Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Silica gel supported ionic liquids as effective and reusable catalysts for the synthesis of highly reactive polyisobutylene in non-polar media

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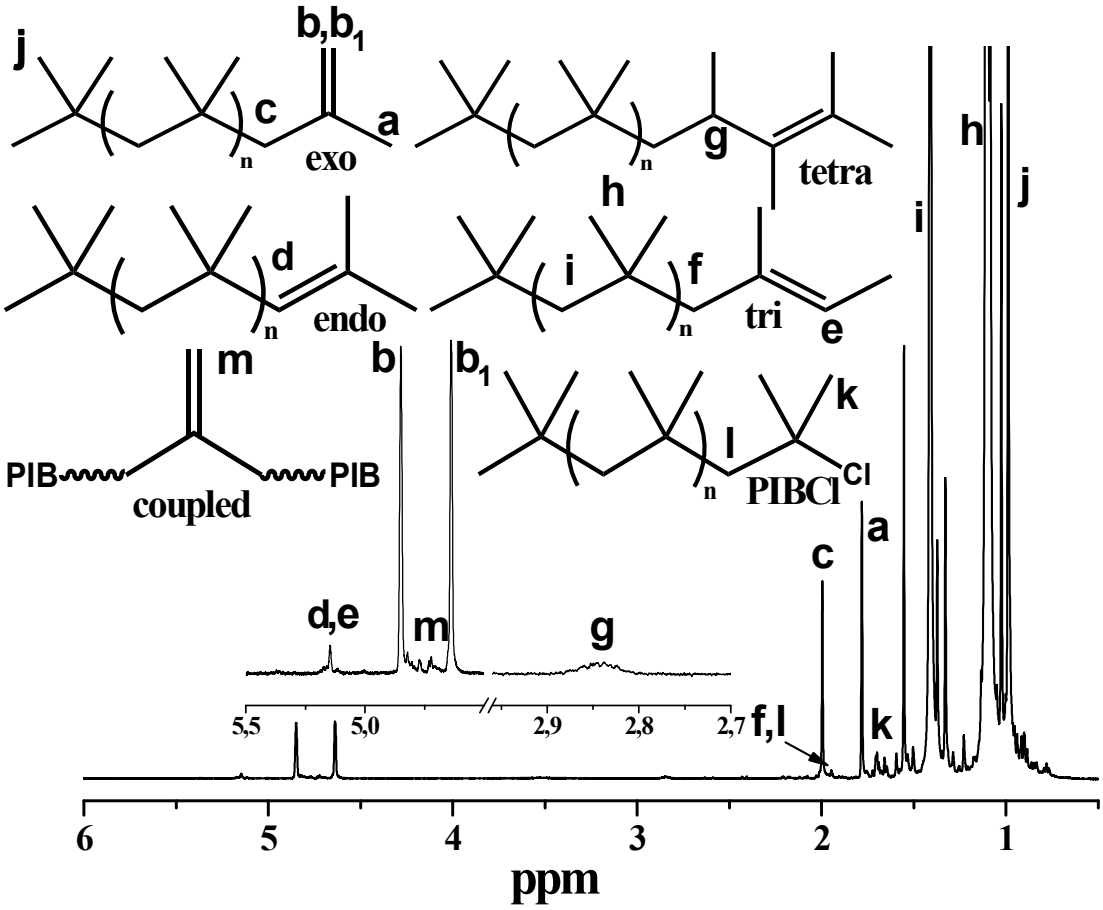


Figure S1. Typical ^{1}H NMR spectrum of polyisobutylene obtained with SILC in the presence of $^{i}Pr_2O$.

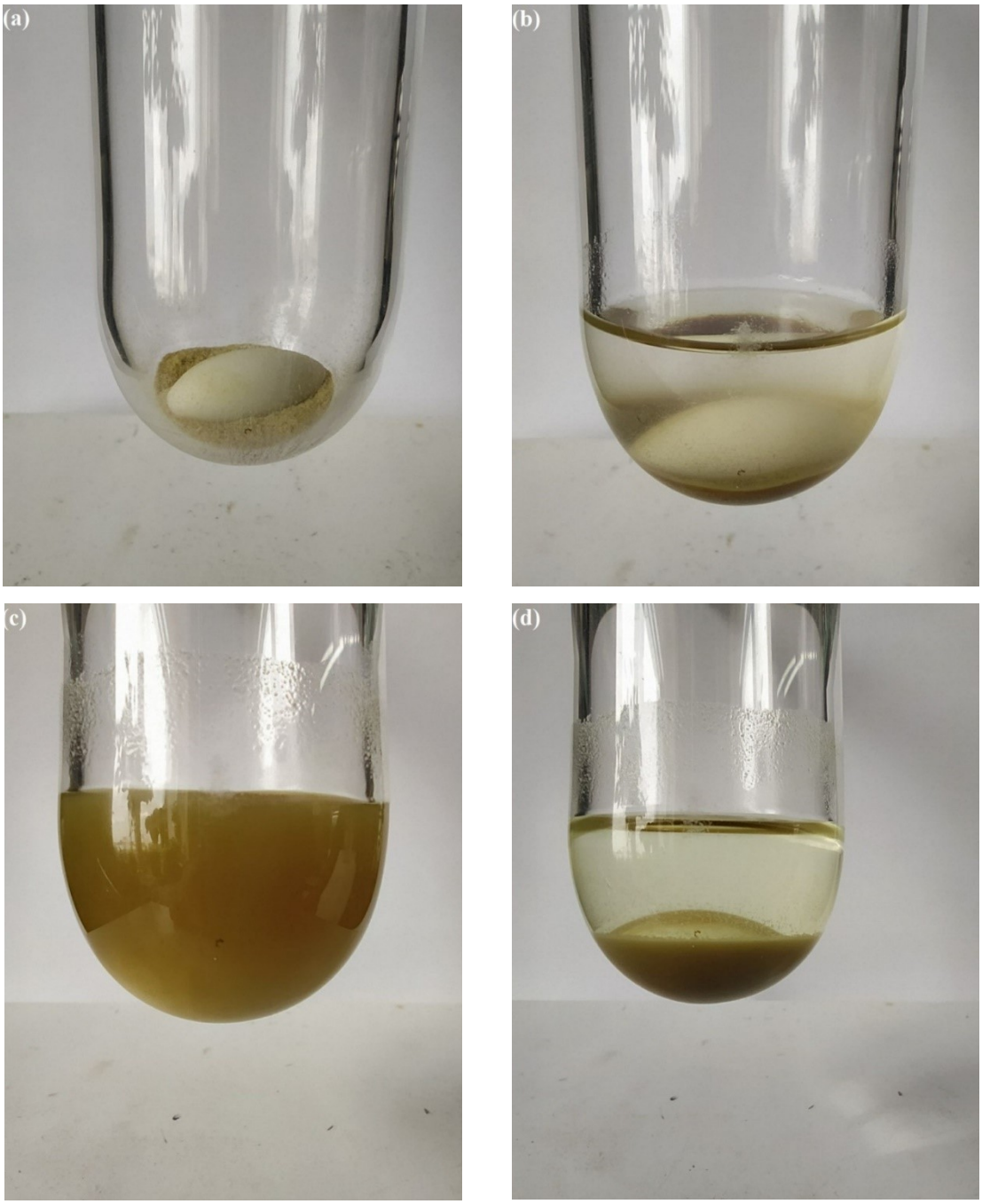


Figure S2. Photos of SiO_2–emimCl-1.5$FeCl_3$ (**a**), mixture of SILC, *n*-hexane and $^{i}Pr_2O$ (**b**), stirred mixture of SILC, *n*-hexane, $^{i}Pr_2O$ and IB (**c**), reaction mixture in 2 minutes after agitation stopping during polymerization cycle (**d**).

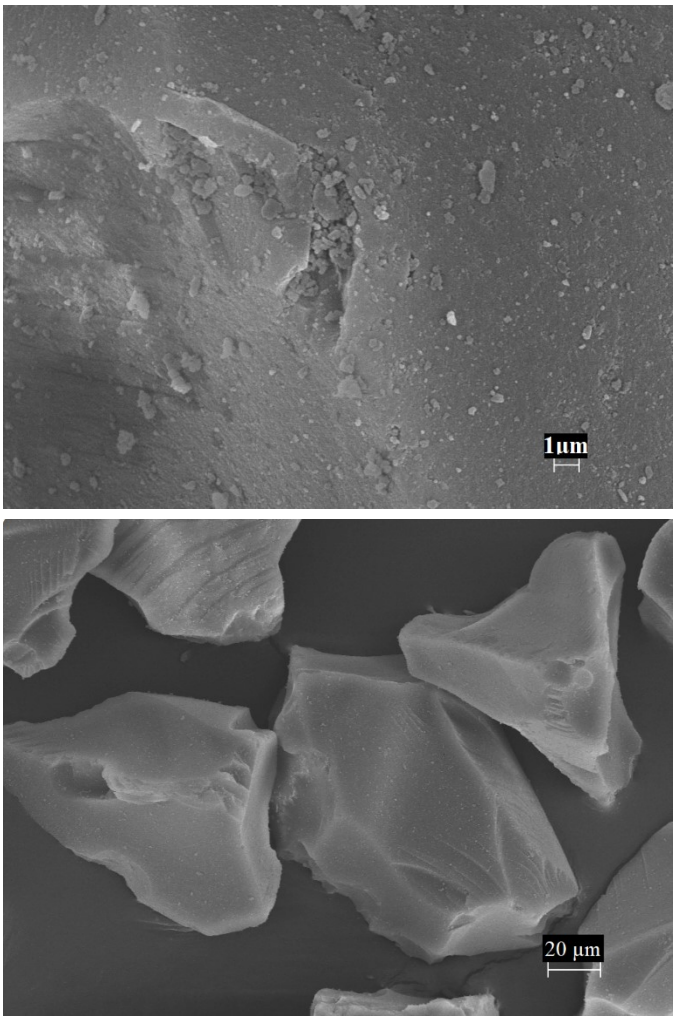


Figure S3. SEM images of silica gel 60

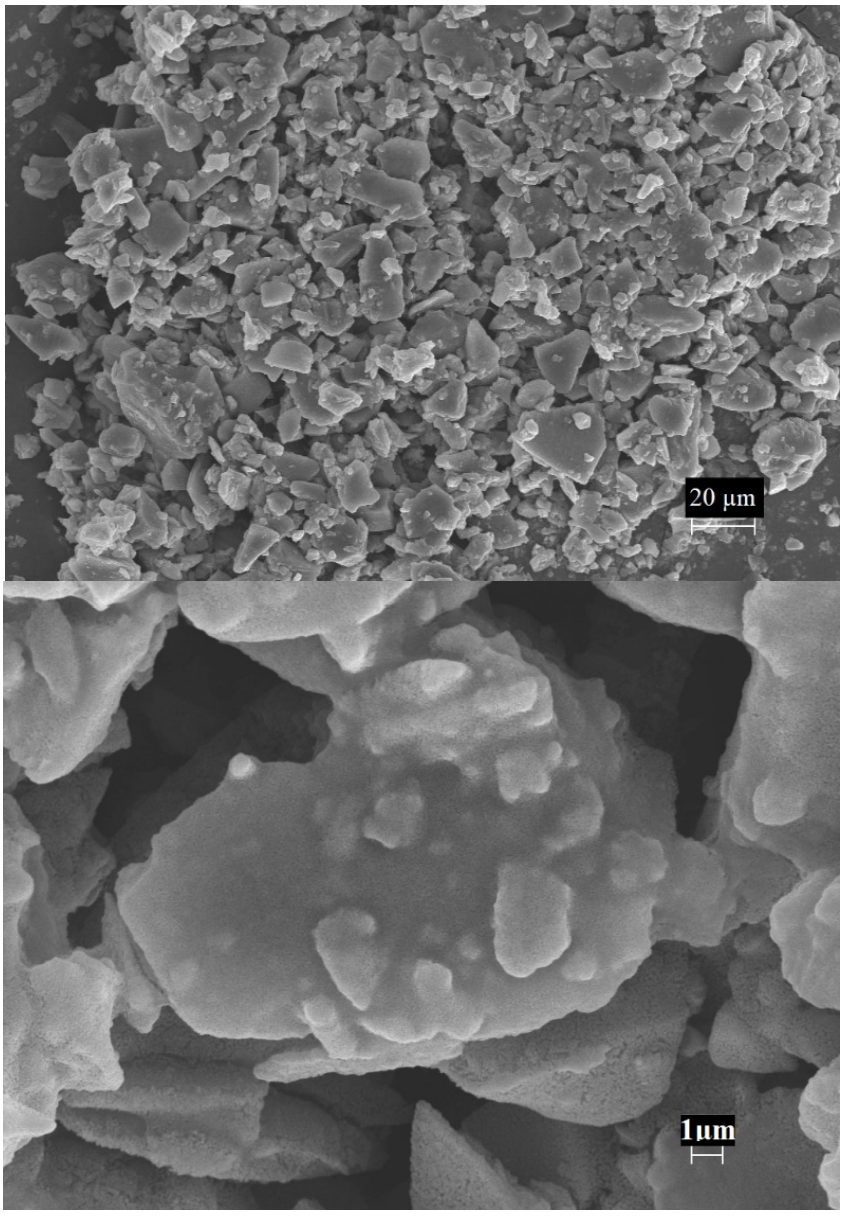
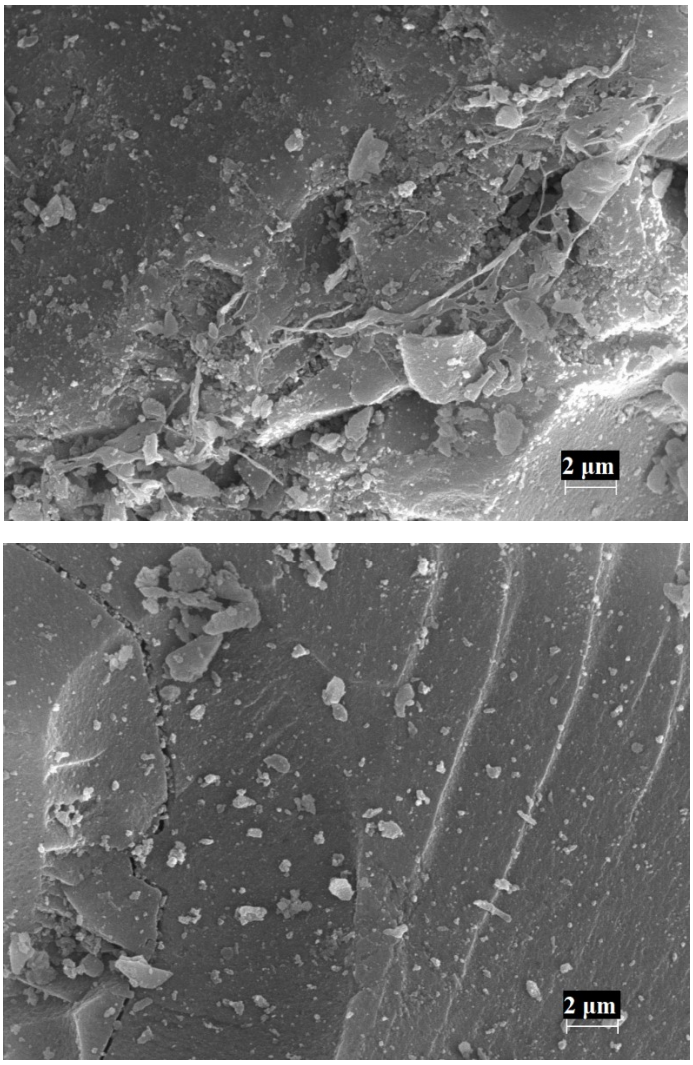

20 µm
1µm

Figure S4. SEM images of SILC based on silica gel 60 (*wt*.(IL) = 60%)



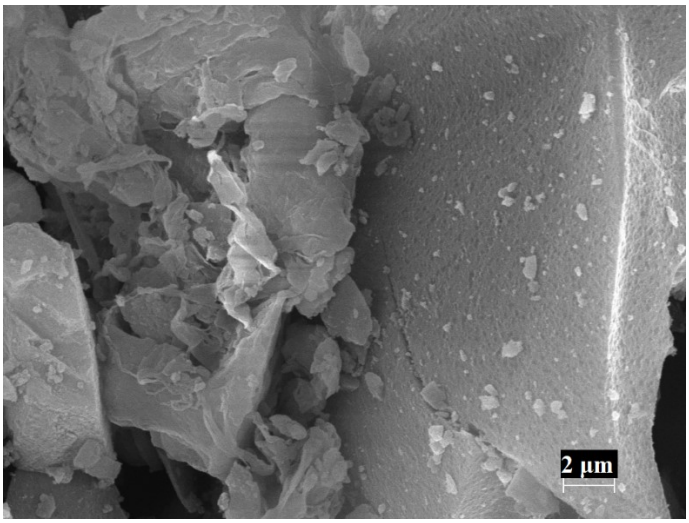


Figure S5. SEM images of SILC based on silica gel 60 (*wt*.(IL) = 30%)

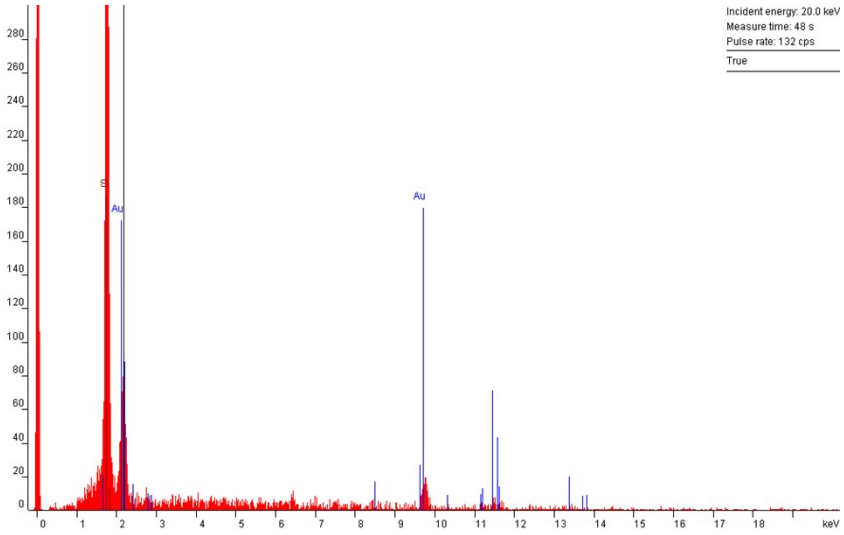


Figure S6. EDX element mapping of silica gel 60

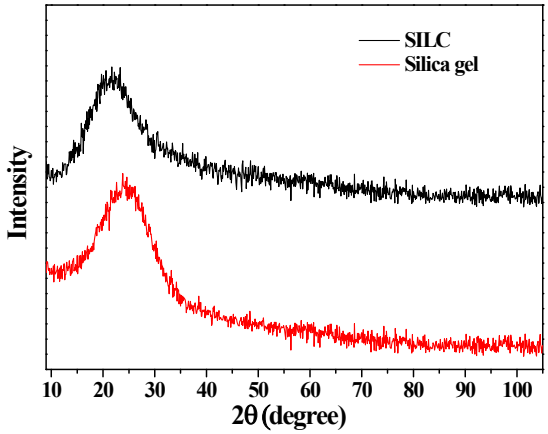


Figure S7. XRD patterns of silica gel (red line) and SILC (black line)

According to the Bragg's law (1) interplanar spacing *d* in the transition from silica gel to SILC slightly increases.

$2d\sin(\theta) = n\lambda$ *(1)*

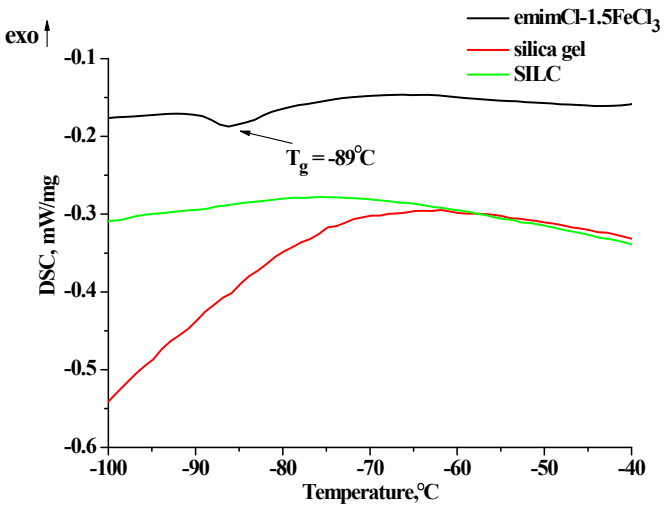


Figure S8. DSC curves of the emimCl-1.5$FeCl_3$, silica gel and SILC

Table S1. Cationic polymerization of isobutylene in *n*-hexane in the presence of SiO_2–emimCl-$FeCl_3$ at 0°C[a]

Entry	[SILC], mM[b]	Conv. (%)	M_n (g/mol)	Đ	End group distribution (mol. %)				
					exo	endo+ tri	tetra	PIBCl	coupl
1	38[c]	0	–	–	–	–	–	–	–
2	38[c, d]	0	–	–	–	–	–	–	–
3	38	50	1500	4.5	69	14	10	3	4

[a] Conditions: (ω(IL) = 60 wt%); [IB] = 5 M; Time = 20 min; Supported catalyst/*n*-hexane mixture was stirred for 3 min before IB addition; [b] In respect to IL content; [c] (ω(IL) = 2 %wt); [d] Time = 60 min

Table S2. Cationic Polymerization of Isobutylene in *n*-Hexane in the Presence of Different Supported Catalysts at 0°C[a]

Entry	Catalyst (mM)[b]	Conv. (%)	M_n (g/mol)	Đ	End group distribution (mol. %)				
					exo	*endo*+ *tri*	*tetra*	*PIB Cl*	*coupl*
1[c]	SiO_2-emimCl-$FeCl_3$ (38)	50	1500	4.5	69	14	10	3	4
2	SiO_2-$FeCl_3$ (38)	100	2000	4.3	39	26	21	0	14
3	SiO_2-emimCl-$FeCl_3$ (56)	65	1300	4.3	67	15	9	3	6
4	SiO_2-emimCl-$FeCl_3$ (80)	92	1200	3.7	61	18	13	6	2
5	SiO_2-emimCl-$AlCl_3$ (38)	50	3500	5.1	10	72	0	18	0
6	SiO_2-$AlCl_3$ (18)	100	1750	7.0	6	66	28	0	0

[a] Conditions: ω(IL/LA) = 60%; [IB] = 5 M; Time = 30 min; Supported catalyst/*n*-hexane mixture was stirred for 3 min before IB addition; [b] In respect to IL or Lewis acid content. [c] Time = 20 min.

Table S3. Cationic polymerization of isobutylene in *n*-hexane in the presence of SiO_2–$FeCl_3$ and $^{i}Pr_2O$ at 0°C[a]

Entry	Ether (mM)	Time (min)	Conv. (%)	M_n (g/mol)	Đ	End group distribution (mol. %)				
						exo	*endo+ tri*	*tetra*	*PIB Cl*	*coupl*
1	no	20	100	2000	4.3	39	26	21	14	0
2	$^{i}Pr_2O$ (19)	10	51	3200	3.0	87	6	3	3	1
3	$^{i}Pr_2O$ (19)	20	100	1500	3.1	43	19	20	18	0
4	$^{i}Pr_2O$ (11)	10	100	2500	4.1	74	10	7	9	0
5	CEE (11)	7	98	2000	3.3	66	16	6	12	0
6	CE (11)	6	62	3500	3.8	75	10	7	7	1

Conditions: [SiO_2-$FeCl_3$]=38 mM; [IB] = 5 M; T = 0 ºC; *n*-hexane. Supported catalyst/*n*-hexane mixture was stirred for 3 min before IB addition.

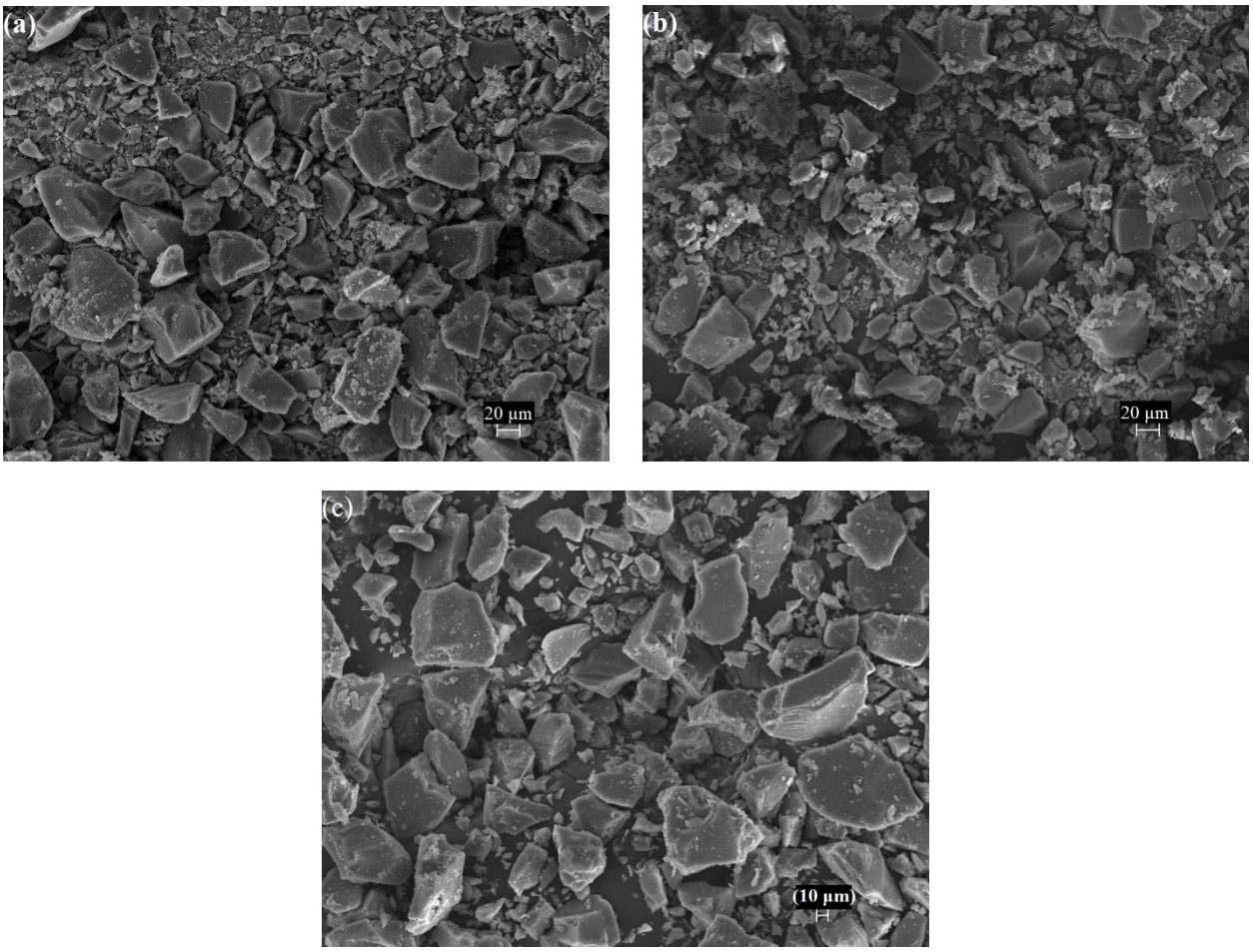


Figure S9. SEM images of SILC based on silica gel 60 (IL = 30 wt%) after (**a**) zero polymerization cycle, (**b**) first polymerization cycle and (**c**) second polymerization cycle.

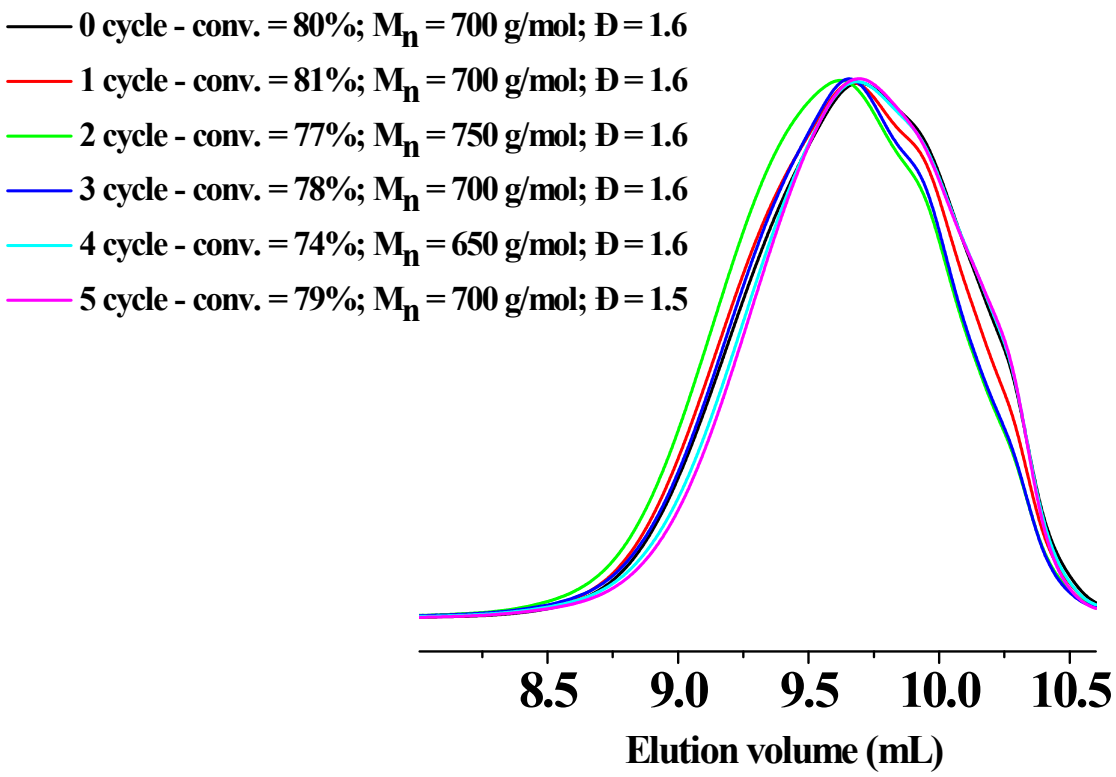


Figure S10. SEC traces of PIB*s* obtained during catalyst recycling in the course of IB polymerization in *n*-hexane at 0ºC: ω(IL) = 30 %wt; $[SILC]_0$ = 38 mM in respect to IL content; $[^iPr_2O]_0$ = 19 mM; $[IB]_n$ = 3 M. Fresh SILC (20 wt%) was added into system after each polymerization run.