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ARTICLE TYPE

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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The cationic polymerization of isobutylene using $RAlCl_2{\times}nO^{i}Pr_2$-based initiating systems (R=Me, Et, ^{i}Bu; n=0.6–1) in non-polar *n*-hexane at 10 °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 $EtAlCl_2{\times}nO^{i}Pr_2$ and $^{i}BuAlCl_2{\times}nO^{i}Pr_2$ where n=0.8–0.9. These initiating systems afforded polyisobutylenes with desired low molecular weight (M_n=1,000–1,500 g mol^{-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 $RAlCl_2$ 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, $RAlCl_2{\times}O^{i}Pr_2$-based initiating systems showed high activity and selectivity towards polymerization of C_4 mixed feed.

Introduction

Low molecular weight polyisobutylene (PIB) (M_n=500-5000 g mol^{-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_4 mixture (IB, 1-butene, 2-butenes and hydrocarbons) using complexes of BF_3 with alcohols and/or ethers as co-initiator in hydrocarbons at moderately high temperatures (–20 to –10 °C).[1,2] The main disadvantage of this technique is gaseous state of BF_3 that makes difficulties to handle and is detrimental to equipments. Another industrial technique to synthesize low molecular weight PIB is based on the $AlCl_3$- or $EtAlCl_2$-co-initiated polymerization of C_4 mixture but the obtained "conventional" PIB contains predominantly tri- and tetra-substituted olefinic end groups,[3] which are far less reactive as compared to *exo*-olefin end group. The recent interest to the synthesis of HR PIB by various research groups[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.[18] Then, one-step method for synthesis of allyl- and isobutenyl-terminated PIB via *in situ* quenching of controlled cationic polymerization of IB with allyltrimethylsilane or isobutenyltrimethylsilane was proposed by the same authors.[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 $TiCl_4$-co-initiated polymerization of IB with strong hindered bases (2,5-dimethylpyrrole, 1,2,2,6,6-pentamethylpiperidine),[4] sulfides (di-*tert*-butyl sulfide, diisopropylsulfide),[5] and, recently, ethers (diisopropyl ether, di-*sec*-butyl ether).[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.[6] In summary, the great advantage of this approach is the possibility to synthesize mono- and difunctional *exo*-olefin terminated PIBs (*exo*~100%) with precisely controlled number-average molecular weight (M_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-diphenylethylene,[20] but the internal double bond usually showed low reactivity towards further modification by maleic anhydride.[1,7]

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The second approach developed by Kühn and Voit[7,8] consists in the using solvent-ligated complexes with weakly coordinating borate or aluminate anions ([M(NCCH$_3$)$_6$] (A$_2$), 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.[8f] These solvent-ligated complexes were successfully used for the synthesis of HR PIB (*exo*=60-95%) with relatively narrow MWD ($M_w/M_n<2.0$) in dichloromethane or even in non-polar toluene at high reaction temperatures (20–60 °C).[7,8] 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)/$AlCl_3 \times OBu_2$ and $H_2O/AlCl_3 \times OBu_2$ for the synthesis of HR PIB.[9,21] Near at the same time, Wu and co-workers reported independently similar initiating system, i.e. $H_2O/AlCl_3 \times OR_2$ (R=Bu or ^{i}Pr)[12] and, later, $H_2O/FeCl_3 \times OR_2$ (R_2O=Et_2O, Bu_2O and $^iPr_2O$).[13] These initiating systems afforded desired low molecular weight PIB (M_n=1,000–3,000 g mol^{-1}) with relatively narrow MWD ($M_w/M_n \leq 2.2$) and high content of *exo*-olefin double bonds (85-97%) in CH_2Cl_2 or CH_2Cl_2/*n*-hexane mixture at temperatures from –40 to 20 °C.[9,12,13] In order to avoid the use of toxic chlorinated solvents, we have investigated the cationic polymerization of IB in toluene. It was shown that $H_2O/AlCl_3 \times OBu_2$ initiating system allowed to synthesize HR PIB (*exo*≥90%) and that molecular weight of obtained PIB*s* can be easily controlled by the reaction temperature.[10] The desired low molecular weight polymers with M_n=2300 g mol^{-1} and 1,000 g mol^{-1} and relatively narrow MWD (M_w/M_n=2.6 and 1.6) were synthesized in a high yield (>80%) in 10 min at 0 °C and 25 °C, respectively.[10]

Since the commercial process of HR PIB production proceeds in aliphatic hydrocarbon solvents, the cationic polymerization of IB with $H_2O/AlCl_3 \times OR_2$ (R_2O=Bu_2O, $^iPr_2O$) initiating systems were then investigated in *n*-hexane.[11,15] 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.[11,15] In addition, the good functionality was observed only at temperatures below 0 °C (–20 °C) and the molecular weight was higher (M_n=3,000–6,000 g mol^{-1}) than required for the application for motor oil/fuel additives (M_n=1,000–2,300 g mol^{-1}) while MWD was relatively broad (M_w/M_n=2–5).[11] In order to overcome above-mentioned limitations of $AlCl_3 \times OR_2$-based initiating systems, the complexes of $FeCl_3$ and $GaCl_3$ with ethers were recently introduced by Faust et al.[16,17] as efficient catalysts for the synthesis of HR PIB in *n*-hexane. The major advantage of these new catalytic complexes in comparison with $AlCl_3 \times OR_2$ is the possibility to use them in a combination with alkyl chlorides due to the chlorophilic nature[22] of $FeCl_3$ and $GaCl_3$. Therefore, the cationic polymerization of IB with *tert*-butyl chloride/$FeCl_3 \times O^iPr_2$ ($GaCl_3 \times O^iPr_2$) 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%).[16] 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] Another $FeCl_3$-based initiating system, $H_2O/FeCl_3/^iPrOH$ was very recently reported for the synthesis of HR PIB in *n*-hexane at temperatures well below 0 °C.[14] Although this initiating system allowed to synthesize PIB*s* 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 (M_n=3,000–6,000 g mol^{-1}).[14] In addition, for all above-mentioned initiating systems the use of CH_2Cl_2 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 $MCl_3 \times OR_2$ (M=Al, Fe, Ga) initiating systems during last years,[9,10,11,12,13,14,15,16,17] 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 alkylaluminum dichlorides with diisopropyl ether in *n*-hexane at room temperature (10 °C) and at high monomer concentrations ([M]=2.8-5.8 M). Under these conditions HR PIB (exo=85-90%) with desired low molecular weight (M_n=1,000–2500 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 $CaCl_2$. C_4 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 methylcyclopropane was purified similarly to isobutylene. *n*-Hexane (Sigma–Aldrich, >95%) were treated with sulphuric acid, washed with aqueous sodium bicarbonate, dried over $CaCl_2$ and distilled twice from CaH_2 under an inert atmosphere. Diisopropyl ether ($^iPr_2O$, Fluka, ≥98.5%) was distilled over CaH_2 under argon. $AlCl_3$ (Aldrich, 99.999%), $^iBu_3Al$ (1 M solution in hexanes, Aldrich), Et_3Al (1 M solution in hexanes, Aldrich), $CDCl_3$ (Euriso-top®), C_6D_6 (Euriso-top®), ethanol (Sigma–Aldrich, >96%), tetrahydrofuran (anhydrous, Sigma-Aldrich, ≥99.9%) were used as received. Isobutylaluminum dichloride ($^iBuAlCl_2$) and ethylaluminum dichloride ($EtAlCl_2$) were obtained as 1 M solutions in hexanes by mixing of $AlCl_3$ and $^iBu_3Al$ (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. For ^1H NMR experiments, the solutions of alkylaluminum dichlorides and their complexes with diisopropyl ether were prepared in C_6D_6 at 20 °C in a separate glass reactor

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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 ºC 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 ^{i}BuAlCl$_2$ (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 EtAlCl$_2$ 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. Tetrahydrofuran (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$_3$ or C$_6$D$_6$ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the residual solvents resonances.

Results and discussion

Preliminary tests

Complexes of isobutylaluminum dichloride (^{i}BuAlCl$_2$) and ethylaluminum dichloride (EtAlCl$_2$) 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.[23] 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 (AlCl$_3$, FeCl$_3$, GaCl$_3$) with ^{i}Pr$_2$O 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 ^{i}BuAlCl$_2$ 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 (^{i}BuAlCl$_2$/^{i}Pr$_2$O 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 ω-end (run 6, Table 1). In addition, the molecular weight of PIBs synthesized with ^{i}BuAlCl$_2$/^{i}Pr$_2$O 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 AlCl$_3$ where the use of even small excess of Lewis acid over ether reduced the *exo*-olefin terminal groups content significantly.[11]

Table 1 Polymerization of isobutylene co-initiated by ^{i}BuAlCl$_2$×nO^{i}Pr$_2$ at different Lewis acid (LA)/O^{i}Pr$_2$ ratios in *n*-hexane at 20 °C[a]

Run	LA:O^{i}Pr$_2$ (mol/mol)	Time (min)	Conversion (%)	M$_n$ (SEC) (g mol^{-1})	M$_n$ (NMR)[b] (g mol^{-1})	M$_w$/M$_n$	[PIB][c] (mM)	End groups distribution (mol%)[d]		
								Exo	Endo+tri	Tetra
1	1:0	3	100	6930	4530	5.3	12	0	77	23
2	1:1	10	5	500	410	2.1	7	95	2.5	2.5
3	1:1	30	9	810	520	2.4	10	93	3.5	3.5
4	1:0.9	30	19	680	490	2.8	22	91	4	5
5[e]	1:0.8	30	27	940	560	2.0	27	91	4	5
6	1:0.6	30	39	2040	3470	2.6	6	53	22	25

[a] [IB]=1.0 M; [^{i}BuAlCl$_2$]=[^{i}BuAlCl$_2$×nO^{i}Pr$_2$]=22 mM. The polymerization was initiated by the addition of monomer into reaction mixture containing catalytic complex and solvent. [b] Determined by ^{1}H NMR as M$_n$(NMR)=56×[(i/2)/((b+b+k)/2+d+e+g)], see Figure 1 for assignments. [c][PIB]=[IB]×56×(conv./M$_{n,\ NMR}$). [d] The content of coupled polymer chains is less than 1 mol% [e] 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

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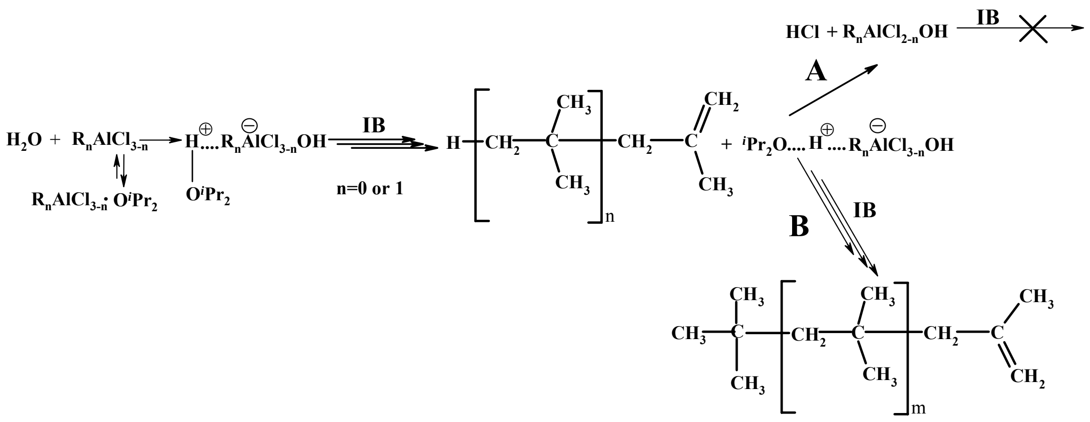
(about 20-30% in the best cases) and the polymerization was quite slow that is inconsistent with the industrial requirements. The low monomer conversion can be connected either with low concentration of water in non-polar *n*-hexane (≤0.4 mM)[11,15] or relatively high probability of ion pair collapse (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[9,10] and Faust et al.[15] 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.[13,17] 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).



Scheme 1 Proposed mechanism for the polymerization of isobutylene with R$_n$AlCl$_{3-n}$×O^{i}Pr$_2$ (n=0 or 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 *exo*-olefin end groups content almost did not change while MWD became slightly broaden 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 *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 Polymerization of isobutylene co-initiated by RAlCl$_2$×0.9O^{i}Pr$_2$ (R=Me, Et, ^{i}Bu) at different monomer concentrations in *n*-hexane at 10 °C[a]

Lewis acid	Run	[IB] (M)	Conversion (%)	M$_n$ (SEC) (g mol^{-1})	M$_n$ (NMR)[b] (g mol^{-1})	M$_w$/M$_n$	[PIB][c] (mM)	End groups distribution (mol%)			
								Exo	Endo+tri	Tetra	Coupled
^{i}BuAlCl$_2$	1	2.8	24	1520	1070	3.0	35	94	3	3	0
	2[d]	5.8	36	1470	1020	3.9	118	91	3	4	2
	3[e]	5.8	29	900	680	3.1	139	96	2	1	1
	4[f]	11.8	17	1270	890	3.8	137	86	3	1	10
EtAlCl$_2$	5[g]	1.9	29	1000	740	2.8	41	89	4	7	<1
	6[g]	2.8	35	1380	840	3.1	61	88	5	6	1
	7[g]	5.8	41	1750	1050	3.7	109	84	6	8	2
	8	5.8	29	1400	1130	3.6	70	92	3	4	1
	9[h]	5.8	55	1400	1060	3.6	151	84	5	7	4
	10[e,h]	5.8	62	1350	930	2.5	194	82	4	8	6
MeAlCl$_2$	11	5.8	19	3050	2550	3.9	24	80	8	12	<1
	12[h]	5.8	37	3090	2715	3.6	44	78	9	13	<1
	13[e,h]	5.8	60	2370	1940	3.1	100	77	10	11	2

[a] [LA×0.9O^{i}Pr$_2$]=22 mM; reaction time: 10 min. The polymerization was initiated by the addition of monomer into reaction mixture containing catalytic complex and solvent [b] Determined by ^{1}H NMR as M$_n$(NMR)=56×[(i/2)/((b+b+k)/2+d+e+g)], see Figure 1 for assignments. [c] [PIB]=[IB]×56×(conv./M$_{n,\ NMR}$). [d] All values are averaged from several runs. [e] [LA×0.9O^{i}Pr$_2$]=33 mM; [f] Polymerization in a neat isobutylene. [g] EtAlCl$_2$×0.8O^{i}Pr$_2$ (22 mM) was used as co-initiator. [h] Reaction time: 30 min.

The effect of Lewis acid nature on the monomer conversion and *exo*-olefin double bond content has been briefly investigated. The monomer conversion gradually increased in the following series MeAlCl$_2$<^{i}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.[24] The molecular weight, the average concentration of PIB chains and the content of *exo*-olefin end groups were quite similar for PIB*s* synthesized with complexes of ^{i}BuAlCl$_2$ and EtAlCl$_2$ (runs 2 and 8 in Table 2). On the contrary, PIB*s* synthesized with MeAlCl$_2$×0.9O^{i}Pr$_2$ as co-initiator were characterized by considerably higher molecular weight, lower concentration of PIB chains and *exo*-olefin end groups content (Table 2). These results indicated that *β*-H abstraction by diisopropyl ether is less

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efficient in this case that can be associated with the formation of relatively strong complex between $MeAlCl_2$ and $^iPr_2O$.

Interestingly, the increase of concentration of the catalytic complex hardly influenced the monomer conversion (with the exception of using $MeAlCl_2\times0.9O^iPr_2$ 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 $EtAlCl_2\times0.8O^iPr_2$ instead of $EtAlCl_2\times0.9O^iPr_2$ 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 PIB*s* synthesized with $RAlCl_2\times O^iPr_2$ initiating system in comparison with PIBs obtained with $AlCl_3\times O^iPr_2$ 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 $H_2O/EtAlCl_2\times0.8O^iPr_2$ 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.

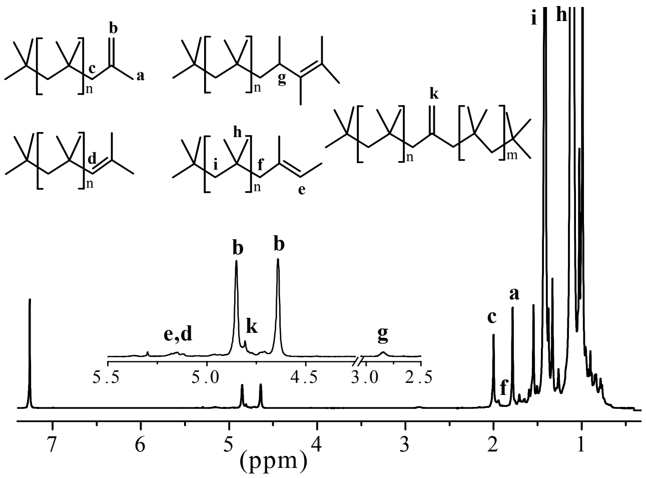

Fig. 1 ^1H NMR spectrum of PIB (run 9, Table 2) obtained with $H_2O/EtAlCl_2\times0.9O^iPr_2$ initiating system at high monomer concentration ([M]=5.8 M) in *n*-hexane at 10 °C.

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 M_n*s* were decreased with increasing monomer conversion reaching the value of M_n 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.

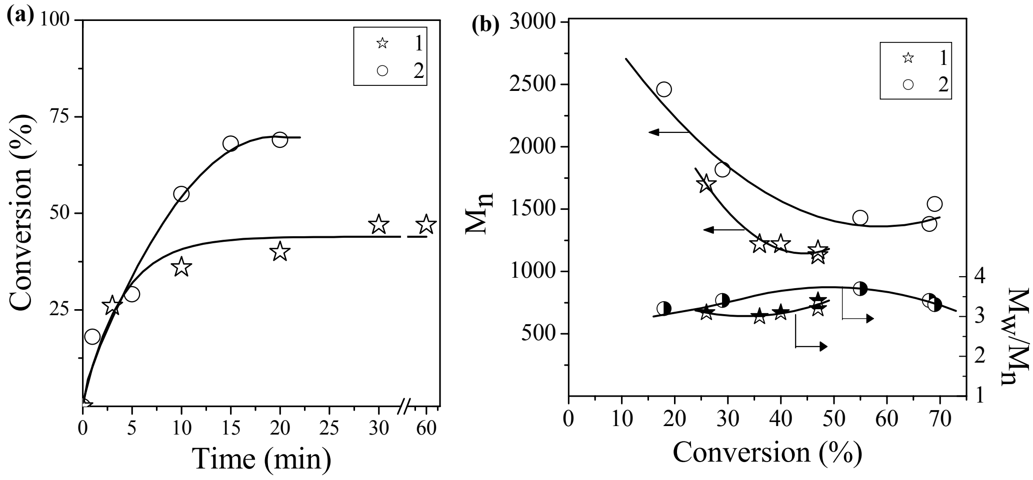

Fig. 2 (a) Conversion vs. time and (b) M_n(NMR), M_w/M_n vs. conversion plots for the isobutylene polymerization co-initiated by $EtAlCl_2\times0.8O^iPr_2$ or $EtAlCl_2$ and separately added diisopropyl ether in *n*-hexane at 10 °C: [$EtAlCl_2$]=22 mM; [$^iPr_2O$]=18 mM; [IB]=2.8 M. The sequence of components addition: (**1**) complex ($EtAlCl_2\times0.8O^iPr_2$) was formed *in situ* and IB was added to system as the last component; (**2**) $EtAlCl_2$ was added to the system containing ether and monomer as the last component.

To summarize, PIBs with desired low molecular weight (M_n=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

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is a strong improvement both in terms of molecular weight and *exo*-olefin content in comparison with $H_2O/AlCl_3{\times}O^iPr_2$ initiating system.[11,15]

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.[15,16] in the cationic polymerization of isobutylene with $H_2O/AlCl_3{\times}O^iPr_2$ and $^tBuCl/GaCl_3{\times}O^iPr_2$ initiating systems. However, under such conditions only conventional PIB*s* containing predominantly *tri*- and *terta*-substituted terminal olefin 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 $H_2O/EtAlCl_2/O^iPr_2$ initiating system allowed to synthesize PIB*s* 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 $RAlCl_2$ (R=^{i}Bu, Et) with diisopropyl 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[a]

Run	Time (min)	Conversion (%)	M_n (SEC) (g mol^{-1})	M_n (NMR)[b] (g mol^{-1})	M_w/M_n	[PIB][c] (mM)	End groups distribution (mol%)[d]		
							Exo	Endo+tri	Tetra
1	1	18	3200	2460	3.2	11	74	10	16
2	5	29	2170	1815	3.4	25	83	6	11
3[e]	10	55	1870	1430	3.7	60	83	7	10
4	15	68	2230	1380	3.4	77	83	6	11
5	20	69	2070	1540	3.3	71	84	6	10
6[f]	10	61	1770	1460	3.8	136	80	6	14

[a] $[EtAlCl_2]$=22 mM; $[^iPr_2O]$=18 mM; [IB]=2.8 M. [b] Determined by ^1H NMR as $M_n(NMR)=56\times[(i/2)/((b+b+k)/2+d+e+g)]$, see Figure 1 for assignments. [c] $[PIB]=[IB]\times56\times(conv./M_{n,\ NMR})$. [d] The content of coupled polymer chains is less than 1 mol%. [e] All values are averaged from several runs. [f] [IB]=5.8 M.

The comparison of data presented in Table 2, Table 3 and Figure 2b showed that "delayed proton abstraction" indeed took place in the case of the separate addition of Lewis acid and ether: the molecular weight is ca. 1.5 times higher in comparison with one obtained using preformed complex of $EtAlCl_2$ with $^iPr_2O$ as catalyst, on the one hand. On the other hand, the change of sequence of the component addition almost did not influence the equilibrium between ion pair collapse and ether-assisted chain transfer (see Scheme 1): the average concentration of PIB chains is almost the same for both approaches (see Table 2 and Table 3). In addition, the evolution of molecular weight with monomer conversion depicted in Figure 2b unambiguously showed that conventional chain transfer-dominated polymerization took place under investigated conditions. The molecular weight distribution was changed insignificantly throughout the polymerization and typically laid around 3.3-3.4 at the ultimate monomer conversion. The "delayed proton abstraction" approach was also efficient at high monomer concentration: desired low molecular weight PIB*s* (M_n~1,500 g mol^{-1}) in a good yield (60% in 10 min) with high content of *exo*-olefin end groups were obtained at [IB]=5.8 M (run 6, Table 3).

In summary, the use of "delayed proton abstraction" approach allowed to increase both the reaction rate and the ultimate monomer conversion (70 % in less than 15 min) keeping at the same time high functionality at the ω-end (*exo*-olefin content about 80-85%). Such of behavior of $RAlCl_2$-based initiating systems is completely different from one observed for conventional metal halides.

Polymerization of C_4 mixed feed

The C_4 mixed feed is generally used for the production of conventional PIB*s* via $AlCl_3$-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 $H_2O/AlCl_3/o$-cresol[25] or $H_2O/FeCl_3/O^iPr_2$[14] initiating systems are availably in the literature. However, although both of these initiating systems afforded PIB*s* with high content of *exo*-olefin end groups (80-95%), the monomer conversion did not exceeded 50% and molecular weight was considerably higher (M_n=3,000–10,000 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 $AlCl_3$-based initiating system.

As shown in Table 4, the polymerization of C_4 mixed feed with $AlCl_3{\times}O^iPr_2$ as co-initiator afforded relatively high molecular weight PIB (M_n=10,800 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).

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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 $H_2O/AlCl_3{\times}O^iPr_2$ initiating system.[11]

Table 4 Polymerization of C_4 mixed feed co-initiated by $AlCl_3{\times}O^iPr_2$ or $^iBuAlCl_2$ and separately added ether [a]

Run	Co-initiator	Temperature (°C)	Conversion[b] (%)	M_n (SEC) (g mol^{-1})	M_n (NMR)[c] (g mol^{-1})	M_w/M_n	End groups distribution (mol%)[d] Exo	Endo+tri	Tetra
1	$AlCl_3{\times}O^iPr_2$	–20	28	10800	9950	2.9	82	11	7
2[e]	$AlCl_3{\times}O^iPr_2$	–20	64	6570	6760	2.7	75	10	16
3	$AlCl_3{\times}O^iPr_2$	0	42	4370	4520	2.4	69	11	20
4[e]	$^iBuAlCl_2$	–20	24	2600	2680	4.2	86	8	6
5[e]	$^iBuAlCl_2$	0	63	1470	1470	2.9	82	8	10

[a] $[AlCl_3{\times}O^iPr_2]=[^iBuAlCl_2]$= 22 mM; $[^iPr_2O]$=18 mM. Reaction time: 30 min. [b] Calculated based on the isobutylene content in C_4 mixed feed. [c] Determined by ^{1}H NMR as $M_n(NMR)=56\times[(i/2)/((b+b+k)/2+d+e+g)]$, see Figure 1 for assignments. [d] The content of coupled polymer chains is less than 1 mol%. [e] H_2O (0.033 mM) was added into the system before the addition of $AlCl_3{\times}O^iPr_2$ or $^iBuAlCl_2$.

The use of $H_2O/^iBuAlCl_2/O^iPr_2$ initiating system, in contrast to $H_2O/AlCl_3{\times}O^iPr_2$ system, allowed to synthesize HR PIB from C_4 mixed feed with desired low molecular weight (M_n=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 M_n=1,500 g mol^{-1}) but, in contrast to polymerization with $H_2O/AlCl_3{\times}O^iPr_2$ initiating system, almost did not influence the *exo*-olefin content (run 5, Table 4).

Taking into account that C_4 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 C_4 mixed feed), the possible incorporation of these olefins into polymer chain has been investigated by ^{1}H NMR spectroscopy (Figure 3).

According to Faust et al.,[26] only monoaddition (capping) of 1-butene and *cis*-2-butene took place, while *trans*-2-butene did not react with growing polyisobutylene macrocations obtained via $TiCl_4$-coinitiated living cationic polymerization. Since the signals of possible terminal $-C\boldsymbol{H}(Cl)-$ groups for PIB–1-butene–Cl at ca. 4 ppm[26] and PIB–2-butene–Cl at ca. 4.6 ppm[26] were not detected in ^{1}H 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]

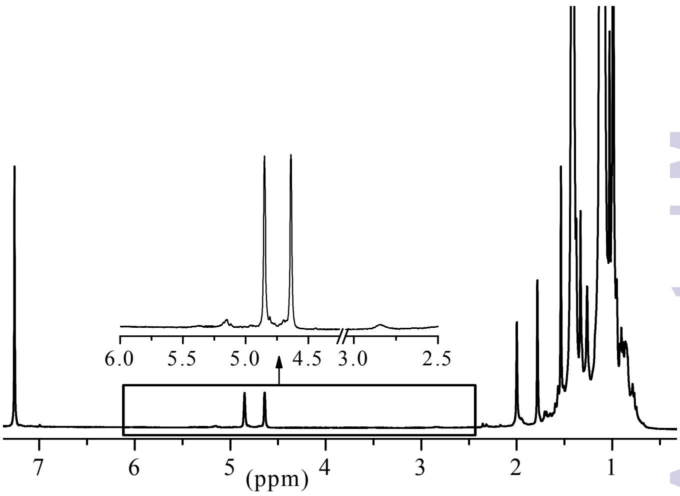
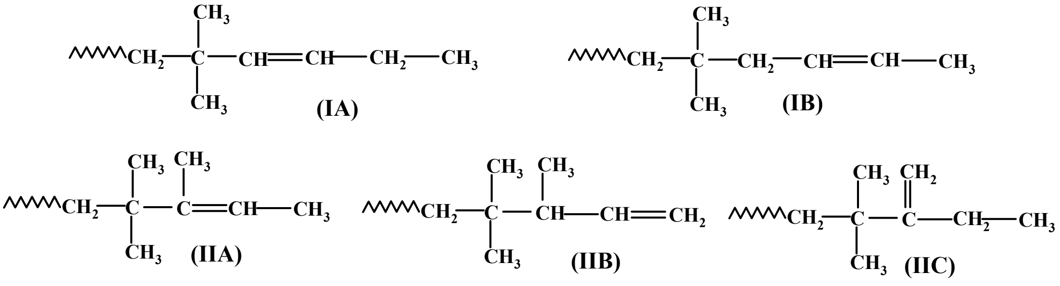


Fig. 3 ^{1}H NMR spectrum of PIB (run 5, Table 4) obtained from C_4 mixed feed with $H_2O/^iBuAlCl_2/^iPr_2O$ initiating system.



Scheme 2 Possible chain end structures after monoaddition of 1-butene and 2-butene to PIB$^+$ macrocation 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 C_4 mixed feed along with isobutylene, should appear near 5.4 ppm.[28] However, no signals were observed in this region of ^{1}H 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 that 1-butene).[26] The capping of PIB$^+$ macrocation with 2-butene following by *β*-H abstraction according to Faust et al.[26] and Mayr et al.[27] will result in the structures **IIA–IIC** (Scheme 2). The structure **IIA** is similar to *tri*-substituted end

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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 distinguish from those formed in the course of isomerization/chain coupling during isobutylene polymerization. On the other hand, the signals of allyl-terminated PIB (structure **IIB**, 5.1 ppm and 5.6-5.7 ppm[19b]) are also absent in the spectrum (Figure 3). Therefore, the reaction of PIB^+ with 2-butene, which is ~294 times less reactive than isobutylene,[26] is also unlikely under investigated conditions. Probably, the β-H abstraction by diisopropyl ether is faster than end capping of PIB^+ by olefins. These results suggest that cationic polymerization of C_4 mixed feed with $H_2O/{}^i BuAlCl_2/O^i Pr_2$ initiating system proceeds with high selectivity towards isobutylene polymerization.

To summarize, a great advantage of $H_2O/{}^i BuAlCl_2/O^i Pr_2$ initiating system, in comparison with known systems,[14,25] is the possibility to synthesize desired low molecular weight polyisobutylenes (M_n=1,500–2,500 g mol^{-1}) in a high yield (above 60%) and good functionality (*exo*=82–86%) via selective cationic polymerization from C_4 mixed feed.

Polymerization mechanism

Complex formation

In order to have an insight into polymerization mechanism, the formation of complexes of ethylaluminum dichloride with diisopropyl ether as well as the interaction of $EtAlCl_2$ and $EtAlCl_2 \times O^i Pr_2$ with water in non-polar C_6D_6 has been studied by ^1H NMR spectroscopy.

As shown in Figure 4, the formation of complex between $EtAlCl_2$ and $^i Pr_2O$, similarly to the formation of $AlCl_3 \times O^i Pr_2$ complex,[11] led to significant downfield shift of OC$\underline{H}$ protons of ether, while C$\underline{H}_3$– protons of $^i Pr_2O$ showed upfield shift. For $EtAlCl_2 \times O^i Pr_2$ two types of complexes with downfield shifts of OC$\underline{H}$ protons of diisopropyl ether of 0.83 ppm and 0.93 ppm were observed. A similar observations were recently reported for $AlCl_3 \times O^i Pr_2$ complex in CD_2Cl_2[15] and C_6D_6.[11] However, the comparison of chemical shifts of OC$\underline{H}$ protons of diisopropyl ether for $EtAlCl_2 \times O^i Pr_2$ and $AlCl_3 \times O^i Pr_2$[11] in C_6D_6 revealed much stronger and uniform interaction of Lewis acid with ether for the former catalytic complex (downfield shifts of OC$\underline{H}$ protons of $^i Pr_2O$ of 0.17 ppm and 0.96 ppm were reported). Interestingly, one resonance of OC$\underline{H}$ protons at 4.26 ppm in $EtAlCl_2 \times O^i Pr_2$ 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 $EtAlCl_2 \times O^i Pr_2$ complex, but its concentration is very low.

The signals of protons of CH_3 and CH_2 groups of $EtAlCl_2 \times O^i Pr_2$ also showed downfield shift of 0.46 ppm and 0.19 ppm in comparison with those for $EtAlCl_2$ that confirms the formation of complex (Figure 4 b, c, Figure S2, Figure S3). No signals of free Lewis acid or ether were detected in ^1H NMR spectrum of $EtAlCl_2 \times O^i Pr_2$ (see Figure 4). Interestingly, only one series of well resolved signals of ethyl group in $EtAlCl_2$ 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 $EtAlCl_2$ is less sensitive towards complexation and we observed on Figure 4c an average signals for both of complexes. Another expalnation can be the formation of dimeric complexes such as $(Et_2Al_2Cl_4) \times O^i Pr_2$. The generation of similar dimeric complexes was observed during the investigation of Et_2AlCl with croton aldehyde.[29]

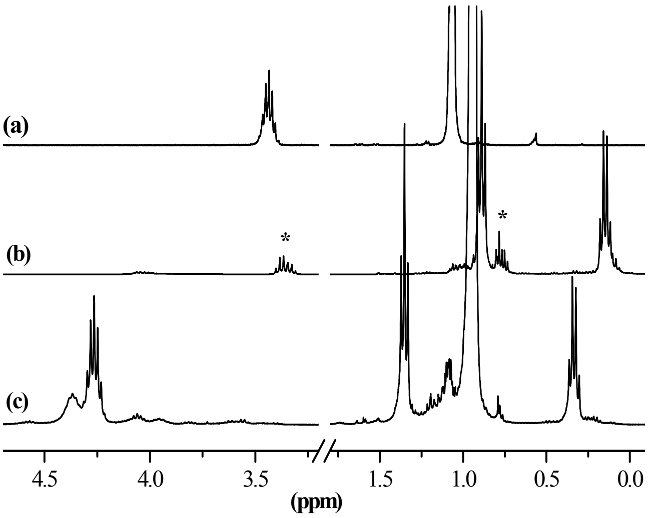

Fig. 4 ^1H NMR spectra overlay of (a) diisopropyl ether, (b) $EtAlCl_2$ and (c) $EtAlCl_2 \times O^i Pr_2$ in C_6D_6 at 25 °C: $[EtAlCl_2]=[EtAlCl_2 \times O^i Pr_2]=0.05$ M. The signals labeled by asterisks correspond to admixtures of oxidized ethylaluminum dichloride.[30]

Initiation

In order to investigate the initiation process, we studied further the interaction of $EtAlCl_2 \times O^i Pr_2$ complex with water. The reaction of water with a 1:1 $EtAlCl_2 \times O^i Pr_2$ complex ($EtAlCl_2 \times O^i Pr_2$: H_2O ratio is 1:0.6 mol/mol) is relatively slow that is fully consistent with low activity of equimolar alkylaluminum complexes with diisopropyl ether in the cationic polymerization of IB (see Table 1 and discussion therein). Indeed, no significant changes were observed in ^1H NMR spectrum of $EtAlCl_2 \times O^i Pr_2$ in 10 min after addition of H_2O except of the appearance of ethane peak at 0.8 ppm indicating slow hydrolysis of C–Al bond in $EtAlCl_2$ (see Figure 5a and Figure S5). After 10 h of reaction of $EtAlCl_2 \times O^i Pr_2$ with water, the signals of ethyl group at 0.33 ppm (C$\underline{H}_2$) and 1.352 ppm (C$\underline{H}_3$) are almost completely disappeared (Figure 5a). The signals of OC$\underline{H}$ protons of diisopropyl ether at 4.36 ppm and 4.26 ppm become broaden 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 diisopropyl ether also became broaden (Figure 5, Figure S2 and Figure S6). These data indicated the formation of several donor-acceptor complexes under investigated conditions. Importantly, no signals of OC$\underline{H}$ protons of free diisopropyl ether at 3.43 ppm are appeared in spectrum (Figure 4a, Figure 5a, Figure S5) as it was reported for the reaction of $AlCl_3 \times O^i Pr_2$ with water[15] that can be associated with different mechanism of initiation with $H_2O/EtAlCl_2 \times O^i Pr_2$ and $H_2O/AlCl_3 \times O^i Pr_2$ initiating systems.

Finally, we also investigated briefly the interaction of free $EtAlCl_2$ with water in order to clarify the difference (if any) in the initiation mechanism in the presence of $EtAlCl_2$ and $EtAlCl_2 \times O^i Pr_2$ (Figure 6).

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The addition of 0.2 equiv of water into NMR tube containing solution of $EtAlCl_2$ (0.05 M) in C_6D_6 led to the fast reaction with intensive evolution of ethane resulting in the formation of precipitate.[31] The ^1H NMR analysis of solution revealed the broadening of peaks of ethyl group as well as the appearance of low intensity signals at 4.06 ppm and 2.43 ppm, which can be attributed to hydroxyl proton of $Et_nAlCl_{2-n}OH$[31,32] (n=0 or 1) and formation of aluminoxane-like structures,[33] respectively (compare Figure 6b and Figure 6c). The reaction of $EtAlCl_2$ with $MgCl_2 \times 6H_2O$ ($EtAlCl_2$: H_2O=1:0.6 mol/mol) proceeds in more controlled fashion up to complete disappearance of signals of ethyl group of $EtAlCl_2$ (Figure 6a). Besides, in this case all products formed during the reaction of $EtAlCl_2$ with $MgCl_2 \times 6H_2O$ are soluble in C_6D_6.

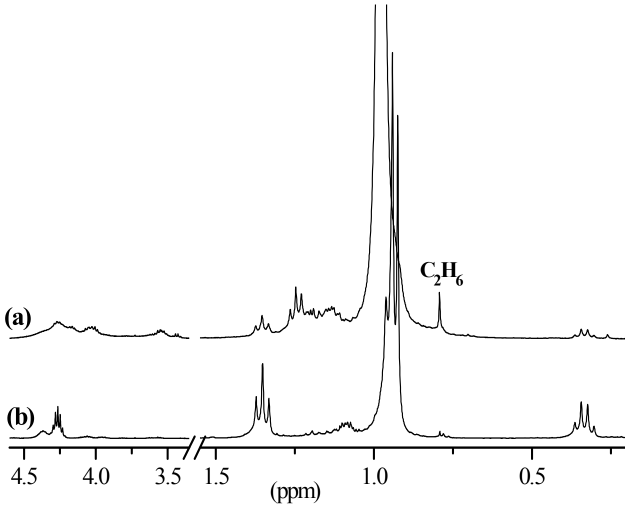

Fig. 5 ^1H NMR spectra overlay of (**a**) $EtAlCl_2 \times O^iPr_2$ after reaction with water (in form of $MgCl_2 \times 6H_2O$) during 10 h ($EtAlCl_2$:H_2O=1:0.6 mol/mol) and (**b**) $EtAlCl_2 \times O^iPr_2$ in C_6D_6 at 25 °C: [$EtAlCl_2 \times O^iPr_2$]=0.05 M.

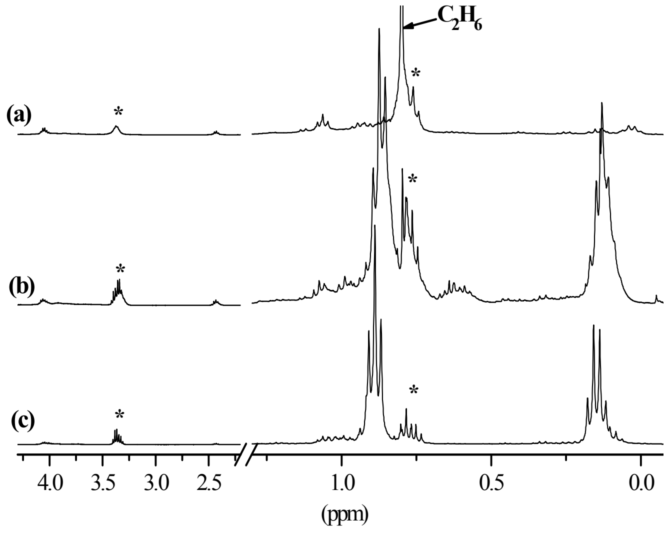

Fig. 6 ^1H NMR spectra overlay of (a) $EtAlCl_2$ (0.05 M) after reaction with water (in form of $MgCl_2 \times 6H_2O$, $EtAlCl_2$:H_2O=1:0.6 mol/mol). (b) $EtAlCl_2$ (0.05 M) after reaction with water ($EtAlCl_2$:H_2O=1:0.2 mol/mol) and (c) $EtAlCl_2$ (0.05 M) in C_6D_6 at 25 °C. The signals labeled by asterisks correspond to admixtures of oxidized ethylaluminum dichloride.[30]

Mechanism

The performed in this study ^1H NMR investigation of interaction of $EtAlCl_2$ with diisopropyl 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.[30,34] Taking into account the nice splitting of signals of ethyl group in $EtAlCl_2$ (Figure 4b and Figure S3) as well as literature data[35], we can postulate the formation of dinuclear chlorine-bridged dimers of $EtAlCl_2$ rather than alkyl-bridged dimers. The addition of ether to these dimers leads to formation of monomeric complex (Scheme 3a) in non-polar C_6D_6 and *n*-hexane[31,32] as it is evidenced by ^1H NMR spectroscopy (Figure 4c).

Based on the ^1H NMR study as well as literature data,[31,36] the reaction of H_2O with $EtAlCl_2 \times O^iPr_2$ is accompanied by the direct hydrolysis of Al–C bond followed by the formation of etherate of corresponding alumoxane[31,32] (Scheme 3b). The similar reaction pathway was also proposed for the interaction of $EtAlCl_2$ with H_2O, which proceeds through the formation of an aqua-complex $EtAlCl_2 \times H_2O$ followed by its transformation into alumoxane derivatives such as $(Cl_2Al)_2O$ and $(C_2H_5AlCl)_2O$.[31] The formation of alumoxane during the interaction of $EtAlCl_2$ with H_2O 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 $EtAlCl_2 \times O^iPr_2$ 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 ($RAlCl_2$:O^iPr_2=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 $AlCl_3$[11,15] and $GaCl_3$[16] etherates). (ii) The relatively low monomer conversion and relatively low average concentration of PIB chains obtained with $H_2O/RAlCl_2 \times O^iPr_2$ initiating system in comparison with complexes of conventional metal halides[13,17] 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 $RAlCl_2$ and separately added ether (PIB*s* containing mainly tri- and tetra- substituted double bonds were formed in the case of separate addition of $AlCl_3$ or $GaCl_3$ and diisopropyl ether[15,16]) 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 typically observed for IB with $H_2O/AlCl_3 \times O^iPr_2$ initiating system in non-polar toluene[10] and *n*-hexane[11]) can indicate that different types of active species (counterions) participate in the initiating and propagating steps of reaction. Finally, we would like to comment on the possible termination during $RAlCl_2 \times O^iPr_2$-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

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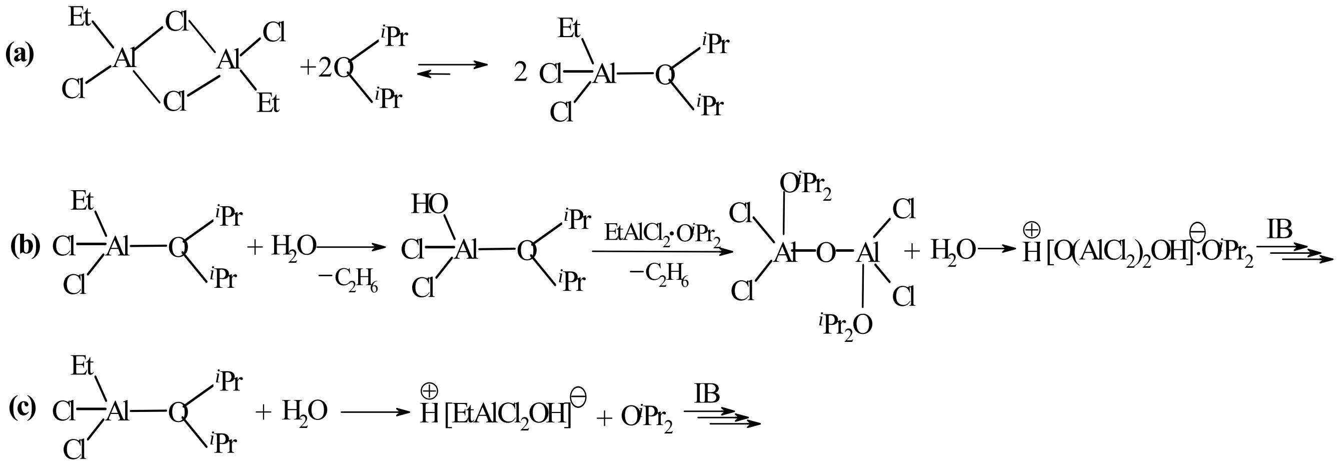
of all monomer that is not observed in the present conditions (see Figure 2a). Therefore, the consumption of Lewis acid (alumoxane) on the process similar to one presented in Scheme 1 (pathway A) is most probably responsible for the termination of polymerization.



Scheme 3 Complex formation and possible pathways for initiation of cationic polymerization of isobutylene with $H_2O/EtAlCl_2{\times}O^iPr_2$ initiating system.

Conclusions

We report here new efficient initiating systems based on complexes of alkylaluminum dichlorides with diisopropyl 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 complexes of $AlCl_3$,[11,15] $FeCl_3$[13,16] and $GaCl_3$[16] with ethers, these new initiating systems are fully soluble in hydrocarbons that allowed to exclude the use of polar co-solvents (CH_2Cl_2) for the preparation of catalytic complexes. Another interesting feature of $RAlCl_2{\times}O^iPr_2$-based initiating systems in comparison with 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 $RAlCl_2$ in the presence of separately added ether. Finally, $RAlCl_2{\times}O^iPr_2$-based initiating systems showed high activity and selectivity towards polymerization of C_4 mixed feed: low molecular weight PIBs (M_n<2,500 g mol^{-1}) in such high yield (above 60%) were synthesized for the *first time*. Mechanistic studies suggests that reaction of $EtAlCl_2{\times}O^iPr_2$ with water during the initiation stage of reaction is accompanied by the direct hydrolysis of Al–C bond followed by the formation of etherates of corresponding alumoxane ($(Cl_2Al)_2O{\times}nO^iPr_2$). From the obtained results it is evident that $RAlCl_2{\times}O^iPr_2$-based initiating systems showed great potential for industrial application and can be a good alternative to currently used BF_3-based systems. The one disadvantage of $RAlCl_2{\times}O^iPr_2$-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.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR spectra of $EtAlCl_2$, $EtAlCl_2{\times}OiPr_2$ and products of their reaction with water.. See DOI: 10.1039/b000000x/

‡ In some ^{1}H NMR spectra of $EtAlCl_2{\times}O^iPr_2$ at higher complex 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.

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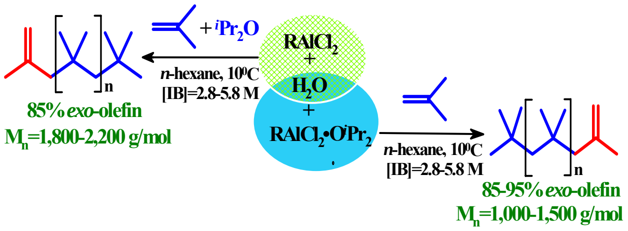
Complexes of alkylaluminum dichlorides with ethers as fully soluble in hydrocarbons catalysts for the synthesis of *exo*-olefin terminated polyisobutylene at room temperature

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



Highly reactive polyisobutylenes with desired low M_n were obtained with $RAlCl_2 \times O^{i}Pr_2$ initiating system at high monomer concentration and room temperature

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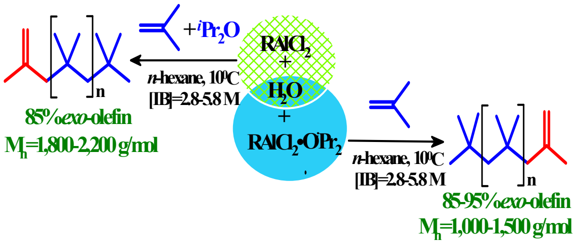

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