Electronic Supplementary Information

Quasiliving carbocationic polymerization of isobutylene using $FeCl_3$ as an efficient and water-tolerant Lewis acid: synthesis of well-defined telechelic polyisobutylenes

Mikalai Bohdan,[a,b] *Dmitriy I. Shiman,*[a, b] *Pavel A. Nikishau,*[a] *Irina V. Vasilenko*[a] *and Sergei V. Kostjuk**[a,b]

[a] Research Institute for Physical Chemical Problems of the Belarusian State University,

14 Leningradskaya st., 220030 Minsk, Belarus

[b]Department of Chemistry, Belarusian State University, Leningradskaya st. 14, 220006, Minsk, Belarus

Contents

EXPERIMENTAL SECTION

Synthesis of 2-Chloro-2-phenylpropan (cumyl chloride). Cumyl chloride was prepared via passing gaseous HCl through a solution of 5 g of α-methylstyrene (99%, Sigma–Aldrich) in 50 mL of CH_2Cl_2 at 0 ºC under stirring. Then the CH_2Cl_2 was evaporated and the cumyl chloride was distilled in vacuum (0.7 Torr) at 35 ºC. The purity of the prepared cumyl chloride was confirmed by ^{1}H NMR spectroscopy.

Synthesis of *exo*-olefin terminated polyisobutylene. The polymerization reaction was carried out in glass tubes under argon atmosphere at –80 ºC. As an example of the typical procedure, polymerization was initiated by addition solution of $FeCl_3 \times 1.4\ ^iPrOH$ in CH_2Cl_2 (1.0 mL, 0.22 M) to a mixture of total volume 11 mL consisting of dicumyl chloride (0.025g, 0.108 mmol), isobutylene (0.813 g, 1.20 mL, 14.5 mmol), *n*-hexane (6.5 mL) and CH_2Cl_2 (3.3 mL). After 3 min, 0.122 mL $^iPr_2O$ was added and reaction mixture was allowed to heated to the room temperature. After 30 min, the reaction was terminated by addition of 2 mL ethanol containing of 0.5%wt of NaOH. The quenched reaction mixture was diluted by *n*-hexane, centrifuged to remove the iron–containing residues, evaporated to dryness under reduced pressure, and dried in vacuum at 40 ºC to give the product polymers.

Preparation of LA×PhOH. The complexes of LA ($FeCl_3$ or $AlCl_3$) with PhOH were prepared under argon atmosphere in CH_2Cl_2 at 0 ºC. As an example of the typical procedure, 0.230 g of $FeCl_3$ or 0.189 g $AlCl_3$ (1.42·mmol) was air-tightly transferred into Schlenk flask, followed by addition of 9.1 mL of phenol solution in CH_2Cl_2 ([PhOH] = 2.55 M) under vigorous stirring. After 5 minutes, a transparent solution was obtained with [LA] = 0.155 M and [PhOH] = 2.55 M.

Synthesis of hydroxyl-terminated PIB (PIBOH). The polymerization and *in situ* functionalization was carried out in glass tubes under argon atmosphere at –80 ºC. As an example of the typical procedure, polymerization was initiated by addition of solution of $FeCl_3 \times 1.4\ ^iPrOH$ in CH_2Cl_2 (1.5 mL, 0.22 M) to a mixture of total volume 22.5 mL consisting of dicumyl chloride (50 mg, 0.216 mmol), isobutylene (1.63 g, 2.40 mL, 29.0 mmol), *n*-hexane (13 mL) and CH_2Cl_2 (7.1 mL). After 10 min, 6.8 mL of solution of LA×PhOH in CH_2Cl_2 was added and the reaction mixture was allowed to heated to room temperature. Samples of ca. 2 mL were taken at predetermined time intervals and precipitated into excess of ethanol. Then the resulting polymer was centrifuged, dissolved in hexane, and re-precipitated into ethanol. The functionalization of PIB was studied by ^1H NMR spectroscopy.

Computational Details. All calculations were performed with Gaussian 09 program[1] using the density functional theory (DFT) BP86[2] method. Optimizations were performed in conjunction with the def2-SVP[3] basis set. Single-point energy, frequency, and Natural bond orbital (NBO) calculations were performed using the def2-TZVP[3] basis set taking into account the highest multiplicity of iron-containing compounds[4]. The solvent effects in both steps were evaluated using the polarized continuum model (PCM)[5] with the default parameters for chloroform (ε = 4.7113). Despite the fact that the reaction was carried out in a mixture of *n*-hexane (ε = 1.8819) and dichloromethane (ε = 8.93) with 60:40 v/v, chloroform was selected for calculations because its ε value is close to the average ε of the specified mixture of solvents ($1.8819\times0.6 + 8.93\times0.4 = 4.7011$). Optimized structures were checked to be minima, with no imaginary frequencies. The Gibbs free energy for reaction at 193 K (or -80 °C, Δ_rG_{193}) was computed from the following equations:

$$\Delta_rG_{193} = \Delta_rH_{193} - T\Delta_rS_{193}$$

$$\Delta_rH_{193} = \Delta E_{\text{total}} + \Delta ZPE + \Delta(H_{193} - H_0)$$

where E_{total} is SCF single point electronic energy, ZPE is the zero-point vibrational energy, $(H_{193} - H_0)$ is the change in enthalpy due to changing the temperature from 0 to 193 K, and S is the entropy at 193 K. Typically, binding energy was calculated us Δ_rG_{193} for the reaction:

$$FeCl_3 + ROR' = FeCl_3{-}OR(R')$$

where R = ^{i}Pr, Bu; R' = H, ^{i}Pr.

Table S1. Effect of Catalyst Preparation on the Cationic Polymerization of IB with DiCumCl/$FeCl_3$×1.4^{i}PrOH Initiating System[a]

entry	Complex preparation	time (min)	conv. (%)	$M_{n,\text{ theor}}$[b] (g mol^{-1})	M_n (g mol^{-1})	Đ	end group distribution (%)		$F_n(\alpha)$[d]
							olefin[c]	PIBCl	
1	–[e]	2	0	–	–	–	–	–	–
2	–[e]	30	0	–	–	–	–	–	–
3[f]	–[e]	10	11	1120	800	2.1	67[g]	0	100
4	I	1	30	2340	2200	1.2	19	81	99
5	II	1	86	6710	7900	1.2	31	69	96
6	I	5	100	7800	10000	1.3	31	69	97
7	II	5	100	7800	9850	1.3	45	55	86

[a] Conditions: [IB] = 1.2 M; [DiCumCl] = 9mM; CH_2Cl_2/*n*-hexane 40: 60 (v/v); [$FeCl_3$×1.4iPrOH]=38 mM;. [b] $M_{n,\text{ theor}}$ = ([IB]/[DiCumCl]×56×Conv.+M_r(DiCumCl)). [c] Total olefinic end groups content including *exo*-, *endo*-olefin, *tri*-, *tetra*-substituted olefin end groups and coupled polymer chains determined by ^{1}H NMR spectroscopy (see Figure 1 for details). [d] Fraction of difunctional PIB calculated from ^{1}H NMR spectroscopy. [e] Neat $FeCl_3$ was used as co-initiator. [f] Polymerization was initiated by simultaneous addition of IB and DiCumCl solution in CH_2Cl_2 into the reactor containing $FeCl_3$, iPrOH and solvents (CH_2Cl_2/n-hexane). [g] Along with exo-olefin end group, the endo-olefin end group (33 mol%) was detected.

Catalytic complex preparation:

Complex I: $FeCl_3$×1.4^{i}PrOH was prepared in CH_2Cl_2 (0.22 M) at 0 °C and then heated to room temperature (20 °C – 25 °C) before use.

Complex 2: $FeCl_3$×1.4^{i}PrOH was prepared in CH_2Cl_2 (0.22 M) at 0 °C and then stored and used at 0 °C.

Table S2. Effect of Solvent on the Cationic Polymerization of Isobutylene with DiCumCl/$FeCl_3$×1.4^{i}PrOH Initiating System [a]

entry	Hex/ CH_2Cl_2	time (min)	conv (%)	$M_{n,\ theor}$^{b} (g mol^{-1})	M_n (g mol^{-1})	Đ	end group distribution (%)				$F_n(\alpha)^{c}$
							exo	endo +tri+ tetra	coup	PIBCl	
1	60/40	0.5	81	6300	7550	1.17	19	2	6	73	96
2	60/40	1.0	93	7250	8320	1.20	26	0	8	66	97
3	80/20	0.5	70	5450	5200	1.44	23	0	5	72	99
4	80/20	1.0	100	7800	7580	1.35	83	15	0	2	91
5	90/10	2.0	83	6500	6740	1.74	80	11	0	9	90
6	98/2	0.5	36	2800	7850	2.39	39	11	0	50	77
7	98/2	1.0	46	3600	7870	2.35	69	13	5	13	77

[a] Conditions: [IB] = 1.2 M; [DiCumCl]= 9mM; [$FeCl_3$×1.4iPrOH]=38 mM; T: –80 ºC; [b]$M_{n,\ theor}$ = ([IB]/[DiCumCl]×56×Conv.+M_r(DiCumCl)). [c] Fraction of difunctional PIB calculated from ^{1}H NMR spectroscopy.

Table S3. Effect of Temperature on the Cationic Polymerization of Isobutylene with DiCumCl/$FeCl_3$×1.4^{i}PrOH Initiating System [a]

entry	T (°C)	time (min)	conv. (%)	$M_{n,\ theor}$^{b} (g mol^{-1})	M_n (g mol^{-1})	Đ	end group distribution (%)				$F_n(\alpha)^{c}$
							exo	endo +tri+ tetra	coup	PIBCl	
1	–80	1	78	6100	6580	1.14	2	1	0	97	100
2	–80	3	97	7600	8320	1.14	7	0	6	86	98
3	–60	1	64	5000	4740	1.20	19	0	2	79	98
4	–60	3	71	5550	5870	1.27	73	9	2	16	97
5	–60	5	97	7600	8510	1.38	89	2	6	3	88
6	–40	1	38	2950	2850	1.40	85	8	2	5	87
7	–40	3	86	6700	3100	1.96	92	2	2	3	42
8	–20	3	55	4300	1350	1.84	89	3	5	3	22

[a] Conditions: [IB] = 1.2 M; [DiCumCl]=9mM; [$FeCl_3$×1.4iPrOH]=19 mM; CH_2Cl_2/*n*-hexane 40:60 v/v; [b]$M_{n,\ theor}$ = ([IB]/[DiCumCl]×56×Conv.+M_r(DiCumCl)). [c] Fraction of difunctional PIB calculated from ^{1}H NMR spectroscopy

Table S4. Cationic Polymerization of Isobutylene with DiCumCl/$FeCl_3$×1.4^{i}PrOH Initiating System at Different Monomer to Initiator Ratios at – 60 °C [a]

entry	I^b (mM)	$FeCl_3$ (mM)	time (min)	conv. (%)	$M_{n, theor}$[c] (g mol^{-1})	M_n (g mol^{-1})	Đ	end group distribution (%)		$F_n(\alpha)$[e]
								olefin[d]	PIBCl	
1	4.5	9.5	15	58	8660	7560	1.23	14	86	97
2	4.5	9.5	30	87	12960	12370	1.27	56	45	94
3	9	19	5	97	7560	8510	1.38	97	3	88
4[e]	9	19	5	0	-	-	-	-	-	-
5	9	19	3	71	5540	5870	1.27	84	16	97
6	18	38	2	100	3730	4760	1.42	99	1	83

[a] Conditions: [IB] = 1.2 M; CH_2Cl_2/*n*-hexane 40:60 v/v. [b] I: DiCumCl. [c] $M_{n, theor}$ = ([IB]/[DiCumCl]×56×Conv.+M_r(DiCumCl)). [d] Total olefinic end groups content including *exo*-, *endo*-olefin, *tri*-, *tetra*-substituted olefin end groups and coupled polymer chains determined by ^1H NMR spectroscopy (see Figure 1 for details). [e] Fraction of difunctional PIB calculated from ^1H NMR spectroscopy. [e] 1.4-Lutidine (Lu, 1.5 mM) was added to the reaction mixture.

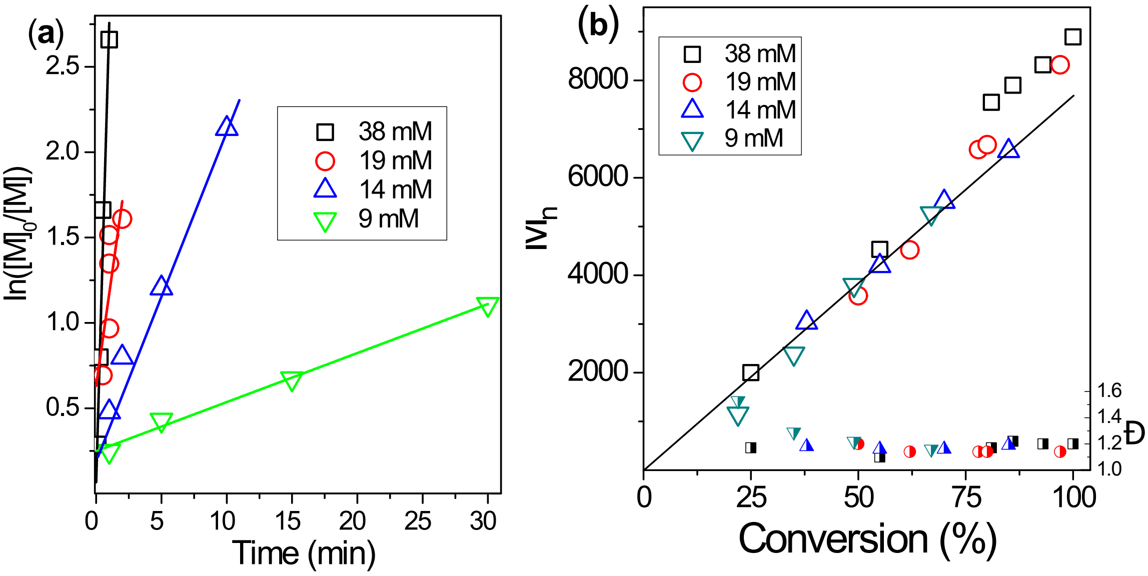


Figure S1. (**a**) First-order plots and (**b**) M_n, Đ vs. conversion plots for the cationic polymerization of isobutylene with DiCumCl/$FeCl_3$×1.4iPrOH initiating system in CH_2Cl_2/*n*-hexane at –80 ºC and at different co-initiator concentrations: [IB] = 1.2 M; [DiCumCl]=9 mM.

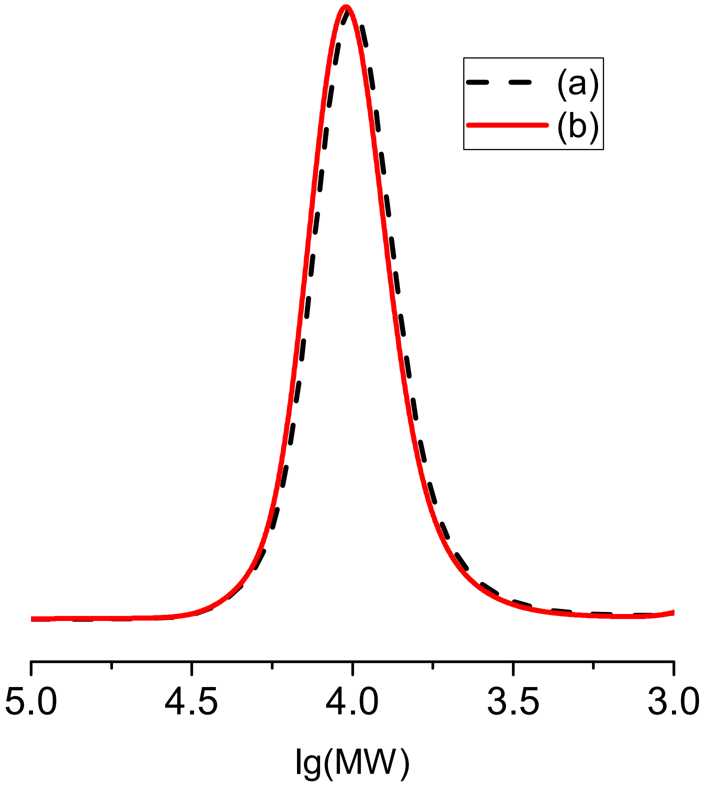


Figure S2. SEC traces of polyisobutylene (**a**) before and (**b**) after end-quenching by $^{i}Pr_2O$ (entries 1 and 3 in Table 2).

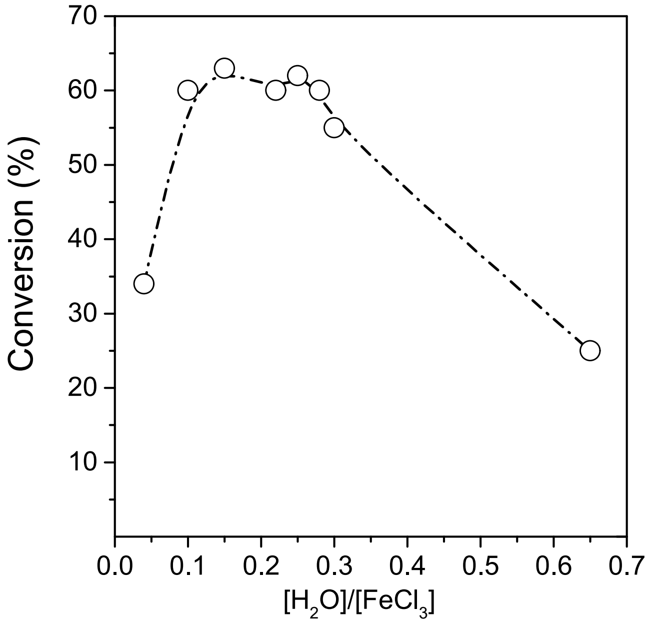


Figure S3. Conversion vs [H_2O]/[$FeCl_3$] dependence for the cationic polymerization of isobutylene with DiCumCl/$FeCl_3$×1.4iPrOH initiating system in CH_2Cl_2/*n*-hexane at –80 ºC: [IB] = 1.2 M; [DiCumCl]=9 mM; [$FeCl_3$×1.4^{i}PrOH]=14 mM. Reaction time: 2 min.

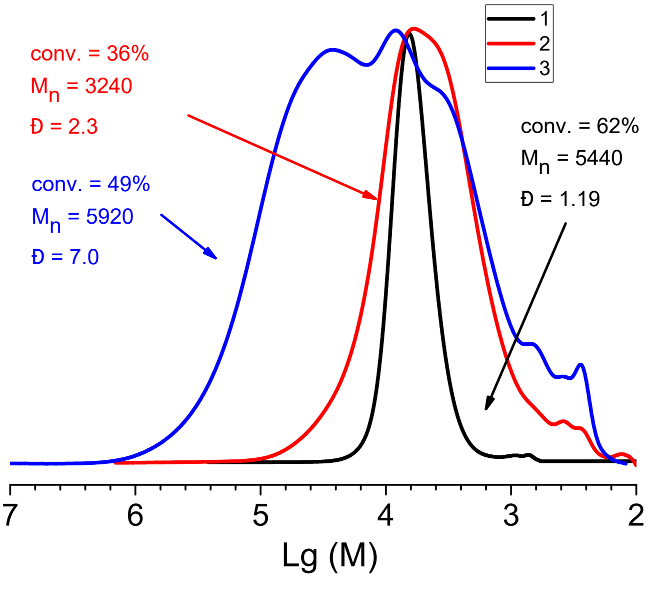


Figure S4. SEC curves of polyisobutylenes synthesized with DiCumCl/LA (LA= $FeCl_3$×1.4^{i}PrOH or $TiCl_4$) initiating systems in CH_2Cl_2/*n*-hexane mixture 40:60 v/v at –80 °C at 10 mol% H_2O to Lewis acid: [IB] = 1.2 M; [DiCumCl]=9 mM; [LA]=14 mM. Lewis acid: $FeCl_3$×1.4^{i}PrOH (**1**) (entry 2, Table 3); $TiCl_4$ in the presence of Lu (**2**) (entry 4, Table 3) and $TiCl_4$ (**3**) (entry 3, Table 3).

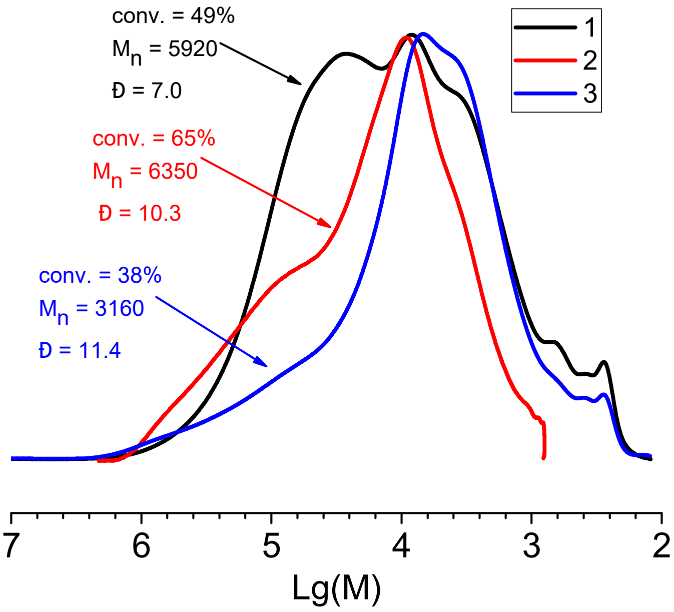


Figure S5. SEC curves of polyisobutylenes synthesized with DiCumCl/$TiCl_4$ initiating system in CH_2Cl_2/*n*-hexane mixture 40:60 v/v at –80 °C at different concentration of H_2O: [IB] = 1.2 M; [DiCumCl]=9 mM; [LA]=14 mM. Concentration of H_2O: 10 mol% to $TiCl_4$ (**1**) (entry 3, Table 3); 25 mol% to $TiCl_4$ (entry 7, Table 3); 65 mol% to $TiCl_4$ (entry 9, Table 3).

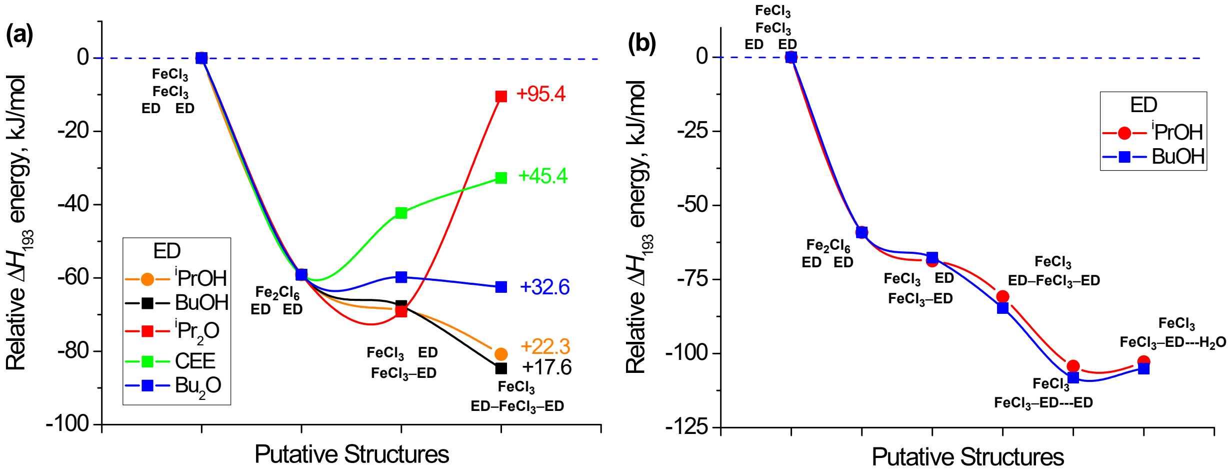
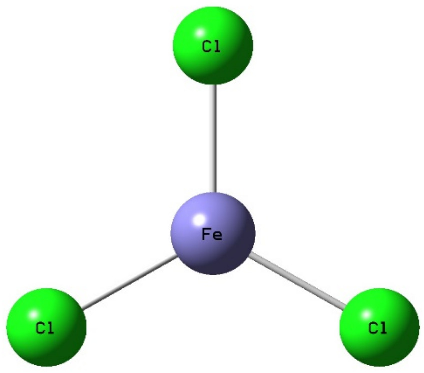


Figure S6. Relative energies ($\Delta_r H_{193}$) and formulas of the structures for the $FeCl_3$-complexes formation reactions. The numbers are $\Delta_r G_{193}$ of the formation reaction of $FeCl_3$×2ROR' complexes (in kJ/mol).

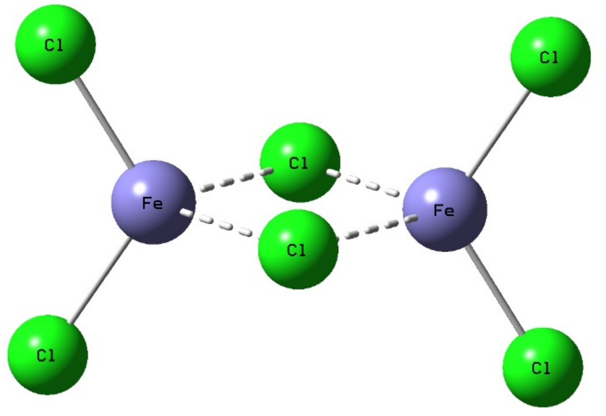
Table S5. Cationic Polymerization of Isobutylene with DiCumCl/$FeCl_3 \times 1.4ROH$ (R=^{i}Pr or Bu) Initiating System at – 80 °C [a]

entry	ROH	$FeCl_3$ (mM)	conv. (%)	M_n (g mol^{-1})	Đ	end group distribution (%)				$F_n(\alpha)$[b]
						exo	endo +tri+ tetra	coup	PIBCl	
1	^{i}PrOH	19	78	6580	1.14	2	0	1	97	100
2	BuOH	19	100	9060	1.30	29	0	1	70	99
3	^{i}PrOH	14	38	3030	1.18	2	0	1	97	100
4	BuOH	14	100	8650	1.20	18	0	1	81	98
5	^{i}PrOH	9	22	1160	1.53	0	0	0	100	100
6	BuOH	9	27	2110	1.40	2	0	0	98	98

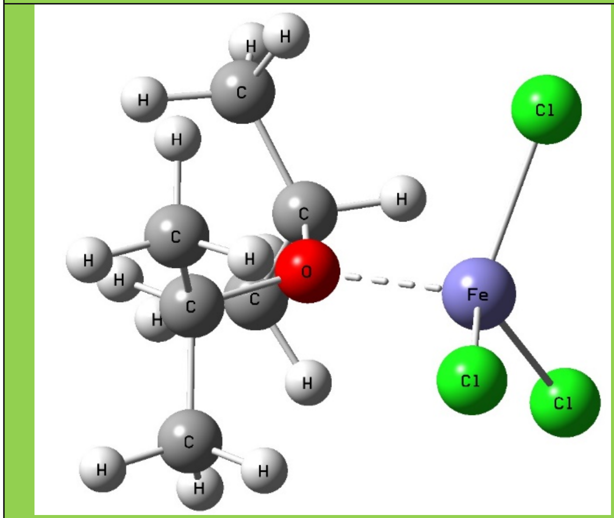
[a] Conditions: [IB] = 1.2 M; [DiCumCl]=9mM; time: 1 min; CH_2Cl_2/*n*-hexane 40:60 v/v; [b] Fraction of difunctional PIB calculated from ^{1}H NMR spectroscopy



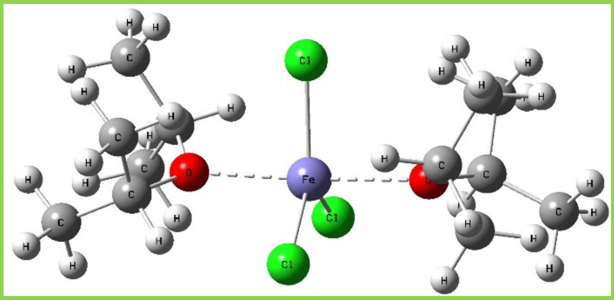
$FeCl_3$



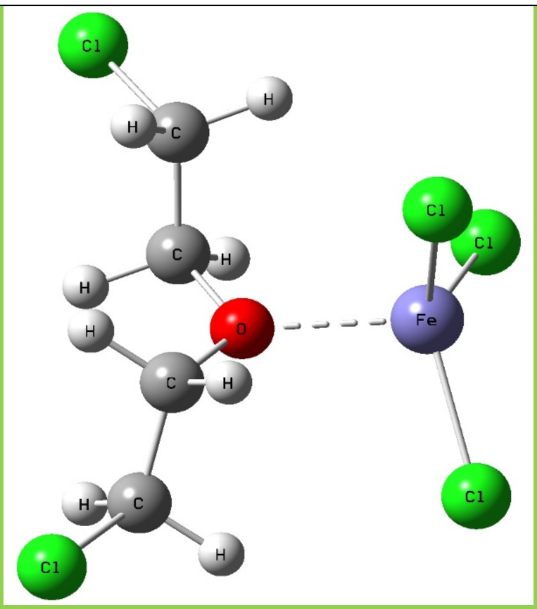
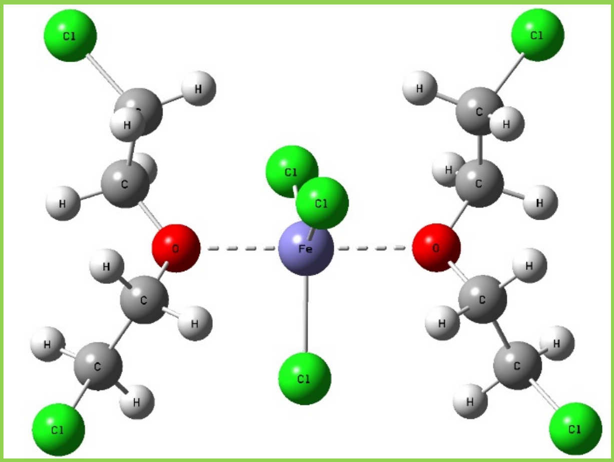
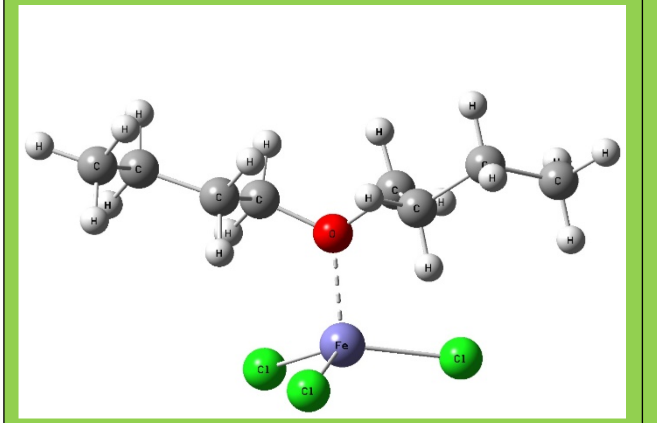
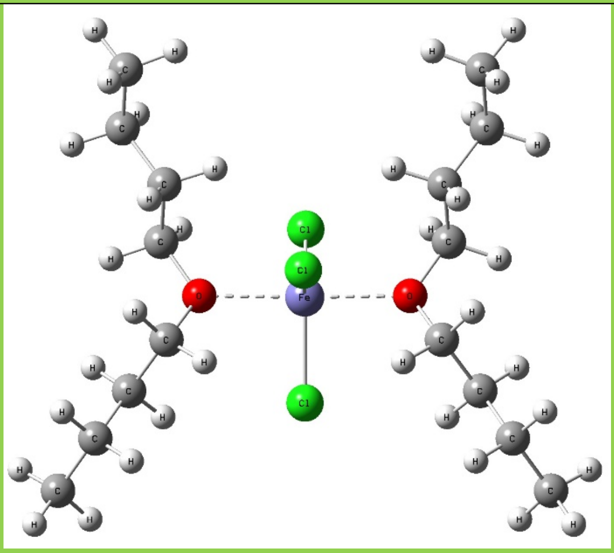
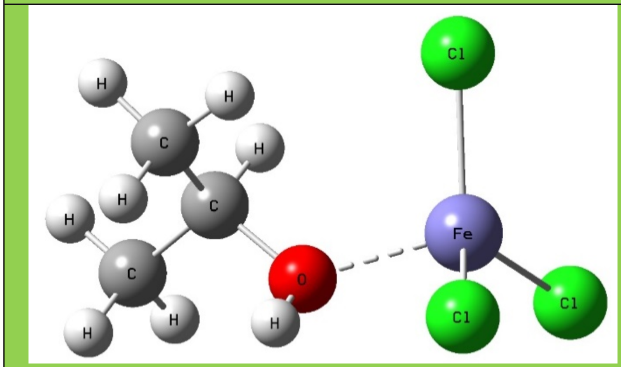
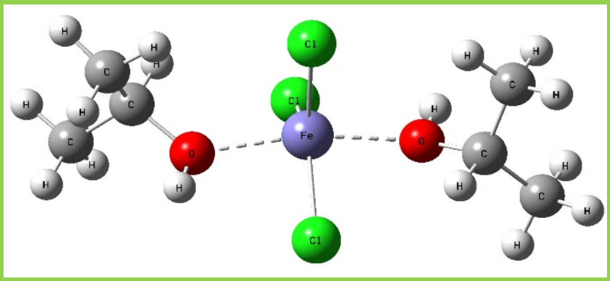
Fe_2Cl_6

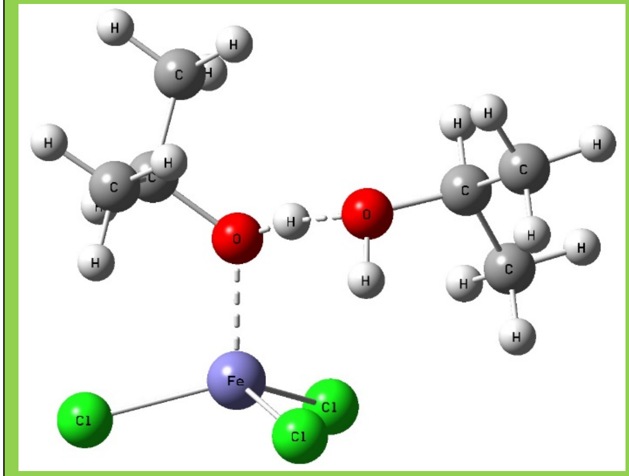


$FeCl_3$– ^{i}Pr_2O

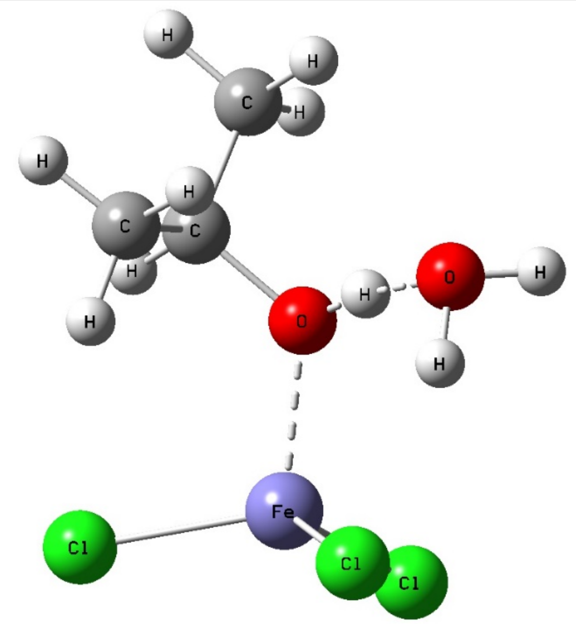


$FeCl_3$– 2^iPr_2O

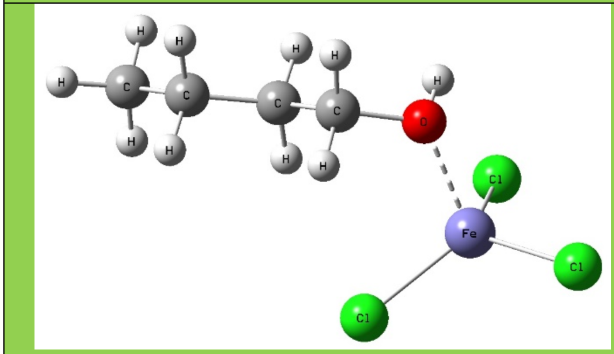
 $FeCl_3$– CEE	 $FeCl_3$– 2CEE
 $FeCl_3$– Bu_2O	 $FeCl_3$– $2Bu_2O$
 $FeCl_3$– $^{i}PrOH$	 $FeCl_3$– $2^{i}PrOH$



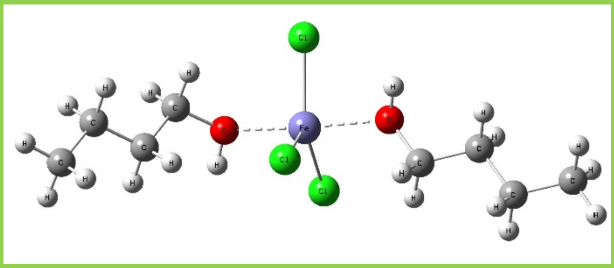
$FeCl_3$– 2^{i}PrOH (HB)



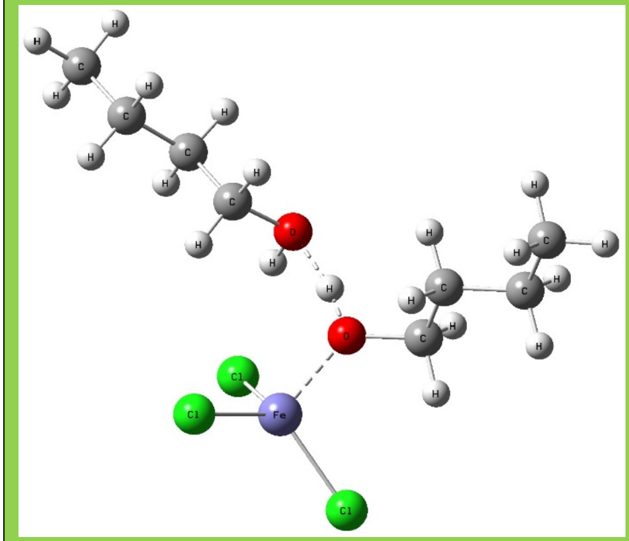
$FeCl_3$– ^{i}PrOH– H_2O (HB)



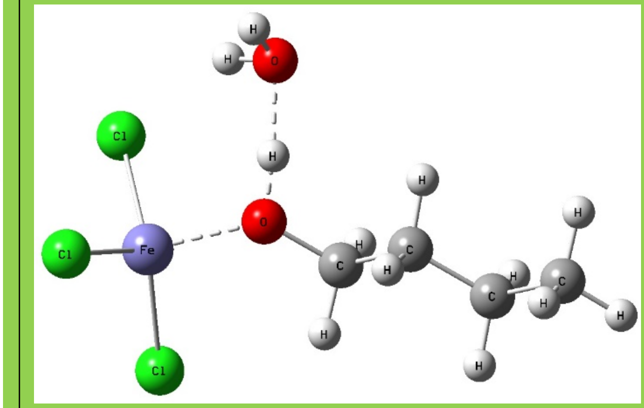
$FeCl_3$– BuOH



$FeCl_3$– 2BuOH



$FeCl_3$– 2BuOH (HB)



$FeCl_3$– BuOH– H_2O (HB)

Figure S7. Geometric representation of optimized structures at BP86/def2-SVP level of theory. HB = hydrogen bond.

Table S6. Average NBO Charges on atoms in different molecules and complexes (HB = hydrogen bond)

Structure	Fe	Cl(Fe)	O	H	O(HB)
$FeCl_3$	0.830	-0.276	-	-	-
Fe_2Cl_6	0.514	-0.171	-	-	-
$^{i}Pr_2O$	-	-	-0.512	-	-
CEE	-	-	-0.482	-	-
$^{i}PrOH$	-	-	-0.707	0.465	-
BuOH	-	-	-0.702	0.468	-
Bu_2O	-	-	-0.490	-	-
H_2O	-	-	-0.932	0.466	-
$FeCl_3$–$^{i}Pr_2O$	0.551	-0.276	-0.491	-	-
$FeCl_3$–CEE	0.578	-0.262	-0.474	-	-
$FeCl_3$–$^{i}PrOH$	0.584	-0.273	-0.659	0.519	-
$FeCl_3$–BuOH	0.588	-0.273	-0.645	0.520	-
$FeCl_3$–Bu_2O	0.574	-0.274	-0.469	-	-
$FeCl_3$–2$^{i}PrOH$	0.567	-0.316	-0.664	0.512	-
$FeCl_3$–2$^{i}PrOH$ (HB)	0.611	-0.298	-0.670	0.509	-0.714
$FeCl_3$–2BuOH	0.546	-0.309	-0.648	0.511	-
$FeCl_3$–2BuOH (HB)	0.614	-0.298	-0.662	0.506	-0.698
$FeCl_3$–2$^{i}Pr_2O$	0.546	-0.298	-0.498	-	-
$FeCl_3$–2CEE	0.512	-0.275	-0.474	-	-
$FeCl_3$–2Bu_2O	0.543	-0.305	-0.474	-	-
$FeCl_3$–$^{i}PrOH$–H_2O	0.613	-0.295	-0.669	0.507	-0.913
$FeCl_3$–Bu_2O–H_2O	0.615	-0.295	-0.659	0.507	-0.909

Table S7. One-Step Alkylation of Phenol by Living PIB Synthesized with CumCl/$FeCl_3$×1.4^iPrOH Initiating System

Entry	Total ratio [living chain]/[PhOH]/[LA]	M_n(SEC) (g/mol)	M_w/M_n	End group distribution (%)			$F_n(\alpha)^a$
				PIBCl	olefin	alkylated	
1	1/0/0.27	1130	1.28	95	5	-	100
2	1/10/0.27	1550	1.20	3	65	32	100
3	1/10/1.3	1890	1.25	0	30	70	100

Polymerization step: T: – 80 ºC; [IB]=1.2 M; [$FeCl_3$×1.4^iPrOH]=18 mM; [CumCl]=67 mM; CH_2Cl_2/*n*-hexane 40:60 v/v; M_n(theor)=1000 g mol^{-1}; time: 2 min. [a] Fraction of PIB chains containing fragment of initiator calculated from ^1H NMR spectroscopy. Alkylation step: T: – 70 ºC; [PIB]/[PhOH]=1:10. time: 5 h. Phenol (5 M solution in CH_2Cl_2) and $FeCl_3$×1.4^iPrOH were added to the system that leads to solidification of the system followed by the dilution of reaction mixture by CH_2Cl_2.

Table S8. One-Step Alkylation of Phenol by Living PIB Synthesized with DiCum/$FeCl_3$×1.4^iPrOH Initiating System [a]

Entry	[PIB]/[PhOH]	Time (h)	End group distribution (%)			$F_n(\alpha)^a$
			PIBCl	olefin	alkylated	
1	-	-	70	30	-	100
2	1:10	2	0	87	13	98
3	1:10	4	0	90	10	89
4	1:10	120	0	86	14	93
5	1:20	2	0	57	43	99
6	1:20	5	0	27	73	99
7	1:40	1	0	31	69	100
8	1:40	2	0	13	87	100
9	1:40	2.5	0	0	100	100
10[b]	1:40	1	0	0	100	100

Polymerization: T = –80 ºC; [IB]=1.2 M; [$FeCl_3$×1.4^iPrOH]=18 mM; [DiCumCl] = 9 mM, CH_2Cl_2/hex 40:60 v/v; time: 2 min. Alkylation: solution of $AlCl_3$/PhOH in CH_2Cl_2 ([PhOH]=2.55 M; [$AlCl_3$] = 0.155 M) was added to the system, the alkylation conducted at room temperature.

[b] Alkylation: solution of $FeCl_3$/PhOH in CH_2Cl_2 ([PhOH]=2.55 M; [$FeCl_3$] = 0.155 M) was added to the system.

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