Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of highly reactive polyisobutylene by catalytic chain transfer in hexanes at elevated temperatures; Determination of the kinetic parameters

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Table S1 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 0 °C with [CEE]/[EADC] = 1.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
2	16	5100			70	18	12
5	46	4500	4800	2.4	69	17	14
10	75	3100	3300	2.6	67	18	15
20	100	2700	2500	3.4	67	20	13
60	100	2500	2300	3.1	66	20	14

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S2 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 10 °C with [CEE]/[EADC] = 1.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	14	3400	3700	2.4	65	21	15
2	38	3000	2900	2.3	66	21	13
3	60	2700	2800	2.5	60	20	20
4	83	2400	2600	2.6	62	24	14
5	100	1900	2000	2.8	62	23	15

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S3 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 15 °C with [CEE]/[EADC] = 1.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	16	3000	3300	2.7	57	23	20
2	40	2400	2600	2.8	58	22	20
3	77	2000	2300	3.1	55	26	19
4	91	1600	1800	2.6	55	28	17
5	100	1400	1600	2.8	52	30	18

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S4 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 20 °C with [CEE]/[EADC] = 1.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	06	3600			63	22	15
2	15	3100	3000	2.8	60	20	18
3	36	2400	2600	2.7	58	23	20
4	52	2200	2400	3.0	55	25	20
5	70	1900	1800	3.1	52	26	22

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S5 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 0 °C with [CEE]/[EADC] = 1.25.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
2	14	3400	3600	3.1	77	12	11
5	38	2800	2700	2.8	76	12	12
10	64	2400	2600	3.0	78	12	11
20	89	1800	2000	3.2	80	11	09
30	100	1500	1700	3.3	81	10	09

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S6 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 10 °C with [CEE]/[EADC] = 1.25.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	07	2100			73	13	14
2	10	1900	2100	2.7	74	15	11
3	16	1700	2000	2.6	78	12	11
4	25	1600	1700	2.7	77	12	11
5	47	1400	1600	3.1	80	10	10
10	92	1100	1300	2.9	80	11	09

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

Table S7 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 15 °C with [CEE]/[EADC] = 1.25.

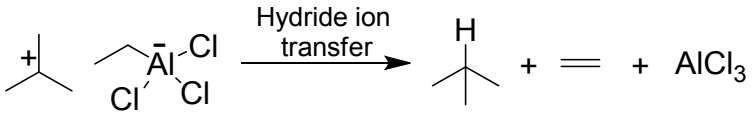
Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	07	2300			74	14	12
2	18	1900	2100	2.8	72	16	12
3	29	1600	1800	2.8	76	13	11
4	38	1500	1700	3.0	80	11	09
5	54	1300	1500	2.9	74	14	12
8	87	1100	1300	3.1	74	14	12
10	100	1000	1200	2.9	75	15	10

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.

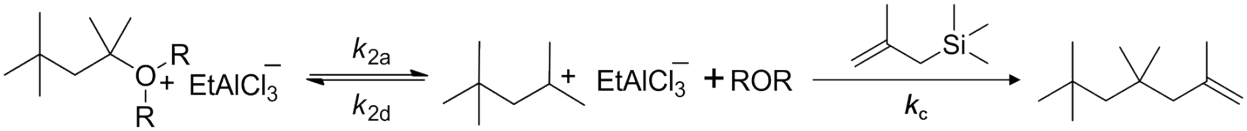
Table S8 Polymerization of IB ([IB] = 1.0 M) using [EADC•CEE] = 0.01 M, and [*t*-BuCl] = 0.01 M in dry hexanes at 20 °C with [CEE]/[EADC] = 1.25.

Time (min)	Conv[a] (%)	$M_{n,NMR}$[b] (g/mol)	$M_{n,SEC}$[c] (g/mol)	PDI[c]	Exo[d] (%)	Tri+ Endo[d] (%)	Tetra[d] (%)
1	05						
2	08						
3	14	2100	2200	2.9	77	11	12
4	20	2000	2100	2.8	79	11	10
5	23	1900	2000	3.1	78	12	10
8	38	1800	1600	3.0	77	12	11
10	49	1600	1400	3.2	75	13	12

[a]Determined gravimetrically based on monomer feed; [b]Determined from NMR analysis; [c]Obtained from SEC measurements; [d]Calculated from ^{1}H NMR spectroscopic study.



Scheme S1 Schematic representation of the hydride ion transfer reaction.



Scheme S2 Schematic representation of the model reactions between carbenium ion (TMP^+) and MATMS.

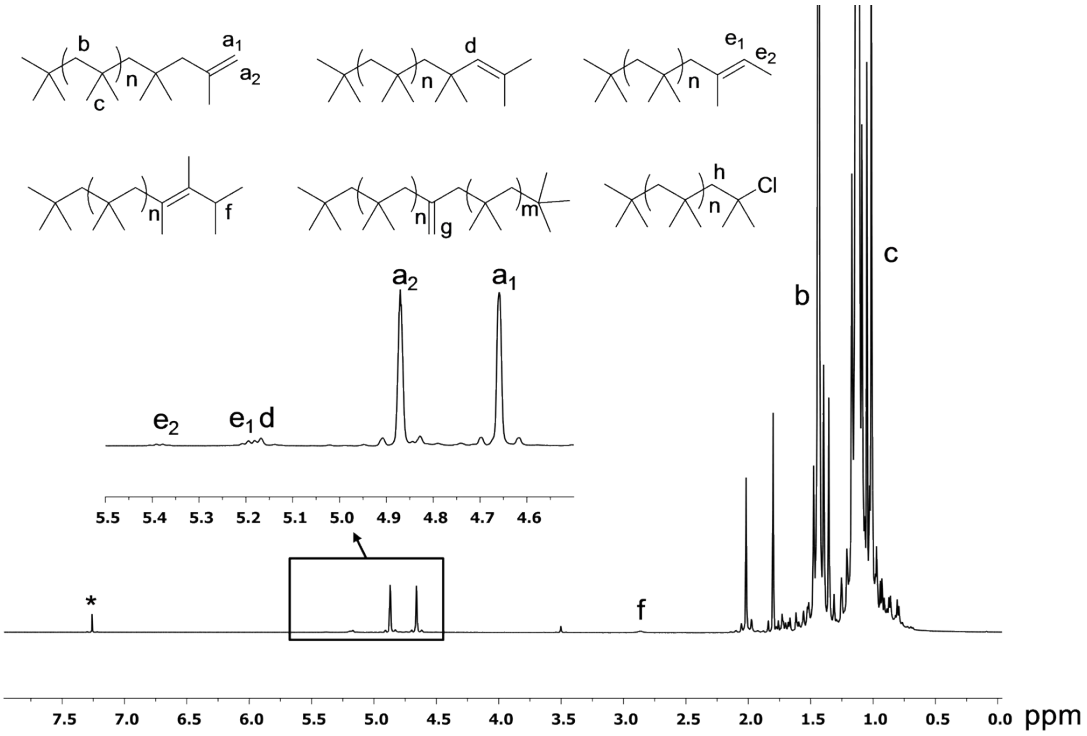


Fig. S1 Typical ^{1}H NMR spectrum of HR PIB obtained in this study. The asterisk represents the $CHCl_3$ resonance.

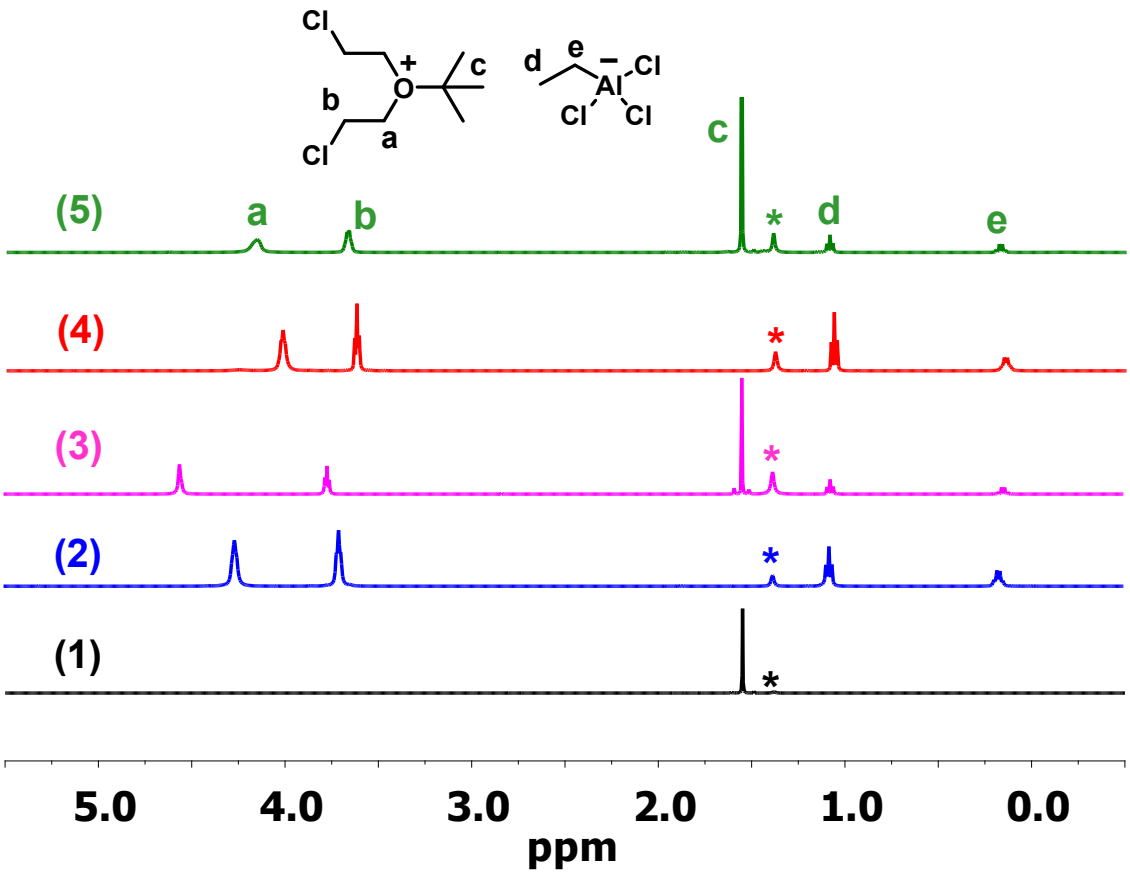


Fig. S2 ^{1}H NMR spectra of 1: [*t*-BuCl]. 2: [EADC·CEE] with [CEE]/[EADC] = 1. 3: [EADC·CEE + *t*-BuCl] with [CEE]/[EADC] = 1. 4: [EADC·CEE] with [CEE]/[EADC] = 1.5. 5: [EADC·CEE + *t*-BuCl] with [CEE]/[EADC] = 1.5 at 10 °C in cyclohexane-d_{12}. The asterisk denotes the cyclohexane-d_{11}H resonance.

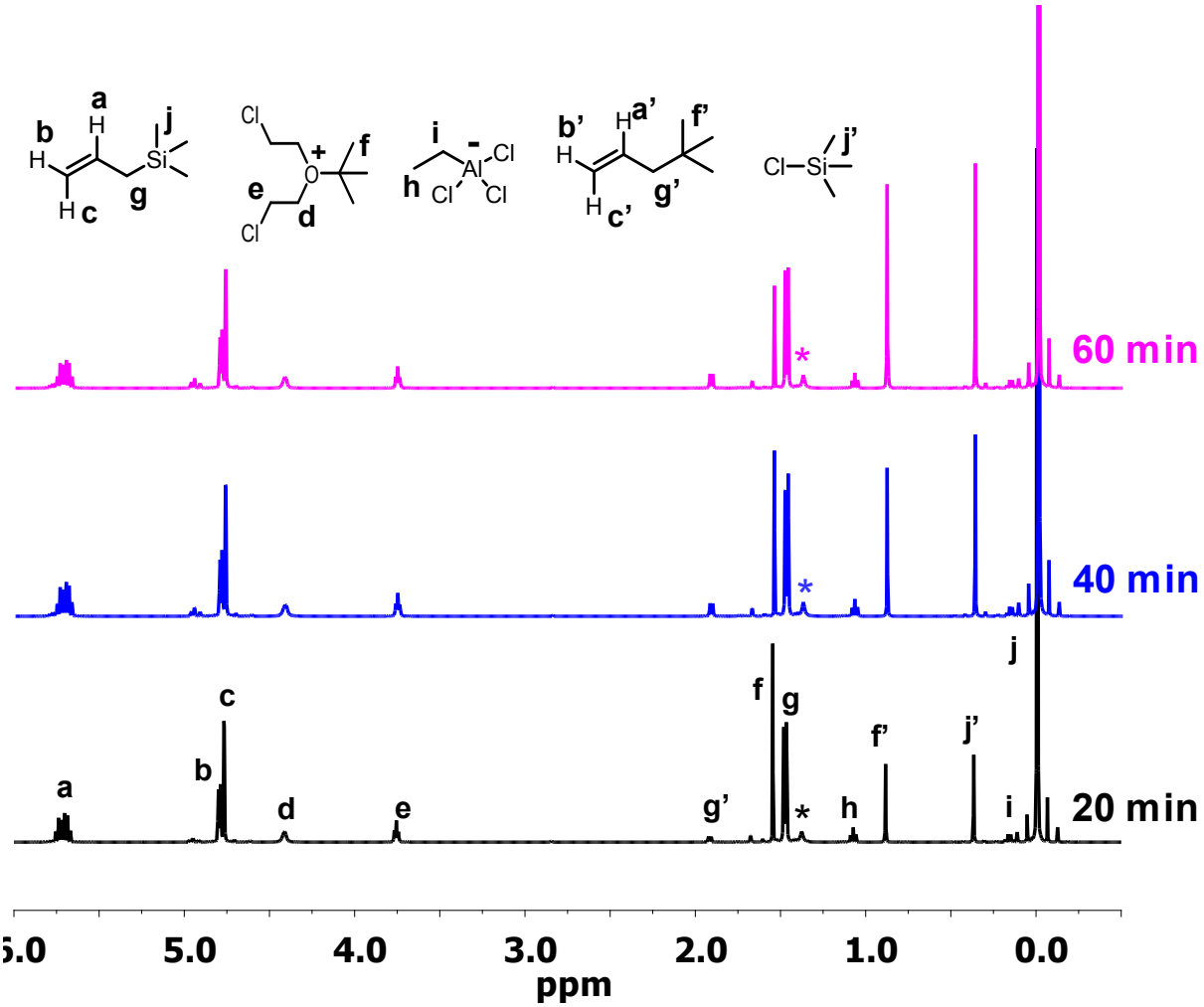


Fig. S3 ^{1}H NMR spectra of [EADC•CEE + *t*-BuCl] in the presence of ATMS at different times at 0 ^{o}C in cyclohexane-d_{12}. [EADC•CEE + *t*-BuCl] = 0.05 M with [CEE]/[EADC] = 1, and [ATMS] = 0.75 M. The asterisk denotes the cyclohexane-d_{11}H resonance.

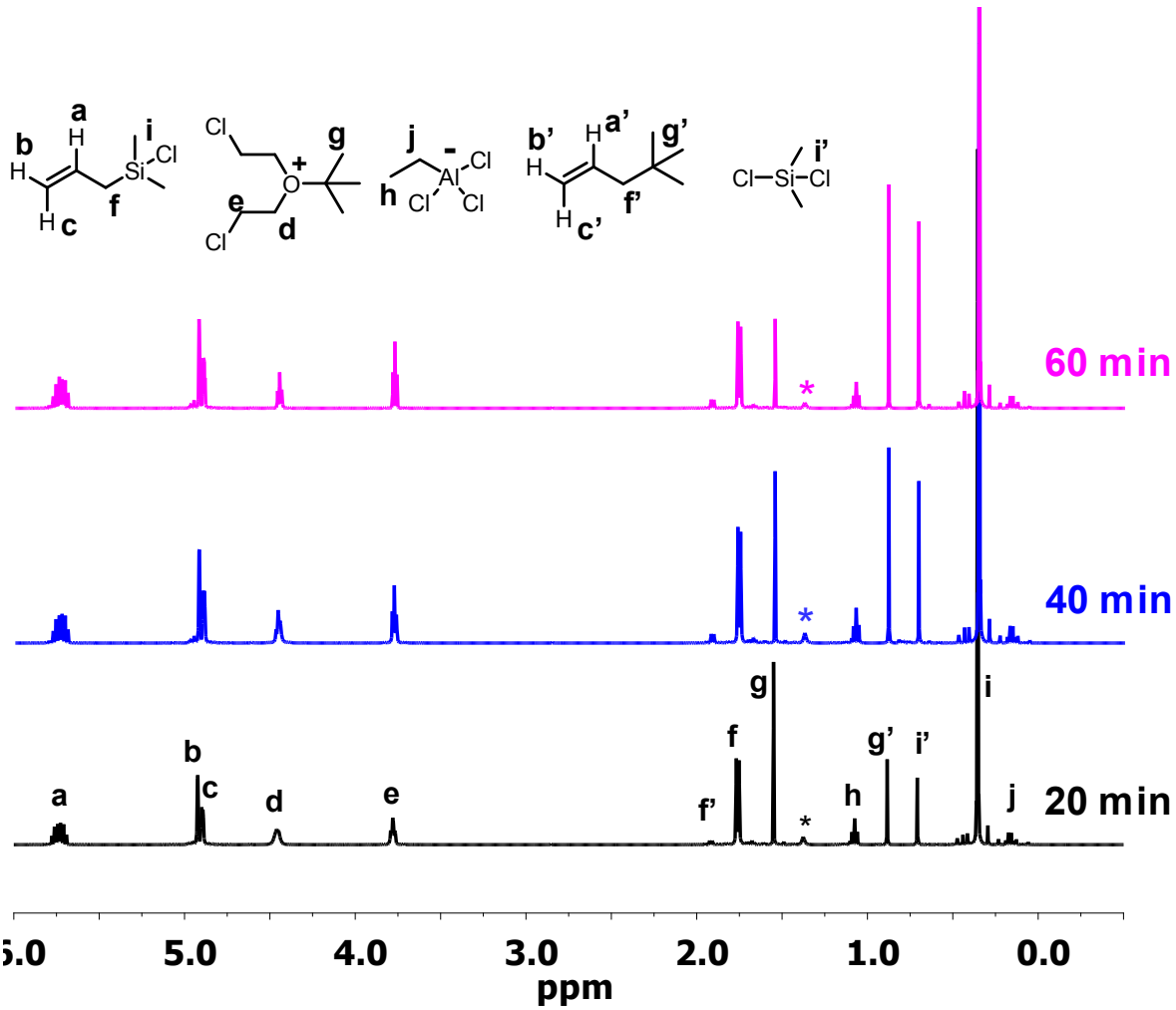


Fig. S4 ^{1}H NMR spectra of [EADC•CEE + *t*-BuCl] in the presence of ADMCS at different times at 0 °C in cyclohexane-d_{12}. [EADC•CEE + *t*-BuCl] = 0.05 M with [CEE]/[EADC] = 1, and [ADMCS] = 0.375 M. The asterisk denotes the cyclohexane-d_{11}H resonance.

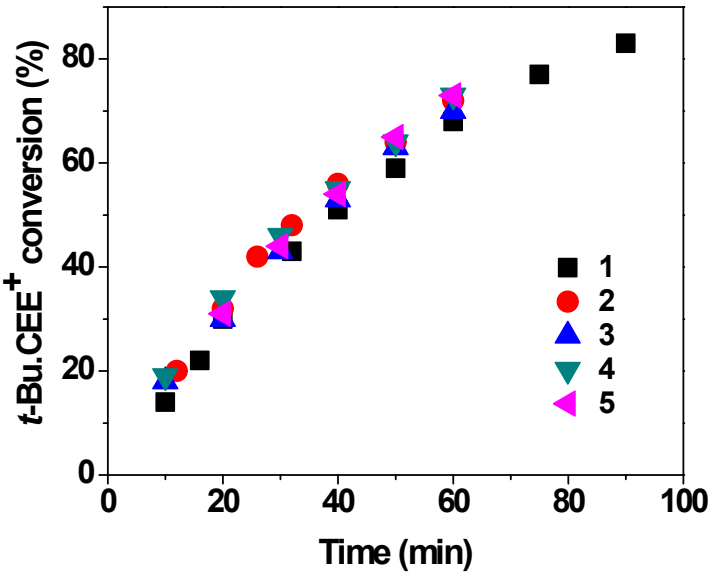


Fig. S5 Conversion vs time plot for reaction of oxonium ion, [EADC·CEE + *t*-BuCl] = 0.05 M with [CEE]/[EADC] = 1, with nucleophile in cyclohexane-d_{12} at 0 °C. 1: [MATMS] = 0.75 M. 2: [MATMS] = 0.375 M. 3: [MATMS] = 0.375 M ([CEE]/[EADC] = 1.5 used). 4: [ATMS] = 0.75 M. 5: [ACDMS] = 0.375 M.

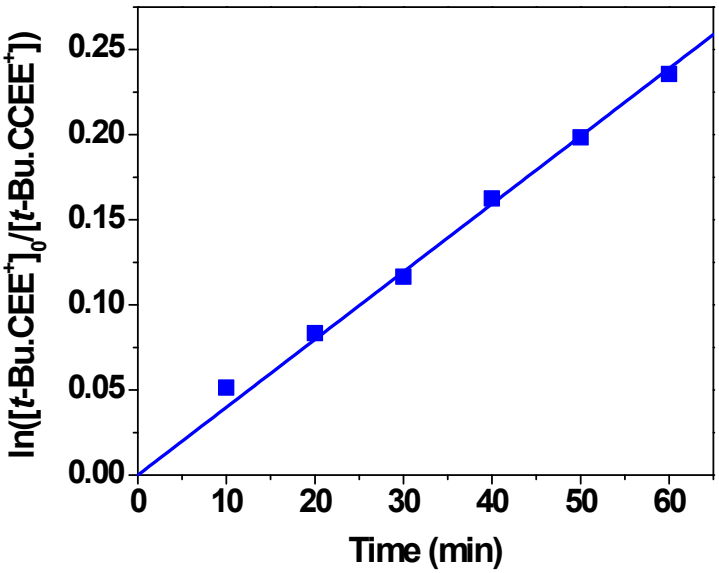


Fig. S6 ln{[*t*-Bu•CEE$^+$]$_0$/[*t*-Bu•CEE$^+$]} vs time plot for reaction of oxonium ion, [*t*-BuCl + EADC•CEE] = 0.05 M where [CEE]/[EADC] = 1, with MATMS in the presence of free CEE in cyclohexane-d_{12} at 0 °C, and [MATMS] = [CEE] = 0.25 M.

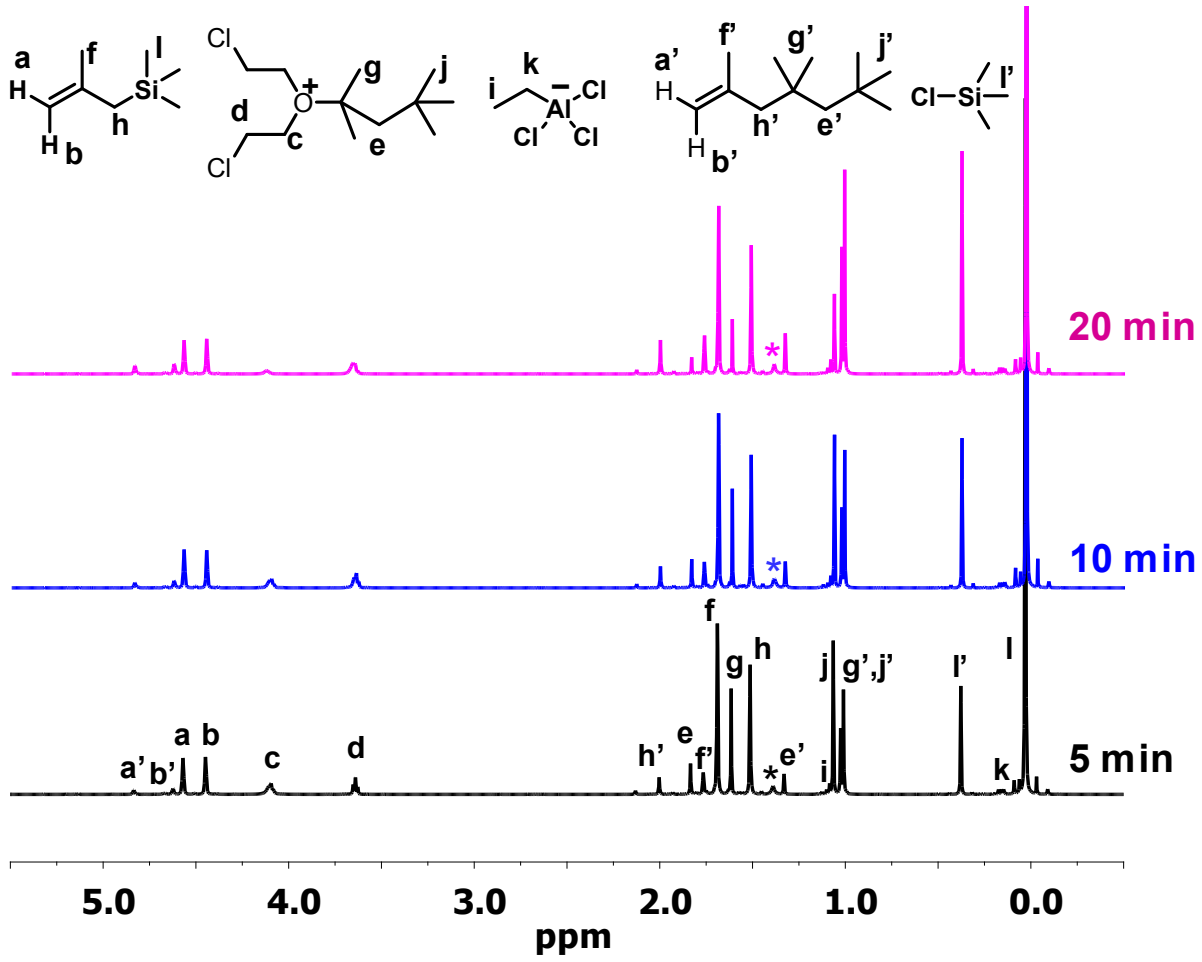


Fig. S7 ^{1}H NMR spectra of [EADC•CEE + TMPCl] in the presence of MATMS at different times at 0 °C in cyclohexane-d_{12}. [EADC•CEE + TMPCl] = 0.05 M with [CEE]/[EADC] = 1.5, and [MATMS] = 0.375 M. The asterisk denotes the cyclohexane-d_{11}H resonance.

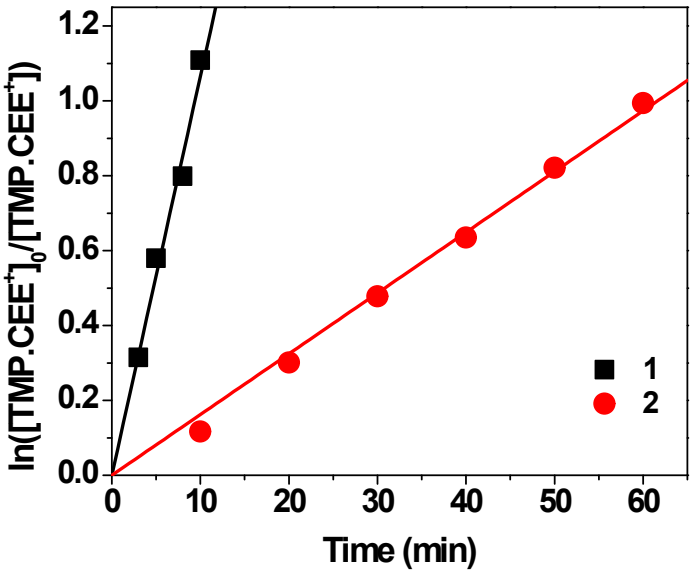


Fig. S8 ln{[TMP•CEE$^+$]$_0$/[TMP•CEE$^+$]} vs time plot for reaction of oxonium ion, [EADC•CEE + TMPCl] = 0.05 M where [CEE]/[EADC] = 1.5, with MATMS in cyclohexane-d_{12} at 0 °C. 1: [MATMS] = 0.375 M. 2: [MATMS] = [CEE] = 0.25 M.

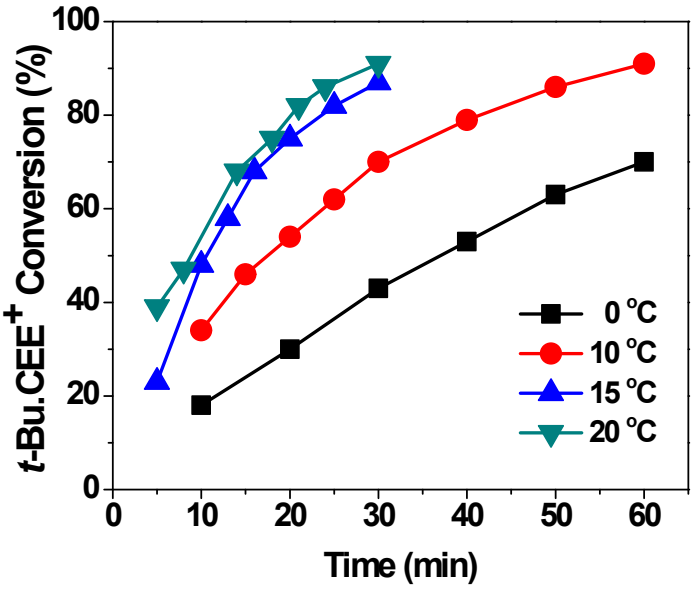


Fig. S9 Conversion vs time plot for reaction of oxonium ion, [EADC·CEE + *t*-BuCl] = 0.05 M where [CEE]/[EADC] = 1, with [MATMS] = 0.375 M in cyclohexane-d_{12} at different temperatures.

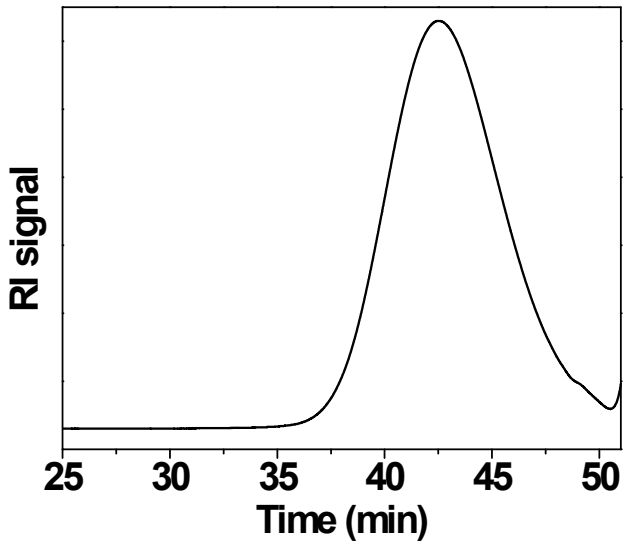


Fig. S10 Typical SEC RI trace of a representative HR PIB sample obtained in this study.