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Electronic Supplementary Information

New Catalysts for the Synthesis of Highly Reactive Polyisobutylene: Chloroaluminate Imidazole-Based Ionic Liquid in the Presence of Diisopropyl Ethers

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Content

Experimental Section

Materials. Isobutylene (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 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%), *tert*-butyl methyl ether (^tBuOMe, Sigma–Aldrich, 99.8%) were distilled over CaH_2 under argon while dibutyl ether (Bu_2O, Sigma–Aldrich, 99.3%) was distilled over CaH_2 at reduced pressure. 1-Ethyl-3-methylimidazolium chloride ([emim]Cl, Aldrich, ≥95%) was dried in vacuum during 5 h before use. [emim]Cl-$AlCl_3$ ($\chi(AlCl_3)=0.6$) was synthesized from 1-ethyl-3-methylimidazolium chloride and $AlCl_3$ by simple mixing of the components under argon atmosphere according to a procedure described in the literature.[1] $AlCl_3$ (Aldrich, 99.999%), Et_3Al (1 M solution in hexanes, Aldrich), $CDCl_3$ (Euriso-top®), ethanol (Sigma–Aldrich, >96%), tetrahydrofuran (anhydrous, Sigma-Aldrich, ≥99.9%) were used as received. The synthesis of $AlCl_3 \times OBu_2$ and $EtAlCl_2$ was performed according to the literature.[2,3]

Instrumentation. 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). ^1H NMR (500 MHz) spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AC-500 spectrometer calibrated relative to the residual solvent resonance. The ultrasonication of ionic liquid/*n*-hexane mixture was performed during 3 min at room temperature using Elmasonic S30H ultrasonic batch (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 –40 °C to 10 °C. As an example of a typical procedure, polymerization was initiated by adding of isobutylene (2.86 g, 5.1×10^{-2} mol)) to a mixture of a total volume 9.8 mL consisting of solutions of diisopropyl ether (0.11 mL, 1 M), [emim]Cl-$AlCl_3$ (0.056 mL) and *n*-hexane (4.9 mL). 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.

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1 (a) Wilkes, J. S.; Levisky, L. A.; Wilson, R. A.; Hussey, C. L. *Inorg.Chem.* **1982**, *21*, 1263. (b) Ambler, P.W.; Hodgson, P.K.G.; Stewart N.J. (BP Chem. Ltd) EP 0558187, **1993**

2 Vasilenko, I. V.; Frolov, A. N.; Kostjuk, S. V. *Macromolecules* **2010**, *43*, 5503.

3 Vasilenko, I. V.; Shiman. D. I.; Kostjuk, S. V. *Polym. Chem.* **2014**, *5*, 3855

Table S1. Polymerization of Isobutylene in *n*-Hexane Catalyzed by [emim]Cl-$AlCl_3$ ($\chi(AlCl_3)=0.6$) at Different Temperatures[a]

run	time (min)	temperature (°C)	conv. (%)	M_n (g/mol)	M_w/M_n	end groups distribution (%)			
						exo	tri+endo	tetra	PIBCl
1	30	0	100	1500	6.8[b]	2	74	24	0
2	30	–20	100	7000	3.8[b]	2	71	27	0
3[c]	30	–20	100	6000	5.9[b]	0	75	25	0
4	5	–40	46	25000	6.3[b]	0	75	25	0
5[d]	5	–40	42	-	-	4	72	24	0
6	30	–40	99	7600	6.7[b]	1	79	20	0

[a] [emim]Cl-$AlCl_3$=22 mM; [IB] = 5.2 M. [b] Bimodal or multimodal MWD. [c] Reproducibility check [d] [emim]Cl-$AlCl_3$=11 mM.

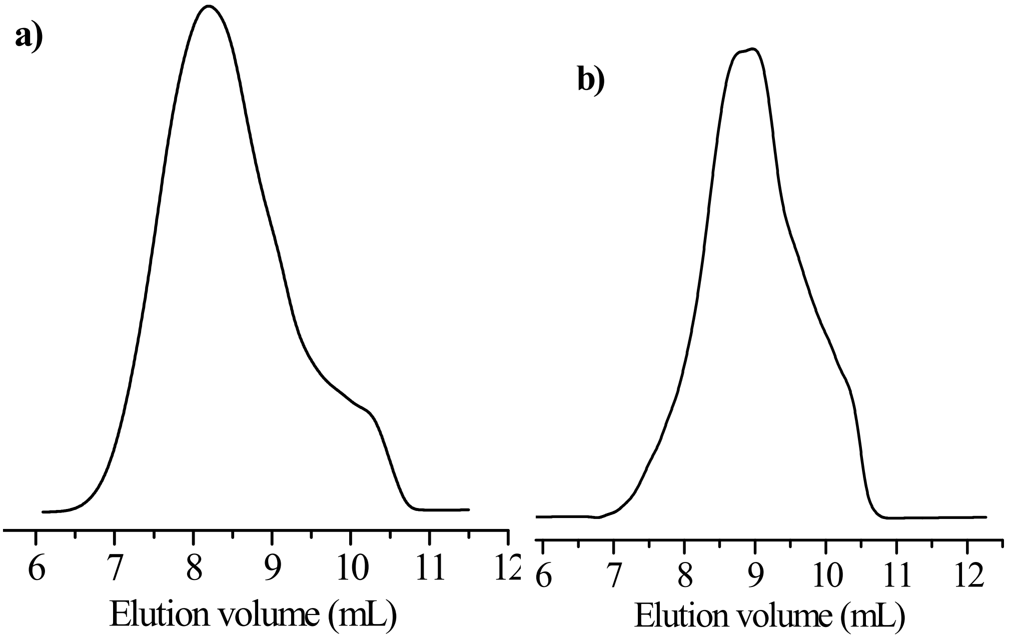

Figure S1. Typical SEC curves of polyisobutylenes synthesized during isobutylene polymerization with [emim]Cl-$AlCl_3$ as catalyst at different temperatures: [emim]Cl-$AlCl_3$=22 mM; [IB] = 5.2 M. Temperature: (**a**) –20 °C (run 3, Table S1) and (**b**) 0 °C (run 1, Table S1).

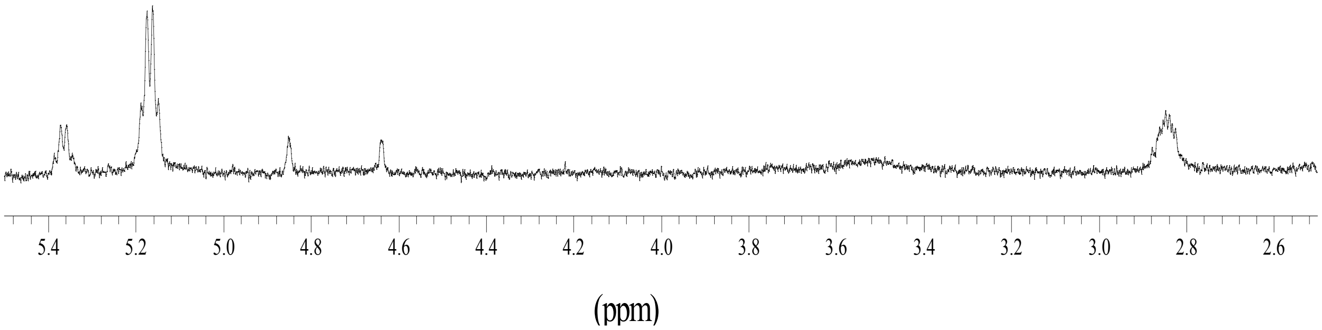

Figure S2. Fragment of ^1H NMR spectrum of polyisobutylene (run 1 in Table S1) synthesized during isobutylene polymerization with [emim]Cl-$AlCl_3$ as catalyst at 0 °C: [emim]Cl-$AlCl_3$=22 mM; [IB] = 5.2 M.

Table S2. Polymerization of IB in Hexane at 0°C for 30 min Catalyzed by [emim]Cl-AlCl$_3$ (χ(AlCl$_3$)=0.6) in the Presence of Diisopropyl Ether at the Different Monomer Concentrations [a]

run	[IB] (M)	conv (%)	M_n (g/mol)	M_w/M_n	$M_{n,NMR}$[b] (g/mol)	end groups distribution (%)			
						exo	tri+endo	tetra	PIBCl
1	1.3	25	2500	2.2	1760	46	40	11	3
2	2.6	40	3170	1.7	2200	87	6	5	2
3	5.2	51	3940	2.0	3340	92	4	3	1
4	7.8	24	7250	2.2	5340	91	4	4	1

[a] [emim]Cl-AlCl$_3$=22 mM; [^{i}Pr$_2$O] = 11 mM.; [b] M_n(NMR)=56.11×[(i/2)/((b+b')/2)+d+e+g+k/6], see Figure 1a.

Table S3. Polymerization of Isobutylene in *n*-Hexane at 0° C for 30 min Catalyzed by [emim]Cl-AlCl$_3$ (χ(AlCl$_3$)=0.6) in the Presence of Diisopropyl Ether at Different IL concentrations [a]

run	IL (mM)	[^{i}Pr$_2$O]/[IL]	conv (%)	M_n (g/mol)	M_w/M_n	$M_{n,NMR}$[b] (g/mol)	end groups distribution (%)			
							exo	tri+endo	tetra	PIBCl
1	11	1.00	28	4900	1.9	3520	95	2	1	2
2	22	0.50	51	3940	2.0	3340	92	4	3	1
3	33	0.35	62	6500	1.9	4510	89	4	4	3
4	44	0.25	74	4700	5.8	3170	49	24	26	1

[a] [IB] = 5.2 M. [b] Calculated based on the end groups content as M_n(NMR)=56.11×[(i/2)/((b+b')/2)+d+e+g+k/6], see Figure 1a.

Table S4. Polymerization of IB in *n*-Hexane at 0°C for 30 min Catalyzed by [emim][AlCl$_4$] (χ(AlCl$_3$)=0.6) in the Presence of Diisopropyl Ether and Different Initiators (H$_2$O, ^{t}BuCl, PhEtCl) [a]

run	initiator (mM)	conv (%)	M_n (g/mol)	M_w/M_n	$M_{n,NMR}$[b] (g/mol)	End groups distribution (%)			
						exo	tri+endo	tetra	PIBCl
1	H_2O (67 mM)	7	-	-	3400	95	1	1	3
2	^{t}BuCl (2.2mM)	47	6400	1.8	5300	0	80	20	0
3[c]	^{t}BuCl (2.2mM)	76	2900	2.2	1800	28	54	17	1
4[d]	PhEtCl (1.1 mM)	93	5400	2.7	2800	24	51	22	3
5[d,e]	PhEtCl (1.1 mM)	49	4200	2.3	3900	51	29	17	3

[a] [emim]Cl-AlCl$_3$=22 mM; [^{i}Pr$_2$O] = 11 mM. [IB]=5.2 M; PhEtCl: 1-chloro-1-phenylethane. Te sequence of components addition: *n*-hexane, [emim]Cl-AlCl$_3$, ^{i}Pr$_2$O, then monomer and initiator were injected simultaneously. [b] Calculated based on the end groups content as M_n(NMR)=56.11×[(i/2)/((b+b')/2)+d+e+g+k/6], see Figure 1a. [c] Ionic liquid was injected as the last component. [d] [emim]Cl-AlCl$_3$, χ(AlCl$_3$)=0.67; [e] [^{i}Pr$_2$O] = 17 mM.

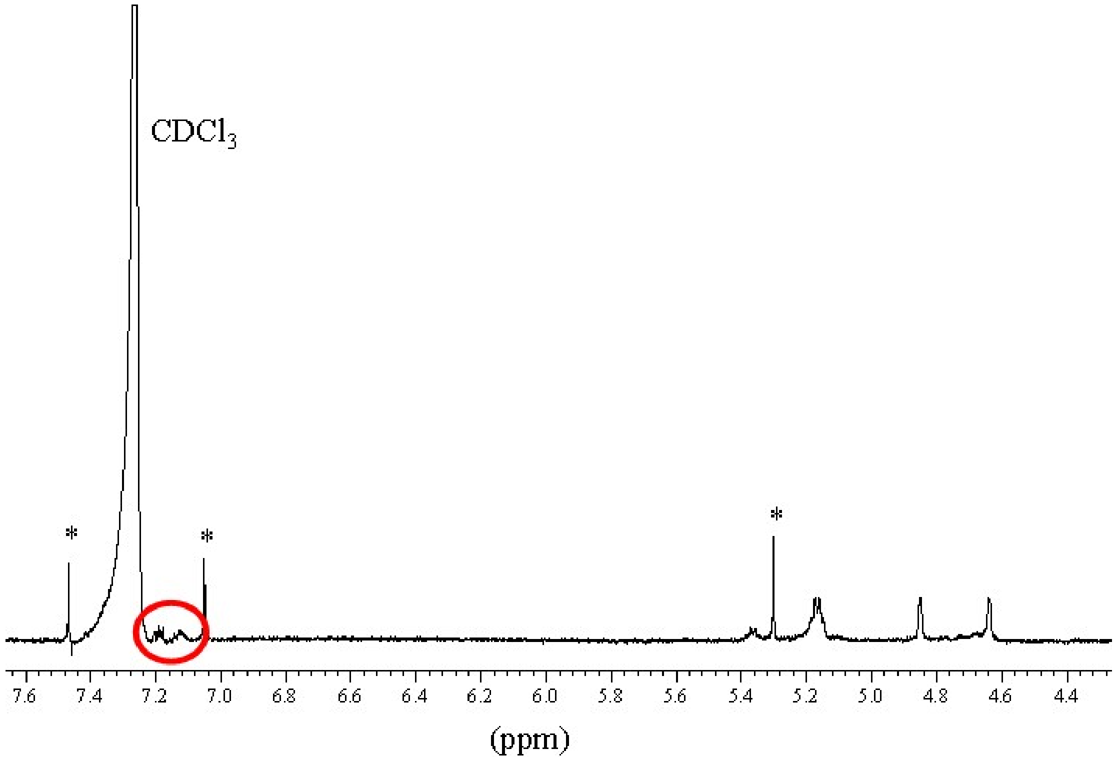

Figure S3. Fragment of ^{1}H NMR spectrum of polyisobutylene (run 4 in Table S4) synthesized during isobutylene polymerization with PhEtCl/[emim]Cl-AlCl$_3$ initiating system at 0 °C. ^{13}C satellites and traces of CH_2Cl_2 labeled by asterisks.