Cationic Polymerization of Isobutylene by Complexes of Alkylaluminum Dichlorides with Diisopropyl Ether: An Activating Effect of Water

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

Research Institute for Physical Chemical Problems, Belarusian State University, 14 Leningradskaya St., 220030 Minsk, Belarus
Correspondence to: S. V. Kostjuk (E-mail: kostjuks@bsu.by or kostjuks@rambler.ru)

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ABSTRACT: The $RAlCl_2 \times O^iPr_2$-co-initiated ($R = {}^iBu$ or Et) cationic polymerization of isobutylene in the presence of externally added water (0.016–0.1 mM) in nonpolar *n*-hexane at 10 °C and high monomer concentration ([IB] = 5.8 M) has been investigated. It was shown that the sequence of H_2O introduction into the system had the crucial effect on the polymerization rate, saturated monomer conversion, and, to a lesser extent, the content of exo-olefin end groups. Particularly, the highest polymerization rate (>70% of monomer conversion in 10 min) and acceptable exo-olefin end groups content (~83%) were observed when ${}^iBuAlCl_2 \times 0.8O^iPr_2$ reacted with suspended in *n*-hexane H_2O before the monomer addition. Better functionality can be obtained when H_2O is introduced into the system in the course of the polymerization (after 3–10 min since the initiation of reaction). Under these conditions, highly reactive polyisobutylenes (exo-olefin content is 86–89%) with desired low molecular weight ($M_n = 1000$–2000 g mol^{-1}) in a high yield (75–90% of monomer conversion in 20 min) were readily synthesized. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2386–2393

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INTRODUCTION The current interest to the synthesis of olefin end-functionalized polyisobutylene (PIB) is connected with its use as a precursor in the preparation of motor oil and fuel additives.[1] PIBs with high content of trisubstituted olefinic chain ends, called conventional PIBs, are commercially produced by the polymerization of C_4 mixture (contained isobutylene (IB), 1-butene, 2-butenes, and hydrocarbons) using $AlCl_3$ or $EtAlCl_2$ as catalysts.[2] The key disadvantage of this technique is the low reactivity of internal double bounds toward further functionalization by maleic anhydride. Highly reactive polyisobutylene (HR PIB) contained predominantly reactive exo-olefin end group is commercially prepared via polymerization of pure IB or, rarely, C_4 mixture using complexes of BF_3 with alcohols or ethers as catalysts.[3] Because chlorination-dehydrochlorination is not necessary for HR PIB before its reaction with maleic anhydride and the final product does not contain any chlorine, HR PIB is more preferably than conventional PIB for the production of ashless dispersants.

Recently, a number of new methods for the synthesis of HR PIB, which can be classified into three main approaches, have been reported. The first approach is based on the use of controlled cationic polymerization of IB followed by the end-quenching of living PIB with allyl- or isobutenyl-trimethylsilane or different bases.[4,5] This technique allowed to synthesize mono- or di-functional exo-olefin terminated PIB with near quantitative functionality (exo = 90–100%), very narrow molecular weight distribution ($M_w/M_n < 1.2$) and precisely controlled molecular weight.[4,5] The second intensively developed approach consists in the using of transition-metal complexes such as $[M(NCCH_3)_6]^{2+}[A]_2^-$ (M = Mn, Mo, Zn, Fe, Cu; $A = [N_2C_3H_3\{B(C_6F_5)_3\}_2)]^-$, $[B(C_6F_5)_4]^-$, $[Al(OR^F)_4]^-$)[6,7] or, recently, univalent gallium salts ($[Ga(C_6H_5F)_2]^+$ $[Al(OR^F)_4]^-$ or $[Ga(1,3,5\text{-}Me_3C_6H_3)_2]^+$ $[Al(OR^F)_4]^-$)[8] as single-site catalysts for the polymerization of IB. These catalytic complexes afforded HR PIBs (exo = 60–95%) with desired low molecular weight ($M_n = 800$–2500 g mol^{-1}) at high reaction temperatures (from −10 °C to 60 °C) both in polar CH_2Cl_2 or nonpolar toluene.[6,8] The advantages and disadvantages of these two approaches were already well discussed in our previous publications on this matter.[9–12]

The third approach is based on using of conventional modified Lewis acids in the cationic polymerization of IB (both under heterogeneous[13] and homogeneous conditions[9–12,14–20]) that allowed synthesizing HR PIB in a cost-effective way and, therefore, this approach is very attractive to industry. Among different catalytic systems including *tert*-butyl

Additional Supporting Information may be found in the online version of this article.

chloride/$EtZnCl_2$ reported by Bochmann and coworkers,[14] the complexes of conventional metal chlorides (MCl_3, M = Al,[9–11,15,18] Fe,[16,17,19,20] Ga[19]) with ethers attract much attention due to their low cost and high efficiency in the synthesis of HR PIB. It should be noted that complexes of $AlCl_3$ with ethers, alcohols, and other electron donors were first investigated in the polymerization of IB in the late 1950s-middle of 1960s.[21] However, these investigations dealt mainly with the establishing of correlation between molecular weight of synthesized PIBs and conductivity of the corresponding complexes of $AlCl_3$ with electron donors of different composition. No information on the chain end structure was reported in these publications.[21]

Initially, the complexes of $AlCl_3$ and $FeCl_3$ with ethers in combination with tertiary alcohols or adventitious water were used to prepare HR PIB with high content of exo-olefin end groups (above 90%) in polar CH_2Cl_2 or its mixture with *n*-hexane at high reaction temperatures (from -20 °C to 20 °C).[9,15,16] Furthermore, the desired HR PIBs (exo content $\geq$ 85%) with controlled by temperature molecular weight ($M_n = 1000–3000$ g mol^{-1}) were successfully synthesized in a high yield in nonpolar toluene even at high monomer concentrations ([IB] = 2.8–5.8 M).[10,22] However, in *n*-hexane $AlCl_3 \times OR_2$-based initiating systems displayed relatively low activity in the cationic polymerization of IB (40–60% in 30 min in the best conditions),[11,18] although acceptable functionality (exo content = 75–85%) can be obtained at low reaction temperatures (-20 °C).[11,22] The using of H_2O/$FeCl_3$/^{i}PrOH initiating system for the IB polymerization in *n*-hexane proposed recently by Wu and coworkers[17] allowed improving the functionality (exo content above 90%), but the polymerization was relatively slow (70% of monomer conversion in 30 min) and the exo-olefin end groups content decreased from ~90% to 83% by the enhancement of reaction temperature from -20 °C to 20 °C. In addition, this initiation system, similarly to $AlCl_3 \times OR_2$-based initiating systems, afforded HR PIB with higher molecular weight ($M_n = 3000–10{,}000$ g mol^{-1}) than required for the application for motor oil/fuel additives.[11,17,22] The interesting initiating systems, based on complexes of $FeCl_3$ and $GaCl_3$ with ethers, were recently reported by Faust and coworkers[19,20] Due to the chlorophilic nature of $FeCl_3$ and $GaCl_3$,[23] the complexes of these Lewis acids with ethers can be used in a combination with alkyl chlorides (*tert*-butyl chloride (^{t}BuCl), or 2-chloro-2,4,4-trimethylpentane) in contrast to $AlCl_3 \times OR_2$, which interacts efficiently only with water[18] or, in some cases, with alcohols[24] due to oxophilic nature of $AlCl_3$.[23] Therefore, the cationic polymerization of IB with ^{t}BuCl/$FeCl_3 \times O^iPr_2$ or ^{t}BuCl/$GaCl_3 \times O^iPr_2$ initiating systems readily proceeded in *n*-hexane at 0 °C resulting in close to complete monomer conversion (ca. 80–90% in 20 min) and PIBs with good functionality (exo ~80%).[19] 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.[1]

Very recently, we reported the new efficient initiating system based on the complexes of alkylaluminum dichlorides (^{i}BuAlCl$_2$ or $EtAlCl_2$) with diisopropyl ether for the synthesis of HR PIB.[12] In contrast to complexes of $AlCl_3$,[11,18] $FeCl_3$,[19] and $GaCl_3$[19], the complexes of alkylaluminum dichlorides as well as alkylaluminum (di)chlorides itself[25] are fully soluble in hydrocarbons that allowed excluding the use of any polar solvents for the preparation of catalytic complexes. Moreover, $RAlCl_2 \times OR_2$-based initiating systems can be used at high monomer concentrations ([IB] = 2.8–5.8 M) and room temperature to afford HR PIB with high content of exo-olefin end groups (85–95%) and desired low molecular weight ($M_n = 1000–2500$ g mol^{-1}) either from pure IB or C_4 mixture.[12] However, the adventitious water was used as initiator with these alkylaluminum dichlorides-based initiating systems that led to the limitation of monomer conversion around 40–75%[12] due to the very limited solubility of H_2O in hydrocarbons. In addition, the content of adventitious water in solvent and monomer depends on the purification/drying conditions that can result in some difference in monomer conversion obtained by various research groups.[11,18]

This study describes the $RAlCl_2 \times 0.8O^iPr_2$-co-initiated (R = ^{i}Bu, Et) cationic polymerization of IB using of externally added water as initiator. We demonstrate here that the sequence of introduction of H_2O into the system has the crucial effect on both the polymerization rate and the content of exo-olefin end groups. Particularly, the delayed addition of H_2O into the polymerization system (in 3 min after the beginning of reaction) allowed synthesizing HR PIB (exo content = 85–90%) with desired low molecular weight ($M_n = 1000–2000$ g mol^{-1}) in high yield (above 80–90% in 20 min) at high monomer concentration ([IB] = 5.8 M).

EXPERIMENTAL

Materials and Methods

IB (Aldrich, 99%) was dried in the gaseous state by passing through the column packed with $CaCl_2$. *n*-Hexane (Sigma–Aldrich, >95%) were treated with sulfuric acid, washed with aqueous sodium bicarbonate, dried over $CaCl_2$, and distilled twice from CaH_2 under an inert atmosphere. Diisopropyl ether (^{i}Pr$_2$O, Fluka, $\geq$98.5%) was distilled over CaH_2 under argon. $AlCl_3$ (Aldrich, 99.999%), ^{i}Bu$_3$Al (1 M solution in hexanes, Aldrich), Et_3Al (1 M solution in hexanes, Aldrich), $CDCl_3$ (Euriso-top®), ethanol (Sigma–Aldrich, >96%), tetrahydrofuran (THF) (anhydrous, Sigma-Aldrich, $\geq$99.9%) were used as received. Isobutylaluminum dichloride (^{i}BuAlCl$_2$) and ethylaluminum dichloride ($EtAlCl_2$) were obtained as 1 M solutions in hexanes by mixing of $AlCl_3$ and ^{i}Bu$_3$Al (Et_3Al) solutions in 2:1 molar ratio at room temperature. The concentration and composition of synthesized alkylaluminum dichlorides solutions in hexanes were controlled by back titration of Al with EDTA by $ZnSO_4$ with diphenylthiocarbazone as an indicator and back titration of chlorine using Volhard's method, respectively.

Size exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7

TABLE 1 Cationic Polymerization of Isobutylene Co-Initiated by ^{i}BuAlCl$_2$ × 0.8O^{i}Pr$_2$ in *n*-Hexane at 10 °C[a]

						End Group Distribution (mol %)			
Entry	Time (min)	Conv. (%)	$M_{n,\ SEC}$ (g mol^{-1})	$M_{n,\ NMR}$ (g mol^{-1})	M_w/M_n	Exo	Endo + Tri	Tetra	Coupled
1[b]	30	27	940	560	2.0	91	4	5	<1
2[c]	10	15	–	1,045	–	85	7	7	2
3[d]	10	4	–	–	–	–	–	–	–

[a] Polymerization conditions: [^{i}BuAlCl$_2$] = 22 mM; [^{i}Pr$_2$O] = 18 mM; [IB] = 1 M. The sequence of components addition: *n*-hexane, diisopropyl ether, ^{i}BuAlCl$_2$, isobutylene.

[b] All values are averaged from several runs.

[c] *n*-Hexane saturated by water at 20 °C was used as a solvent.

[d] BuAlCl$_2$ × 0.8O^{i}Pr$_2$ was reacted with water (0.033 mM) before the addition to the system.

column and one precolumn (PL gel 5 μm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. THF was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). ^{1}H NMR (400 MHz) spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the residual solvent resonance.

Polymerization Procedures

The polymerization reactions were carried out in glass tubes equipped with a cold finger condenser under argon atmosphere at 0 °C or 10 °C. As an example of a typical procedure, polymerization was initiated by adding of IB (3.25 g, 5.8 × 10^{-2} mol) to a mixture of a total volume 5.25 mL consisting of solutions of diisopropyl ether (0.18 mL, 1 M) and ^{i}BuAlCl$_2$ (0.22 mL, 1 M) in *n*-hexane and *n*-hexane (4.8 mL). Then, in 3 min after the beginning of reaction 6 μL (3.3 × 10^{-4} mol) of deionized H_2O was introduced into the system via microsyringe. After a predetermined time, about 2 mL of ethanol was poured into the glass reactor to terminate the polymerization. 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 °C) to give the product polymers. Monomer conversions were determined gravimetrically. Because the significant variations in the sequence of components addition were applied in this work, the exact sequence for the components addition for each series of experiments is indicated in table footnotes.

RESULTS AND DISCUSSION

Preliminary Tests

In a first series of experiments, we investigated the influence of different ways of introduction of H_2O into the system on the monomer conversion and the content of exo-olefin end groups. An attempt to increase monomer conversion by saturating *n*-hexane with water through their mixing with deionized H_2O at 20 °C ([H_2O] ~ 4 × 10^{-4} M)[18] did not improve the conversion (entries 1, 2 in Table 1). This result is consistent with the much better solubility of H_2O in monomer rather than in *n*-hexane,[26] that is, the main part of initiator comes from IB, not from *n*-hexane. Then, we tried to activate the catalytic complex (^{i}BuAlCl$_2$ × 0.8O^{i}Pr$_2$) by its pre-mixing with H_2O before addition into the system. However, upon the addition of H_2O into 1 M solution of ^{i}BuAlCl$_2$ × 0.8O^{i}Pr$_2$ in *n*-hexane or toluene, the white precipitate was immediately formed. As it can be seen from Table 1, the soluble part of this "preactivated" catalytic complex displayed very low activity in the cationic polymerization of IB (entry 3). However, as it is stated in the work of Gronowski,[27] the preactivation of catalyst (diluted solution of Et_2AlCl and $EtAlCl_2$ in *n*-hexane) had strong effect on the polymer yield in the copolymerization of IB with isoprene in *n*-hexane. In this publication,[27] it was also noted that the mixture of diethylaluminum chloride and ethylaluminum dichloride, after preactivation with H_2O, formed the suspension and this suspension was used as a catalyst. Because we did not observe the formation of fine suspension in our case (probably due to the using more concentrated solution of ^{i}BuAlCl$_2$), we decided to introduce the initiator (H_2O) directly into the system just before the addition of Lewis acid (see below).

Effect of H_2O Addition

In this series of experiments, we added H_2O into a mixture of IB, solvent, and ether and after vigorous stirring we observed visually the formation of the suspension of water in this nonpolar reaction medium. Then, the polymerization was initiated by the addition of solution of ^{i}BuAlCl$_2$ in *n*-hexane into reaction mixture. As it is shown in Table 2, the addition of H_2O into the system led to the increase of monomer conversion, on the one hand, and to some decrease of exo-olefin end groups content, on the other hand (cf. entries 1, 2 and entries 6, 7).

The influence of H_2O concentration on the monomer conversion and exo-olefin end groups content was then investigated. Initially, the rise of H_2O concentration up to [H_2O] = 0.016–0.033 mM and 0.033–0.066 mM resulted in some increase of monomer conversion for cationic polymerization of IB at [IB] = 2.9 M and 5.8 M, respectively, whereas the further raising of [H_2O] led to decrease of conversion (Table 2). In addition, the increase of H_2O concentration led to some increase of the molecular weight and polydispersity

TABLE 2 Effect of H_2O Addition on the Cationic Polymerization of Isobutylene Co-Initiated by $^{i}BuAlCl_2$ in the Presence of Diisopropyl Ether in *n*-Hexane at 10 °C[a]

Entry	[IB] (M)	$[H_2O]$ (mM)	Conv. (%)	$M_{n,\ SEC}$ (g mol^{-1})	$M_{n,\ NMR}$ (g mol^{-1})	M_w/M_n	End Group Distribution (mol %) Exo	Endo + Tri	Tetra	Coupled
1	2.9	–	24	1,520	1,070	3.0	94	3	3	<1
2	2.9	0.016	44	1,690	980	3.9	86	7	5	<1
3	2.9	0.033	43	1,500	1,140	3.9	81	7	12	<1
4	2.9	0.066	28	1,630	1,460	4.2	80	7	13	0
5	2.9	0.1	31	1,490	1,360	4.8	76	9	15	<1
6	5.8	–	36	1,470	1,020	3.9	91	3	4	2
7	5.8	0.033	48	1,720	1,140	3.5	82	7	10	1
8	5.8	0.066	61	1,770	1,430	4.2	81	6	12	1

[a] Polymerization conditions: $[^{i}BuAlCl_2] = 22$ mM; $[^{i}Pr_2O] = 18$ mM; reaction time: 10 min. The sequence of components addition: *n*-hexane, diisopropyl ether, H_2O, isobutylene, $^{i}BuAlCl_2$.

(especially when $[H_2O] = 0.066$ mM) (see Supporting Information Fig. S1 for SEC curves), whereas the content of exo-olefin end groups gradually decreased with raising of $[H_2O]$. According to Table 2, the fractions of tri- and especially tetra-substituted olefinic end groups increased with increasing H_2O concentration, while the amount of coupled polymer chains did not depend on $[H_2O]$. The observed decrease of the content of exo-olefin end groups with increasing $[H_2O]$ can be explained by the high local concentration of initiating species (H^+) due to the localization of the initiation reaction around H_2O droplets in reaction mixture, which can induce the side reactions such as isomerization or even chain scission.[28]

Interestingly, even the external addition of H_2O into the system did not result in the significant increase of the polymerization rate, although saturated monomer conversion doubled reaching 80% in 60 min (cf. curves 1 and 2 in Fig. 1).

In addition, the molecular weight slightly decreased while exo-olefin content almost did not change in the course of polymerization (see Supporting Information Table S1 and Fig. S2). We supposed that the relatively low reaction rate in this case can be explained by slowing down of cationation (reaction of Lewis acid with H_2O) due to the competitive complexation of Lewis acid with IB.[26] Therefore, we assumed that the preactivation of Lewis acid through its interaction with H_2O before the addition of monomer would help to increase the reaction rate.

Co-Initiator Preactivation

As it is evident from Table 3 and Figure 1, the preactivation of Lewis acid, that is, its reaction with H_2O before the addition of monomer, allowed increasing the reaction rate significantly and saturated monomer conversion (~80%) reached in less than 15 min. Besides the change in the mode of the initiation of polymerization, that is, the initiation of reaction by the addition of free Lewis acid into the system (Table 2, Supporting Information Table 1S and Fig. S2) or monomer (Table 3, Supporting Information Fig. S2) did influence significantly neither the molecular weight, molecular weight distribution, nor the content of exo-olefin terminal groups. In addition, the decrease of the polymerization temperature

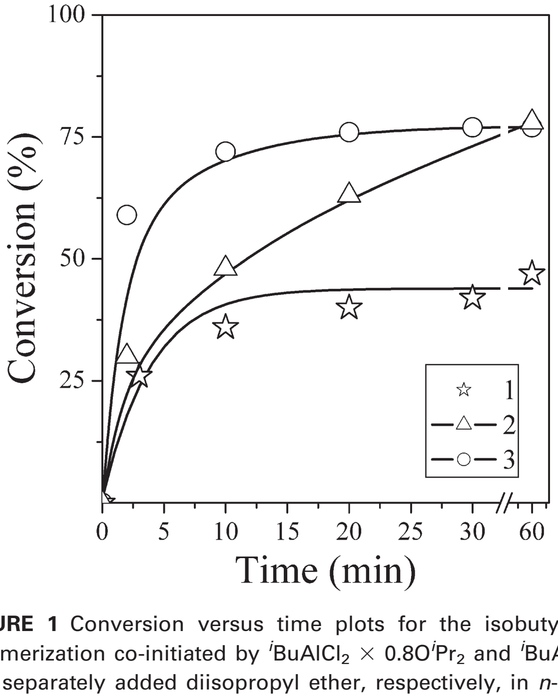


FIGURE 1 Conversion versus time plots for the isobutylene polymerization co-initiated by $^{i}BuAlCl_2 \times 0.8O^{i}Pr_2$ and $^{i}BuAlCl_2$ and separately added diisopropyl ether, respectively, in *n*-hexane at 10 °C without (**1**) or with (**2**, **3**) externally added water: $[^{i}BuAlCl_2] = 22$ mM; $[^{i}Pr_2O] = 18$ mM; $[IB] = 5.8$ M. The sequence of components addition: (**1**) *n*-hexane, diisopropyl ether, $^{i}BuAlCl_2$, isobutylene; (**2**) *n*-hexane, diisopropyl ether, H_2O, isobutylene, $^{i}BuAlCl_2$; (**3**) *n*-hexane, diisopropyl ether, H_2O, $^{i}BuAlCl_2$, isobutylene. The concentration of water: (**1**) no water; (**2**), (**3**) $[H_2O] = 0.033$ mM.

TABLE 3 Influence of Co-Initiator Preactivation on the Cationic Polymerization of Isobutylene Co-Initiated by ^{i}BuAlCl$_2$ in the Presence of Diisopropyl Ether in *n*-Hexane[a]

Entry	Time (min)	Temp. (°C)	Conv. (%)	$M_{n,\ SEC}$ (g mol^{-1})	$M_{n,\ NMR}$ (g mol^{-1})	M_w/M_n	End Group Distribution (mol %) Exo	Endo + Tri	Tetra	Coupled
1	10	10	73	1,485	800	2.9	83	6	10	1
2	2	2	59	1,790	1,340	4.2	80	6	14	<1
3	10	2	71	2,070	1,350	3.6	82	7	10	1
4	20	2	79	1,440	1,060	2.7	83	7	10	<1
5	30	2	77	1,880	1,160	3.9	84	6	8	2
6	60	2	77	1,720	1,120	3.9	85	6	8	1

[a] Polymerization conditions: [^{i}BuAlCl$_2$] = 22 mM; [^{i}Pr$_2$O] = 18 mM; [H_2O] = 0.033 mM; [IB] = 5.8 M. The sequence of components addition: *n*-hexane, diisopropyl ether, H_2O, ^{i}BuAlCl$_2$, isobutylene.

from 10 °C to 2 °C led to some increase of molecular weight but, again, did not affect the exo-olefin content (cf. entries 1 and 3 in Table 3).

These data showed that the sequence of the components addition, especially the mode of water introduction into the system, played a key role in the attainment of high monomer conversion in a very short period of time during the synthesis of HR PIB using RAlCl$_2$ × O^{i}Pr$_2$-based initiating systems. However, the high local concentration of initiating species (H^+) formed in the presence of externally added H_2O led to some decrease of exo-olefin content due to the loss the selectivity of β-H abstraction, on the one hand, and to the increase of the intensity of such side reactions as isomerization and/or chain scission.

Delayed Addition of H_2O

In order to decrease the local concentration of initiating species (H^+), we decided to introduce the external H_2O in the course of the polymerization, that is, when adventitious H_2O will be mostly consumed. We assumed that delayed addition of H_2O into the system would allow decreasing the concentration of initiating species (H^+) and this, in turn, would afford more selective β-H abstraction by free ether and also would suppress the side reactions (isomerization and chain scission). From the kinetic profile of the cationic polymerization of IB initiated by adventitious H_2O (curve 1 in Fig. 1), we can see that close to saturated monomer conversion was achieved from 3 min to 10 min since the beginning of reaction, that is, most of adventitious H_2O was consumed for the initiation during this period of time. Therefore, in the initial series of experiments, we tried to determine an optimal time for H_2O introduction into the system.

According to Table 4, the introduction of H_2O into the system after 10 min since the beginning of the polymerization led to the increase of monomer conversion in about 1.5 times, but did not affect significantly the molecular weight, molecular weight distribution and, most important, exo-olefin end groups content (cf. entries 1 and 2 in Table 4). The introduction of H_2O after 3 min since the beginning of the polymerization resulted in even higher monomer conversion (74% in 20 min), whereas the exo-olefin content remained very high (cf. entries 1, 2, and 4 in Table 4). Based on these preliminary results, we conclude that the most efficient time for H_2O addition into the system is 3 min after the beginning of the polymerization.

The brief kinetic investigation of ^{i}BuAlCl$_2$ × 0.8O^{i}Pr$_2$-co-initiated cationic polymerization of IB where an additional H_2O was introduced into the system after 3 min since the beginning of reaction revealed that saturated monomer conversion (80%) was achieved in 40 min, although relatively high conversion (74%) can be already obtained in 20 min (see entries 3, 4, and 7 in Table 4). The comparison of these results with those obtained under "preactivation of catalyst" approach (see previous section) allowed to conclude that the polymerization is slower in the present case: 46% and 73% of monomer conversion was obtained in 10 min for the polymerization experiments performed under "delayed H_2O addition" and "preactivation of catalyst" approaches, respectively (cf. entry 1 in Table 3 and entry 3 in Table 4). On the other hand, the functionality (exo-olefin content) is much higher when "delayed H_2O addition" approach was used and lies around 88–90% (Table 4). The comparison of end groups distribution in PIBs obtained in this study using different ways of H_2O addition into the system revealed the very low amount of tri- (~3.5 mol %) and tetra-substituted (~3.5 mol %) end groups in the polymers prepared using "delayed H_2O addition" approach (cf. data presented in Tables 2 and 3 with data of Table 4). This indicates that side reactions (isomerization and/or chain scission) were significantly suppressed under these conditions that can be explained by the decrease of the instantaneous concentration of active species due to the delayed addition of external H_2O. On the contrary, the fraction of coupled polymer chains is slightly increased from about 1–2 mol % to 2–4 mol % because of creating a relatively high amount of growing macrocations upon addition of external H_2O, which can interact with exo-olefin-terminated PIBs generated during the first stage of reaction initiated by adventitious H_2O.

TABLE 4 Influence of "Delayed" Addition of H_2O on the Cationic Polymerization of Isobutylene with $^iBuAlCl_2 \times 0.8O^iPr_2$ in *n*-Hexane at 10 °C[a]

							End Group Distribution (mol %)			
Entry	H_2O Addition[b] (min)	Total Reaction Time (min)	Conv. (%)	$M_{n,\,SEC}$ (g mol^{-1})	$M_{n,\,NMR}$ (g mol^{-1})	M_w/M_n	Exo	Endo + Tri	Tetra	Coupled
1	–[c]	20	42	1,470	1,020	3.9	91	3	4	2
2	10	20	64	1,260	760	3.4	90	4	3	3
3	3	10	46	1,300	820	3.8	90	3	4	3
4	3	20	74	1,230	730	3.4	88	4	3	5
5[d]	3	20	62	1,280	620	3.2	88	5	4	4
6[d,e]	3	20	77	1,740	1,090	2.9	89	5	5	1
7	3	40	80	1,480	870	3.4	88	5	6	1
8[f]	3	20	77	1,400	770	3.5	87	4	5	4
9[e,f]	3	20	92	1,880	1,300	3.3	88	5	7	<1

[a] Polymerization conditions: $[^iBuAlCl_2] = 22$ mM; $[^iPr_2O] = 18$ mM; $[H_2O] = 0.033$ mM; [IB] = 5.8 M. The sequence of components addition: *n*-hexane, diisopropyl ether, $^iBuAlCl_2$, isobutylene, and then H_2O.

[b] Time of introduction of H_2O after beginning of the polymerization.

[c] H_2O was not introduced into the system.

[d] [Lewis acid] = 33 mM; $[^iPr_2O] = 26.8$ mM.

[e] $EtAlCl_2$ instead of $^iBuAlCl_2$.

[f] The second portion of $^iPr_2O$ (8.8 mM) and Lewis acid (11 mM) were sequentially introduced into reactor after 10 min of polymerization.

The use of higher co-initiator concentration (33 mM instead of 22 mM) did not improve the monomer conversion but also did influence neither the molecular weight nor the content of exo-olefin end groups (entries 4 and 5 in Table 4). On the other hand, the addition of the catalytic complex into two shots (22 mM + 11 mM) allowed raising the monomer conversion up to 77% and almost did not affect the exo-olefin content (entries 5 and 8, Table 4). Interestingly, the use of $EtAlCl_2 \times 0.8O^iPr_2$ instead of $^iBuAlCl_2 \times 0.8O^iPr_2$ led to significant increase of monomer conversion and synthesized PIBs were characterized by slightly higher molecular weight, narrower MWD and high content of exo-olefin end groups (cf. entries 5, 6 and 8, 9 in Table 4). Looking at the end groups distribution, we can see that PIBs synthesized with $EtAlCl_2 \times 0.8O^iPr_2$ as co-initiator contained slightly higher amount of tri- and tetra-substituted olefinic end groups, whereas the content of coupled polymer chains decreased to ~1 mol % (see Table 4). Finally, the addition of the catalytic complex into two shots (22 mM + 11 mM) in the case of $EtAlCl_2 \times 0.8O^iPr_2$-co-initiated polymerization of IB allowed to synthesize HR PIB (exo-olefin content 88%) with near quantitative monomer conversion (92%) in 20 min at high monomer concentration 5.8 M and close to room temperature (entry 9, Table 4).

The typical ^{1}H NMR spectrum of PIB synthesized using "delayed H_2O addition" approach is presented in Figure 2.

The expansion of olefinic region (2.5–5.5 ppm) shows two major signals at 4.64 and 4.85 ppm for the terminal exo-olefin (vinylidene) end groups. The small fraction of endo- and tri-substituted (7 mol %) as well as tetra-substituted (7 mol %) olefinic end groups are observed as broad resonances centered at 5.15 and 2.84 ppm, respectively. The two very small signals at 4.80 and 4.79 ppm (<1 mol %) correspond to coupled[29] and/or isomerized[15,16] polymer chains. Importantly, the signals of *tert*-chloride end groups at 1.68 and 1.96 ppm are virtually absent in the spectrum of PIB sample synthesized with $H_2O/EtAlCl_2 \times 0.8O^iPr_2$ initiating system (Fig. 2).

The polymerization mechanism proposed previously[9,12] adequately explain all the results obtained in this work (the formation of alumioxane-like structures described in ref. 12). The main difference is that in the present case the polymerization proceeds into two stages: at the beginning of the

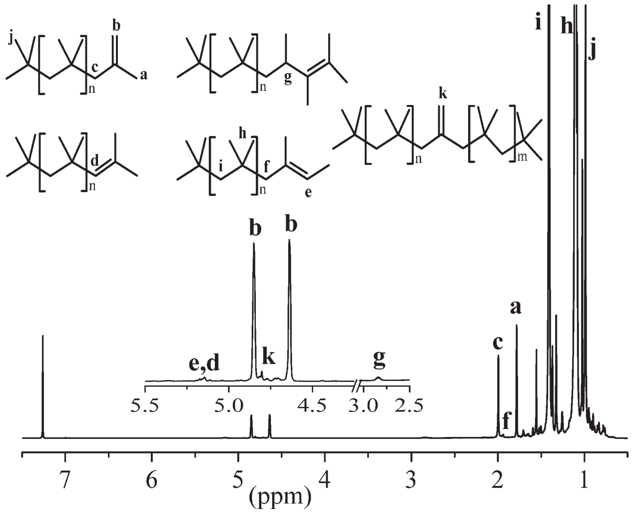
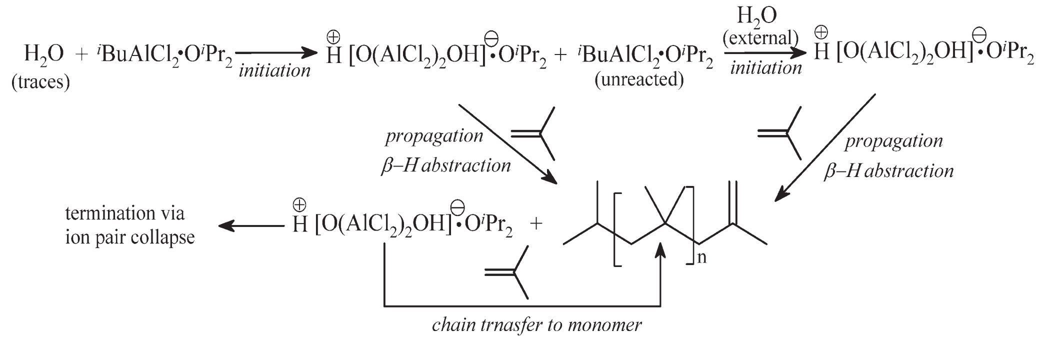


FIGURE 2 ^{1}H NMR spectrum of PIB (entry 9, Table 4) obtained with $H_2O/EtAlCl_2 \times 0.8O^iPr_2$ initiating system at high monomer concentration ([M] = 5.8 M) in *n*-hexane at 10 °C.



SCHEME 1 Proposed mechanism for isobutylene polymerization using externally added $H_2O/^iBuAlCl_2 \times O^iPr_2$ initiating system.

polymerization adventitious water acts as initiator, while externally added water participates in the initiation at the latter stages of the reaction (Scheme 1). This approach allowed reaching high monomer conversion keeping at the same time high functionality. The initial active species regenerated after ether-assisted chain transfer to monomer (β-H abstraction) can initiate new polymer chain or undergo the ion pair collapse leading to the destruction of active species (Scheme 1).

CONCLUSIONS

A systematic study of the cationic polymerization of IB with $H_2O/EtAlCl_2 \times 0.8O^iPr_2$ initiating system in the presence of externally added water was performed in this study. First of all, we demonstrated here that externally added water, which is not fully soluble in the reaction mixture and rather forms the suspension, can be an efficient initiator of the cationic polymerization of IB in nonpolar solvents. The sequence of H_2O introduction into the system has the crucial effect on the polymerization rate, saturated monomer conversion and, to a lesser extent, the content of exo-olefin end groups, but almost does not influence the molecular weight and molecular weight distribution. The highest polymerization rate (>70% of monomer conversion in 10 min) was observed for the polymerization experiments performed using "preactivation of catalyst" approach where $^iBuAlCl_2 \times 0.8O^iPr_2$ was reacted with H_2O before the monomer addition to initiate the polymerization. However, the exo-olefin end groups content is slightly decreased in this case in comparison with experiments without addition of H_2O (from ~90% to 83%) probably due to the high local concentration of initiating species (H^+) formed in the course of catalyst preactivation that leads to some loss the selectivity of β-H abstraction and to the increase of intensity of side reactions (isomerization and/or chain scission). Much better functionality (exo-olefin content is 88–90%) was obtained when H_2O was introduced into the system in the course of the polymerization (after 3–10 min since the initiation of reaction). In this case, the side reactions were significantly suppressed that can be explained by the decrease of the instantaneous concentration of active species due to the delayed addition of external H_2O.

Shortly, this work provides with the simple and industrially relevant initiating system consists of H_2O (in form of suspension in reaction mixture) as initiator and $RAlCl_2 \times 0.8O^iPr_2$ ($R = {}^iBu$ or Et) as co-initiator. This initiating system allows synthesizing HR PIB (exo-olefin content is 83–89%) with desired low molecular weight ($M_n = 1000–2000$ g mol^{-1}) in a high yield (70–90% of monomer conversion in 20 min) at close to room temperature (10 °C) and high monomer concentration ([IB] = 5.8 M). To best of our knowledge, this is a first example of the synthesis of predominantly exo-olefin terminated PIB in a high yield in a relatively short period of time (<20 min) at such high monomer concentration and high reaction temperature.

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