic protons of internal double bond at the chain end formed due to 1-butene addition followed by β-H abstraction. These data allowed for explaining the much lower activity of [emim]Cl-FeCl<sub>3</sub> in cationic polymerization of C<sub>4</sub> mixed feed in comparison with IB as well as the necessity to use quite high concentrations of ionic liquids to reach high monomer conversions. Indeed, the formation of CH–Cl group led to irreversible termination and, in turn, to the decrease of active species concentration. On the other hand, the formation of olefinic end group after capping of PIB<sup>+</sup> with 1-butene resulted in regeneration of active center and therefore, did not influence the concentration of active species.

In summary, [emim]Cl-FeCl<sub>3</sub> is a quite promising catalyst for the preparation of HR PIB with the high *exo*-olefin end group content (> 80%) and relatively low polydispersity (M<sub>w</sub>/M<sub>n</sub> < 2.8) *via* cationic polymerization of C<sub>4</sub> mixed feed. However, due to the irreversible termination after end-capping of PIB<sup>+</sup> with 1-butene, a relatively high concentration of ionic liquid catalyst was required to achieve the high reaction rate and monomer conversion. This limitation of using [emim]Cl-FeCl<sub>3</sub> for the polymerization of C<sub>4</sub> mixed feed can be overcome by sonication of reaction mixture before polymerization. The sonication allowed to decrease the molecular weight of HR PIB synthesized from C<sub>4</sub> mixed feed as well.

## CONCLUSIONS

Three generations of catalysts, namely the complexes of AlCl<sub>3</sub>, <sup>t</sup>BuAlCl<sub>2</sub>, and [emim]Cl-FeCl<sub>3</sub> with diisopropyl ether, for the synthesis of highly reactive polyisobutylene from C<sub>4</sub> mixed feed were tested in this work. The key difference in the polymerization behavior of C<sub>4</sub> mixed feed as compared to IB is the lower activity of all above-mentioned catalytic systems, which can be connected with the end-capping of PIB<sup>+</sup> by 1-butene that led to the decrease of polymerization rate. Another difference is the systematically higher molecular weight of polyisobutylenes obtained from C<sub>4</sub> mixed feed in comparison with those prepared from IB. Among the catalysts studied, <sup>t</sup>BuAlCl<sub>2</sub> pre-activated by MgSO<sub>4</sub>·7H<sub>2</sub>O in

the presence of equimolar mixture of <sup>t</sup>Pr<sub>2</sub>O and Et<sub>2</sub>O represents the most promising catalyst for the synthesis of HR PIB from C<sub>4</sub> mixed feed. This catalytic system induced fast cationic polymerization of C<sub>4</sub> mixed feed (> 90% of monomer conversion in 10 min) to afford HR PIB with desired low molecular weight (M<sub>n</sub> ~ 1200 g·mol<sup>-1</sup>) as well as reasonable functionality (*exo*-olefin end group content of 80%) and polydispersity (M<sub>w</sub>/M<sub>n</sub> = 3.3). Acidic ionic liquids in conjunction with <sup>t</sup>Pr<sub>2</sub>O could be considered as an alternative to <sup>t</sup>BuAlCl<sub>2</sub>-based initiating system for the cationic polymerization of C<sub>4</sub> mixed feed. Although [emim]Cl-FeCl<sub>3</sub>-co-initiated cationic polymerization of C<sub>4</sub> mixed feed was slower in comparison with <sup>t</sup>BuAlCl<sub>2</sub>-based initiating system, it resulted in HR PIB with lower polydispersity (M<sub>w</sub>/M<sub>n</sub> = 2.5).

## ACKNOWLEDGMENTS

This work was financially supported by BASF SE.

## REFERENCES

- Mach, H.; Rath, P. Highly reactive polyisobutene as a component of a new generation of lubricant and fuel additives. *Lubr. Sci.* **1999**, *11-2*, 175–185.
- Kostjuk, S. V.; Yeong, H. Y.; Voit, B. Cationic polymerization of isobutylene at room temperature. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 471–486.
- Kostjuk, S. V. Recent progress in the Lewis acids co-initiated cationic polymerization of isobutylene and 1,3-dienes. *RSC Adv.* **2015**, *5*, 13125–13144.
- Li, Y.; Cokoja, M.; Kühn, F. E. Inorganic/organometallic catalysts and initiators involving weakly coordinating anions for isobutene polymerization. *Coord. Chem. Rev.* **2011**, *255*, 1541–1557.
- Ummadisetty, S.; Storey, R. F. Quantitative synthesis of *exo*-olefin-terminated polyisobutylene: Ether quenching and evaluation of various quenching methods. *Macromolecules* **2013**, *46*, 2049–2059.
- Lichtenthaler, M. R.; Higelin, A.; Kraft, A.; Hughes, S.; Stefani, A.; Plattner, D. A.; Slattery, J. M.; Krossing, I. Univalent gallium salts of weakly coordinating anions: Effective initiators/catalysts for the synthesis of highly reactive polyisobutylene. *Organometallics* **2013**, *32*, 6725–6735.
- Guerrero, A.; Kulbaba, K.; Bochmann, M. “Highly reactive” poly(isobutene)s *via* room temperature polymerization with a new zinc-based initiator system. *Macromolecules* **2007**, *40*, 4124–4126.
- Burrington, J. D.; Johnson, J. R.; Pudelski, J. K. Cationic poly-

- merization using heteropolyacid salt catalysts. *Topics in Catal.* **2003**, *23*, 175–181.
- 9 Vasilenko, I. V.; Frolov, A. N.; Kostjuk, S. V. Cationic polymerization of isobutylene using  $\text{AlCl}_3\text{OBU}_2$  as a co-initiator: Synthesis of highly reactive polyisobutylene. *Macromolecules* **2010**, *43*, 5503–5507.
- 10 Liu, Q.; Wu, Y. X.; Zhang, Y.; Yan, P. F.; Xu, R. W. A cost-effective process for highly reactive polyisobutylenes via cationic polymerization coinitiated by  $\text{AlCl}_3$ . *Polymer* **2010**, *51*, 5960–5969.
- 11 Liu, Q.; Wu, Y.; Yan, P.; Zhang, Y.; Xu, R. Polyisobutylene with high *exo*-olefin content via  $\beta$ -H elimination in the cationic polymerization of isobutylene with  $\text{H}_2\text{O}/\text{FeCl}_3$ /dialkyl ether initiating system. *Macromolecules* **2011**, *44*, 1866–1875.
- 12 Guo, A. R.; Yang, X. J.; Yan, P. F.; Wu, Y. H. Synthesis of highly reactive polyisobutylenes with *exo*-olefin terminals via controlled cationic polymerization with  $\text{H}_2\text{O}/\text{FeCl}_3$ /*i*PrOH initiating system in nonpolar hydrocarbon media. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4200–4212.
- 13 Kumar, R.; Dimitrov, P.; Bartelson, K. J.; Emert, J.; Faust, R. Polymerization of isobutylene by  $\text{GaCl}_3$  or  $\text{FeCl}_3$ /ether complexes in nonpolar solvents. *Macromolecules* **2012**, *45*, 8598–8603.
- 14 Bartelson, K. J.; De, P.; Kumar, R.; Emert, J.; Faust, R. Cationic polymerization of isobutylene by  $\text{FeCl}_3$ /ether complexes in hexanes: An investigation of the steric and electronic effects of ethers. *Polymer* **2013**, *54*, 4858–4863.
- 15 Kumar, R.; De, P.; Zheng, B.; Huang, K. W.; Emert, J.; Faust, R. Synthesis of highly reactive polyisobutylene with  $\text{FeCl}_3$ /ether complexes in hexane; kinetic and mechanistic studies. *Polym. Chem.* **2015**, *6*, 322–329.
- 16 Yang, X. J.; Guo, A. R.; Xu, H. C.; Wu, Y. H. Direct synthesis of highly reactive polyisobutylenes via cationic polymerization of isobutylene co-initiated with  $\text{TiCl}_4$  in nonpolar hydrocarbon media. *J. Appl. Polym. Sci.* **2015**, *132*, 42232–42244.
- 17 Li, X.; Wu, Y.; Zhang, J.; Li, X.; Zhang, M.; Yang, D.; Wang, H.; Shang, Y.; Guo, W.; Yan, P. Synthesis of highly reactive polyisobutylene via cationic polymerization in ionic liquids: Characteristic and mechanism. *Polym. Chem.* **2019**, *10*, 201–208.
- 18 Faust, R.; Dimitrov, P.; Kumar, R.; Emert, J.; Hua, J., **2013**, U.S. Pat., 20130158217A1.
- 19 Vasilenko, I. V.; Shiman, D. I.; Kostjuk, S. V. Highly reactive polyisobutylenes via  $\text{AlCl}_3\text{OBU}_2$ -coinitiated cationic polymerization of isobutylene: Effect of solvent polarity, temperature, and initiator. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 750–758.
- 20 Kostjuk, S. V.; Vasilenko, I. V.; Shiman, D. I.; Frolov, A. N.; Gaponik, L. V. Highly reactive polyisobutylenes via cationic polymerization of isobutylene by  $\text{AlCl}_3$ /ether complexes in non-polar media: Scope and limitations. *Macromol. Symp.* **2015**, *349*, 94–103.
- 21 Shiman, D. I.; Vasilenko, I. V.; Kostjuk, S. V. Cationic polymerization of isobutylene by  $\text{AlCl}_3$ /ether complexes in non-polar solvents: Effect of ether structure on the selectivity of  $\beta$ -H elimination. *Polymer* **2013**, *54*, 2235–2242.
- 22 Kumar, R.; Zheng, B.; Huang, K. W.; Emeret, J.; Faust, R. Synthesis of highly reactive polyisobutylene catalyzed by  $\text{EtAlCl}_2$ /bis(2-chloroethyl) ether soluble complex in hexanes. *Macromolecules* **2014**, *47*, 1959–1965.
- 23 Banerjee, S.; Emert, J.; Wright, P.; Skourlis, T.; Severt, R.; Faust, R. Polymerization of isobutylene catalyzed by  $\text{EtAlCl}_2$ /bis(2-chloroethyl) ether complex in steel vessels. *Polym. Chem.* **2015**, *6*, 4902–4910.
- 24 Banerjee, S.; Jha, B. N.; De, P.; Emert, J.; Faust, R. Kinetic and mechanistic studies of the polymerization of isobutylene catalyzed by  $\text{EtAlCl}_2$ /bis(2-chloroethyl) ether complex in hexanes. *Macromolecules* **2015**, *48*, 5474–5480.
- 25 Rajasekhar, T.; Emert, J.; Faust, R. Synthesis of highly reactive polyisobutylene by catalytic chain transfer in hexanes at elevated temperatures: Determination of the kinetic parameters. *Polym. Chem.* **2017**, *8*, 2852–2859.
- 26 Rajasekhar, T. atalytic chain transfer polymerization of isobutylene: The role of nucleophilic impurities. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 3697–3704.
- 27 Rajasekhar, T.; Emert, J.; Wolf, L. M.; Faust, R. Controlled catalytic chain transfer polymerization of isobutylene in the presence of *tert*-butanol as *exo*-enhancer. *Macromolecules* **2018**, *51*, 3041–3049.
- 28 Vasilenko, I. V.; Shiman, D. I.; Kostjuk, S. V. Alkylaluminum dichloride-ether complexes which are fully soluble in hydrocarbons as catalysts for the synthesis of *exo*-olefin terminated polyisobutylene at room temperature. *Polym. Chem.* **2014**, *5*, 3855–3866.
- 29 Shiman, D. I.; Vasilenko, I. V.; Kostjuk, S. V. Cationic polymerization of isobutylene by complexes of alkylaluminum dichlorides with diisopropyl ether: An activating effect of water. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2386–2393.
- 30 Vasilenko, I. V.; Nikishev, P. A.; Shiman, D. I.; Kostjuk, S. V. Cationic polymerization of isobutylene in toluene: Toward well-defined *exo*-olefin terminated medium molecular weight polyisobutylenes under mild conditions. *Polym. Chem.* **2017**, *8*, 1417–1425.
- 31 Shiman, D. I.; Vasilenko, I. V.; Kostjuk, S. V. Cationic polymerization of isobutylene catalyzed by  $t\text{-BuAlCl}_2$  in the presence of ethers: Effect of catalyst pre-activation and mixture of two ethers. *Polymer* **2016**, *99*, 633–641.
- 32 Zhu, S.; Lu, Y.; Faust, R. Micromixing enhanced synthesis of HRPIBs catalyzed by EADC/(bis(2-chloroethyl)ether) complex. *RSC Adv.* **2017**, *7*, 27629–27636.
- 33 Vasilenko, I. V.; Bereziianko, I. A.; Shiman, D. I.; Kostjuk, S. V. New catalyst for the synthesis of highly reactive polyisobutylene: Chloroaluminate imidazole-based ionic liquid in the presence of diisopropyl ether. *Polym. Chem.* **2016**, *7*, 5615–5619.
- 34 Bereziianko, I. A.; Vasilenko, I. V.; Kostjuk, S. V. Acidic imidazole-based ionic liquids in the presence of diisopropyl ether as catalysts for the synthesis of highly reactive polyisobutylene: Effect of ionic liquid nature, catalyst aging, and sonication. *Polymer* **2018**, *145*, 382–390.
- 35 Zhang, L. B.; Wu, Y. X.; Zhou, P.; Xu, R. W. Synthesis of highly reactive polyisobutylene by selective polymerization with *o*-cresol/ $\text{AlCl}_3$  initiating system. *Polym. Adv. Technol.* **2012**, *23*, 522–528.
- 36 Zhang, L. B.; Wu, Y. X.; Zhou, P.; Wu, G. Y.; Yang, W. T.; Yu, D. S. Synthesis of highly reactive polyisobutylenes with  $\text{BF}_3$ /cyclohexanol initiating system. *Chinese J. Polym. Sci.* **2011**, *29*, 360–367.
- 37 Rajasekhar, T.; Haldar, U.; De, P.; Emert, J.; Faust, R. Cationic copolymerization and multicomponent polymerization of isobutylene with C4 olefins. *Macromolecules.* **2017**, *50*, 8325–8333.
- 38 De, P.; Faust, R. Relative reactivity of C4 olefins toward the polyisobutylene cation. *Macromolecules* **2006**, *39*, 6861–6870.