Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Cationic Polymerization of Isobutylene in Toluene: Toward Well-Defined *exo*-Olefin Terminated Medium Molecular Weight Polyisobutylenes under Mild Conditions

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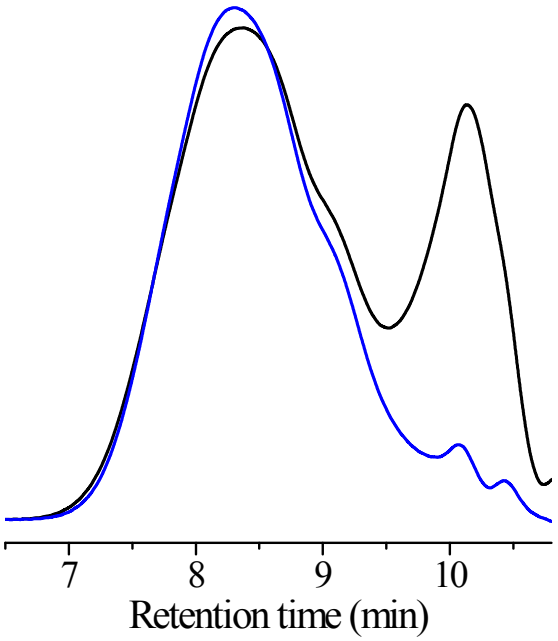

Figure S1. SEC traces for polyisobutylenes obtained by $^{i}BuAlCl_2$-co-initiated cationic polymerization of isobutylene in toluene at –20 °C before (black line) and after (blue line) re-precipitation of sample (run 3, Table 1) into ethanol.

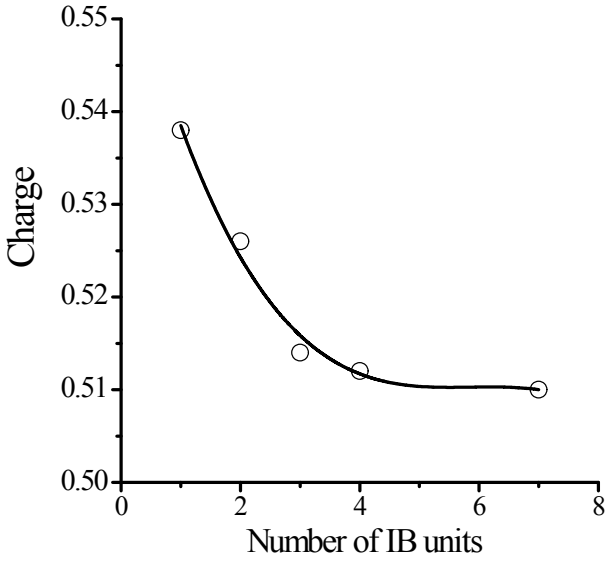

Figure S2. The dependence of NBO atomic charge on the number of isobutylene units in a polymer chain.

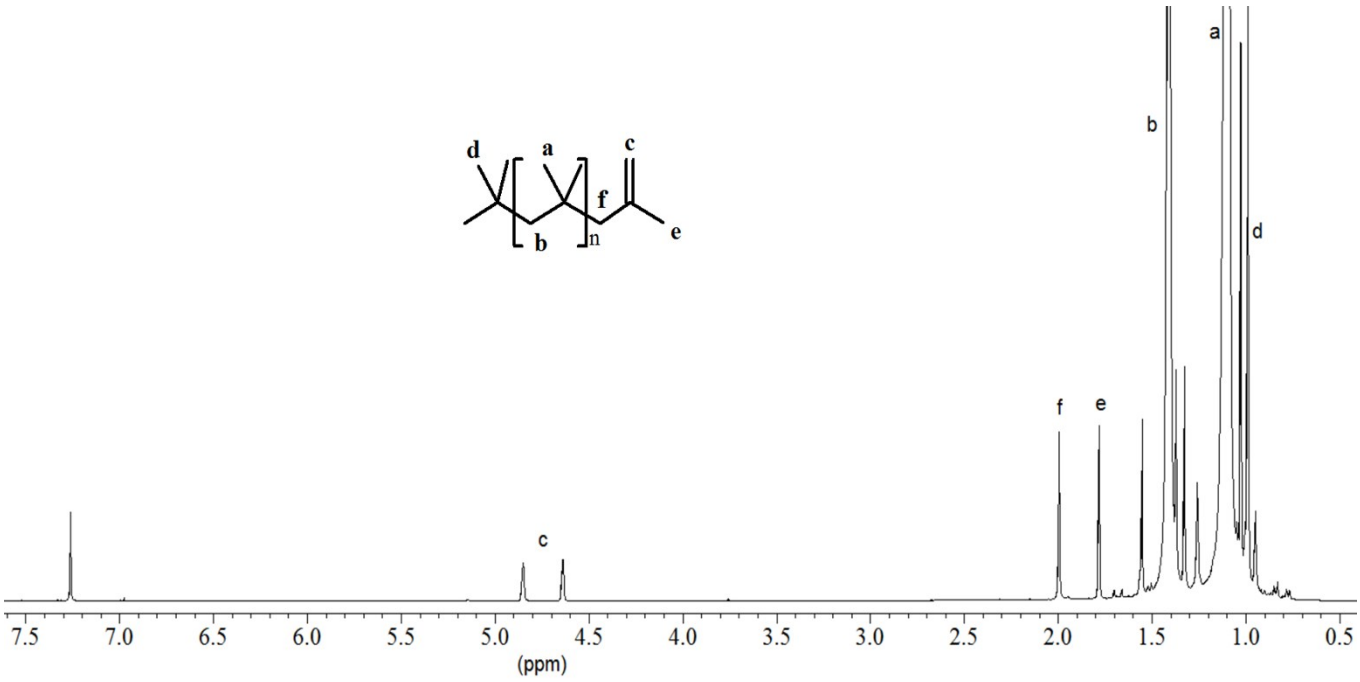

Figure S3. ^{1}H NMR spectrum of polyisobutylene synthesized with $^{i}BuAlCl_2$ in the presence of dibutyl ether in toluene at –20 °C (run 2, Table 3).

Table S1. Cationic Polymerization of IB Co-initiated by $^{i}BuAlCl_2$ Complexes with Dihexyl Ether in Toluene at –20 °C at Different $Hex_2O/iBuAlCl2$ ratios[a]

Run	Co-initiator	Conv. (%)	M_n(SEC) (g mol^{-1})	M_n(NMR) (g mol^{-1})	M_w/M_n	End groups distribution (mol%)		
						Exo	Endo+Tri	Tetra
1	$^{i}BuAlCl_2\times OHex_2$	17	940	780	2.1	96	4	0
2	$^{i}BuAlCl_2\times 0.9OHex_2$	31	2600	2400	2.4	96	4	0
3[b]	$^{i}BuAlCl_2\times 0.6OHex_2$	47	36100	37900	2.0	83	8	9

[a] Polymerization conditions: [IB] = 1 M; [$^{i}BuAlCl_2$] = 22 mM; toluene: 25 mL; reaction time: 30 min. [b] The content of chlorine end groups less than 1 %.

Table S2. Cationic Polymerization of IB Co-initiated by Complexes of $^{i}BuAlCl_2$ with Diisopropyl Ether in Toluene at –20 °C at Different $^{i}Pr_2O/^{i}BuAlCl_2$ Ratios [a]

Run	Co-initiator	Conv. (%)	M_n(SEC) (g mol^{-1})	M_n(NMR) (g mol^{-1})	M_w/M_n	End groups distribution (mol%)		
						Exo	Endo+Tri	Tetra
1	$^{i}BuAlCl_2\times0.9O^{i}Pr_2$	38	2200	2000	2.3	85	15	0
2	$^{i}BuAlCl_2\times0.8O^{i}Pr_2$	67	25000	26300	2.2	82	14	6
3	$^{i}BuAlCl_2\times0.6O^{i}Pr_2$	81	20200	21800	2.0	81	15	4

[a] Polymerization conditions: [IB] = 1 M; [$^{i}BuAlCl_2$] = 22 mM; toluene: 25 mL; reaction time: 30 min.

Table S3. Cationic Polymerization of IB Co-initiated by $^{i}BuAlCl_2$ in the Presence of *tert*-Butyl Methyl Ether in Toluene at –20 °C at Different $BuOMe/^{i}BuAlCl_2$ Ratios [a]

Run	Co-initiator	Conv. (%)	M_n(SEC) (g mol^{-1})	M_n(NMR) (g mol^{-1})	M_w/M_n	End groups distribution (mol%)		
						Exo	Endo+Tri	Tetra
1[b]	$^{i}BuAlCl_2\times0.8^{t}BuOMe$	109	6400	–	5.7	0	11[c]	89[c]
2	$^{i}BuAlCl_2\times^{t}BuOMe$	100	16400	16400	3.9	10	76	14
3[e]	$^{i}BuAlCl_2\times1.2^{t}BuOMe$	99	2900	2500	2.7	96	4	0
4[e]	$^{i}BuAlCl_2\times2^{t}BuOMe$	0.5	–	–	–	–	–	–

[a] Polymerization conditions: [IB] = 1 M; [$^{i}BuAlCl_2$] = 22 mM; toluene: 25 mL; reaction time: 30 min. [b] A fraction (41%) of short PIB chains terminated by toluene was detected. [c] For high molecular weight fraction [e] Reaction time: 10 min.

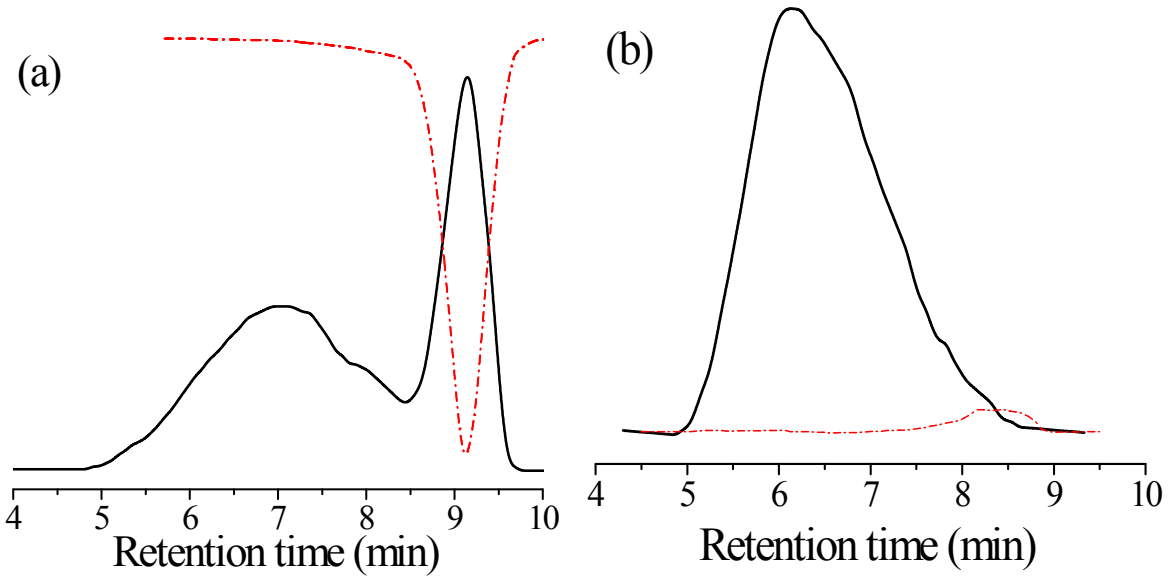

Figure S4. RI (solid line) and UV (dot line) SEC traces for polyisobutylenes obtained with $^{i}BuAlCl_2$ in the presence of *tert*-butyl methyl ether in toluene at –20 °C: (**a**) run 1, Table S3; (**b**) run 2, Table S3.

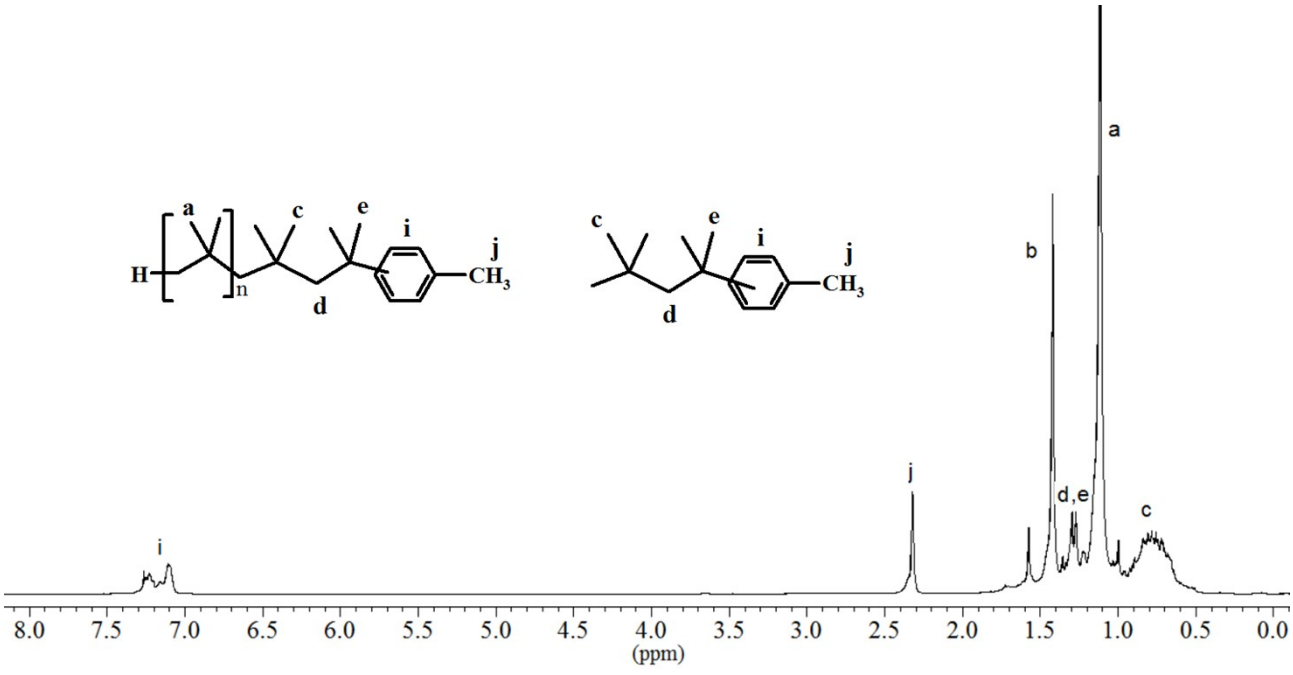

Figure S5. ^{1}H NMR spectrum of polyisobutylene synthesized with $^{i}BuAlCl_2$ in the presence of *tert*-butyl methyl ether in toluene at –20 °C (run 1, Table S3).