Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Imidazolium Triflimide-based Bronsted acidic ionic liquid as organocatalyst to trigger the cationic ring-opening polymerization of cyclotrisiloxanes

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Content

▪Screening of 6 commercial ionic liquids as initiators for ROP of D_3

Table S1. Ring-opening polymerization (ROP) of D_3 initiated by selected ionic liquids in bulk at 90°C.

				SEC composition[a] (% wt)			
Entry	Ionic liquid (IL)	$[D_3]_0/[IL]_0$	Time	D_3	$D_4 + D_5 + D_6$	PDMS	M_n (kg.mol^{-1}) (*Đ*) [a]
S1	$[BMIM]HSO_4$	250/1	5h	100	0	0	No polymer[b]
S2	$[BMIM]HSO_4$	50/1	5h	96.1	3.9	0	No polymer[b]
S3	$[BMIMSO_3H]HSO_4$	250/1	5h	100	0	0	No polymer[b]
S4	$[BMIMSO_3H]HSO_4$	50/1	5h	97.5	2.5	0	No polymer[b]
S5	[BMIM]OTf	250/1	5h	100	0	0	No polymer[b]
S6	[BMIM]OTf	50/1	5h	99.3	0.7	0	No polymer[b]
S7	$[BMIMSO_3H]OTf$	250/1	15min	0.1	13.0	86.9	317 (1.4)
S8	$[BMIM]NTf_2$	250/1	5h	100	0	0	No polymer[b]
S9	$[BMIM]NTf_2$	50/1	5h	100	0	0	No polymer[b]
S10	$[BMIMSO_3H]NTf_2$	250/1	5min	0.1	9.2	90.7	271 (1.4)

a) SEC conducted in toluene using polystyrene (PS) for calibration.

b) As confirmed by FTIR analysis

Table S2. Polymerization of D_3 induced by $[BMIMSO_3H]OTf$ as BAIL in bulk at 90°C.

			NMR composition[a] (%)			M_n (kg.mol^{-1})	
Entry	$[D_3]_0/[IL]_0$	Time	D_3	$D_4 + D_5 + D_6$	PDMS	Theo[b]	SEC (*Đ*)[c]
S11	250/1	2h	7.0	28.7	71.3	45	288 (2.2)
S12	1,000/1	2h	8.7	22.7	77.3	174	249 (2.4)
S13	2,500/1	2h	9.4	15	85.0	458	277 (2.1)

a) Determined by ^{29}Si NMR in $CDCl_3$ at 298

b) Theoretical molar masse $M_n^{Theo} = \frac{[D_3]_0}{[BAIL]_0} * 3 * conv * 74.1$,where $[D_3]_0$ and $[BAIL]_0$ are the initial molar content of D_3 and BAIL. conv is the conversion of D_3: $conv = 100 - \%wt^{SEC}D_3$

c) SEC conducted in toluene using polystyrene (PS) for calibration

Table S3. Polymerization of D_3 induced by $[BMIMSO_3H]NTf_2$ as BAIL in bulk at 90°C.

			NMR composition[a] (%)			M_n (kg.mol^{-1})	
Entry	$[D_3]_0/[IL]_0$	Time	D_3	$D_4 + D_5 + D_6$	PDMS	Theo[b]	SEC (*Đ*)[c]
S14	250/1	10min	0	13	87.0	47	274 (2.3)
S15	1,100/1	10min	0	9.1	90.9	247	257 (2.2)
S16	2,000/1	10min	0	8.0	92.0	405	218 (2.7)
S17	2,800/1	15min	0	8.1	91.9	619	160 (2.3)

a) Determined by ^{29}Si NMR in $CDCl_3$ at 298

b) Theoretical molar masse $M_n^{Theo} = \frac{[D_3]_0}{[BAIL]_0} * 3 * conv * 74.1$,where $[D_3]_0$ and $[BAIL]_0$ are the initial molar content of D_3 and BAIL. conv is the conversion of D_3: $conv = 100 - \%wt^{SEC}D_3$

c) SEC conducted in toluene using polystyrene (PS) for calibration

- **([BMIMSO$_3$H]NTf$_2$) catalyzed ROP of D$_3$**
  - **Selection of chain regulators**
    - **Chain regulators = YOH**

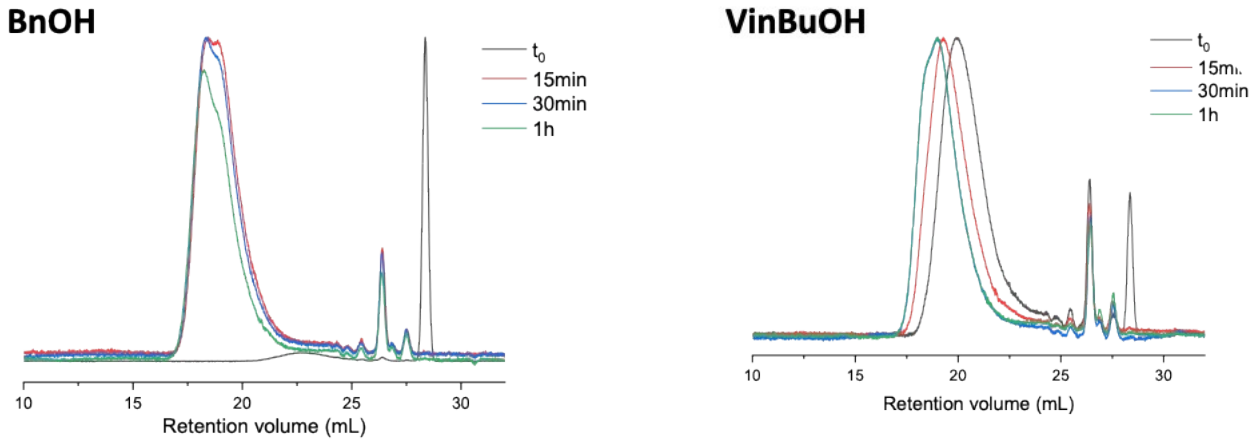


Figure S1. SEC traces (RI detector) of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C using alcohols as chain regulators (YOH) (Table 1, entries 2-3).

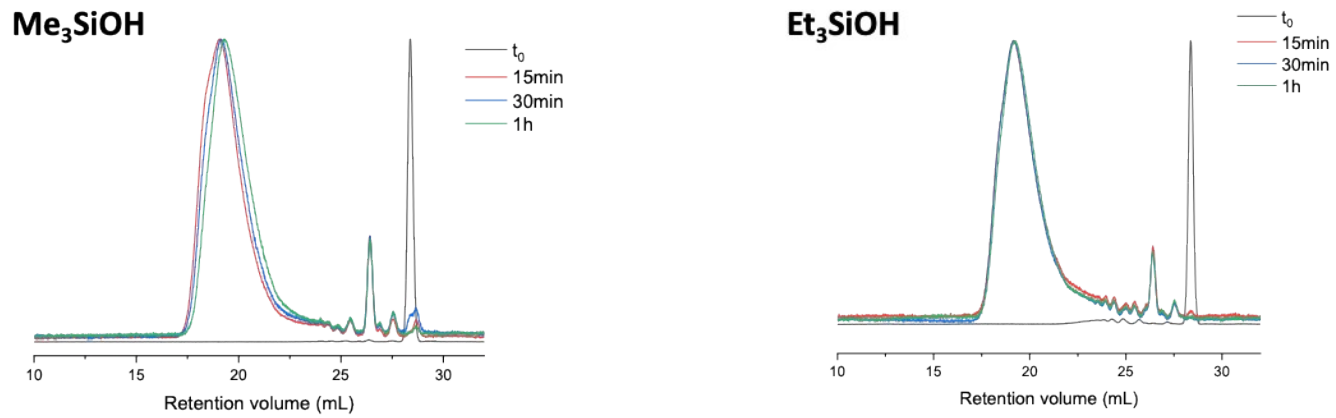


Figure S2. SEC traces (RI detector) of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C using silanols as chain regulators (YOH) (Table 1, entries 4-5).

- **Chain regulators = M_x**

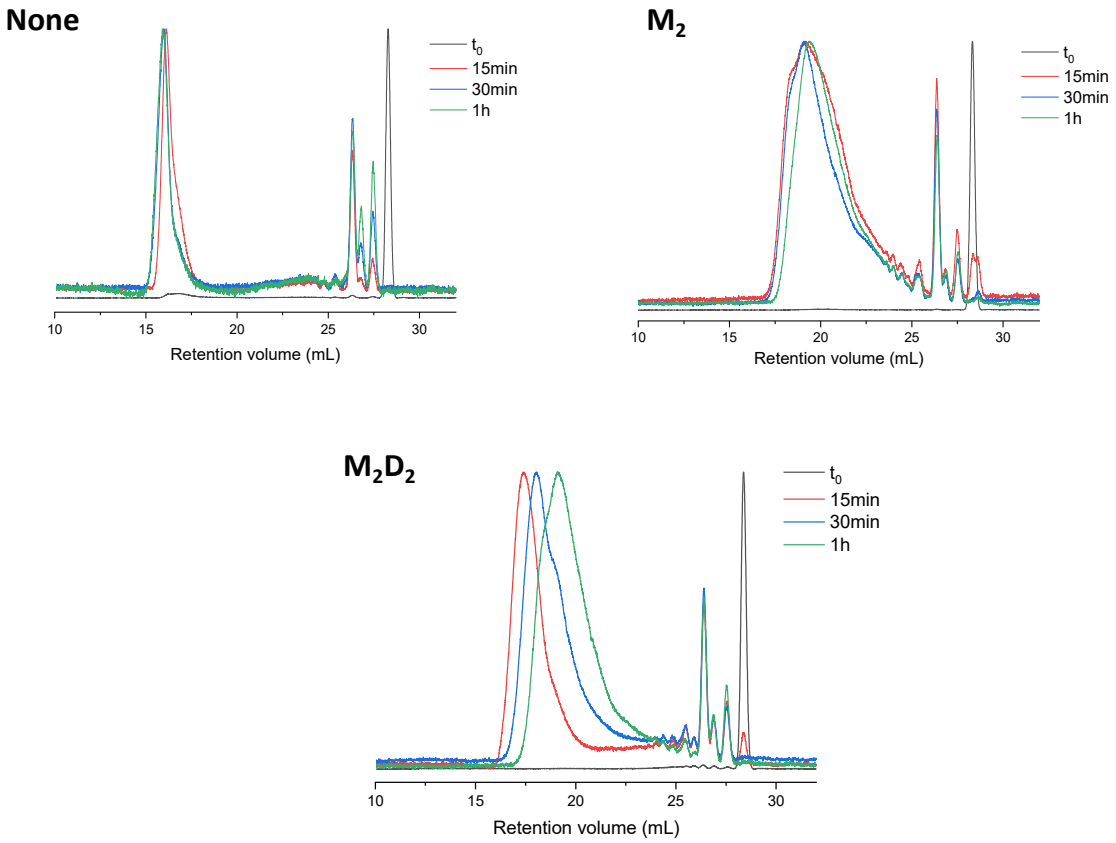


Figure S3. SEC traces (RI detector) of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C using disiloxanes as chain regulators (Mx) (Table 2, entries 7-8)

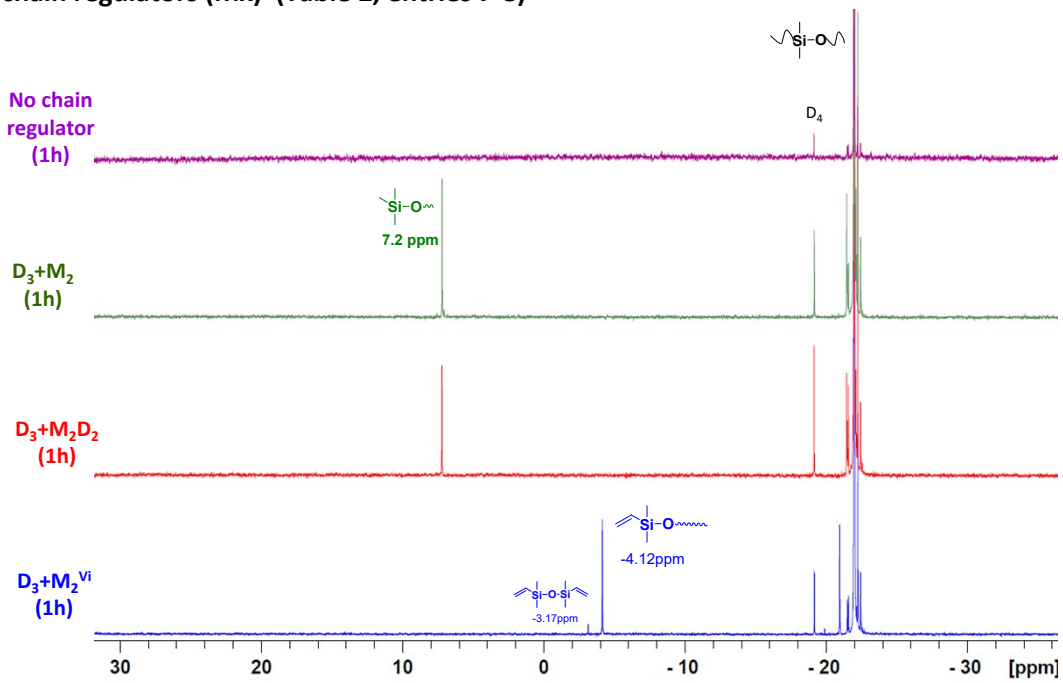


Figure S4. ^{29}Si NMR (in CDCl$_3$) of reaction mixture of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C using disiloxanes as chain regulators (Mx) (see legend) (Table 2)

▪ Influence of $[D_3]_0/[M_2]_0$ initial ratio

Table S4. Polymerization of D_3 at 90°C in bulk using different $[D_3]_0/[M_2]_0$ ratios and $[D_3]_0/[BMIMSO_3H]NTf_2]_0$ = 1,400.

				SEC composition[a] (%)			M_n (kg.mol^{-1})	
Entry	Experiment	$[D_3]_0/[M_2]_0$	Time	M_2 +D_3	D_4 + D_5 + D_6	PDMS	Theo[b]	SEC (*Đ*)[a]
S18	WR-146	8	0	100	0	0	-	-
			5min	10.6	11.0	78.4	-	3.0 (2.2)
			10min	5.3	9.7	85.0	-	3.9 (2.7)
			15min	3.4	9.2	87.4	-	4.3 (2.7)
			25min	2.1	9.3	88.6	-	4.4 (2.6)
			35min	1.8	9.4	88.8	-	4.3 (2.5)
			45min	1.6	9.5	88.9	-	4.2 (2.4)
			1h	1.4	8.7	89.9	1.9	4.0 (2.3)
S19	WR-180	21	0	100	0	0	-	-
			4min	10.9	13.2	75.9	-	4.3 (2.7)
			8min	3.2	8.1	88.7	-	5.8 (3.1)
			15min	0.5	7.2	92.3	-	6.8 (3.7)
			25min	0.4	7.5	92.3	-	6.8 (3.4)
			35min	0.1	7.3	92.4	-	6.5 (3.2)
			45min	0.2	7.9	92.0	-	6.1 (3.1)
			1h	0.2	5.8	94.0	5.0	6.8 (2.7)
S20	WR-181	48	0	100	0	0	-	-
			4min	8.5	11.1	80.4	-	7.1 (3.6)
			8min	0.8	7.7	91.5	-	9.4 (4.0)
			15min	0.8	6.3	92.9	-	10.5 (4.7)
			25min	1.8	8.0	90.2	-	10.3 (3.9)
			35min	1.9	6.2	91.9	-	10.2 (3.7)
			45min	1.8	6.7	91.5	-	9.9 (3.6)
			1h	1.1	7.0	91.9	10.8	9.6 (3.4)
S21	WR-182	83	0	100		0	-	-
			4min	19.0	10.6	70.4	-	9.0 (3.8)
			8min	1.6	8.9	89.5	-	11.4 (4.5)
			15min	0.4	8.2	91.4	-	12.0 (5.2)
			25min	0.3	7.1	92.6	-	12.5 (4.8)
			35min	0.6	7.1	92.3	-	11.3 (4.7)
			45min	0.5	6.5	93.0	-	11.4 (4.4)
			1h	0.2	6.3	93.5	19.1	11.5 (4.0)

a) Determined by SEC conducted in toluene using polystyrene (PS) for calibration

b) Theoretical molar masse $M_n^{Theo} = \frac{[D_3]_0}{[BAIL]_0} * 3 * conv * 74.1$,where $[D_3]_0$ and $[BAIL]_0$ are the initial molar content of D_3 and BAIL. conv is the conversion of D_3: $conv = 100 - \%wt^{SEC}D_3$

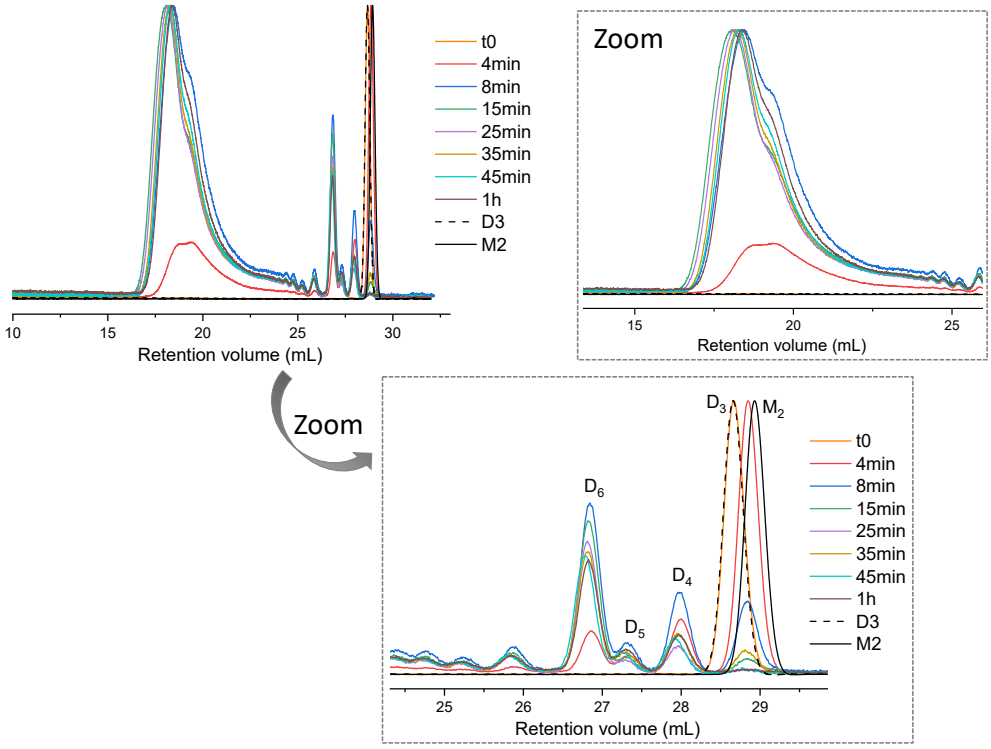


Figure S5. Example of SEC traces (RI detector) of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C using [D$_3$]$_0$/[M$_2$]$_0$/[BAIL]$_0$ = 21/1/0.01 (Table S4, entrey 9).

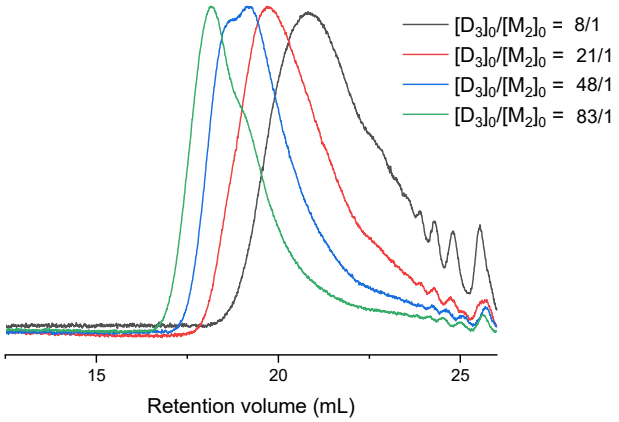


Figure S6. SEC traces (RI) of [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_3$ in bulk at 90°C with various [D$_3$]$_0$/[M$_2$]$_0$ ratios. (Table 3, entries 9-12).

- **Polymerization of functionalized cyclosiloxanes D_n^F**

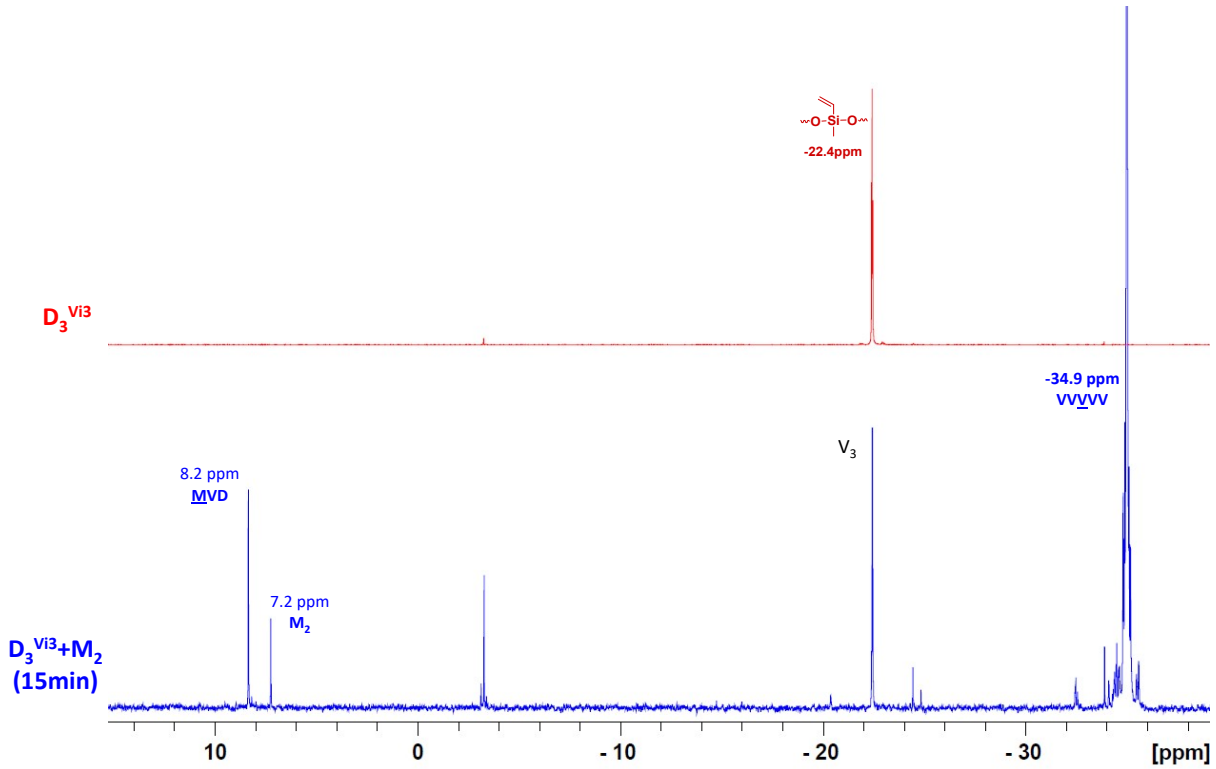


Figure S7. ^{29}Si NMR spectra (in $CDCl_3$) of D_3^{Vi3} and [BMIMSO$_3$H]NTf$_2$-catalyzed copolymerization of D_3^{Vi3} in bulk at 90°C using $[D_3^{Vi3}]_0/[M_2]_0/[BAIL]_0$ = 21/1/0.01 (Table 4, entry 13).

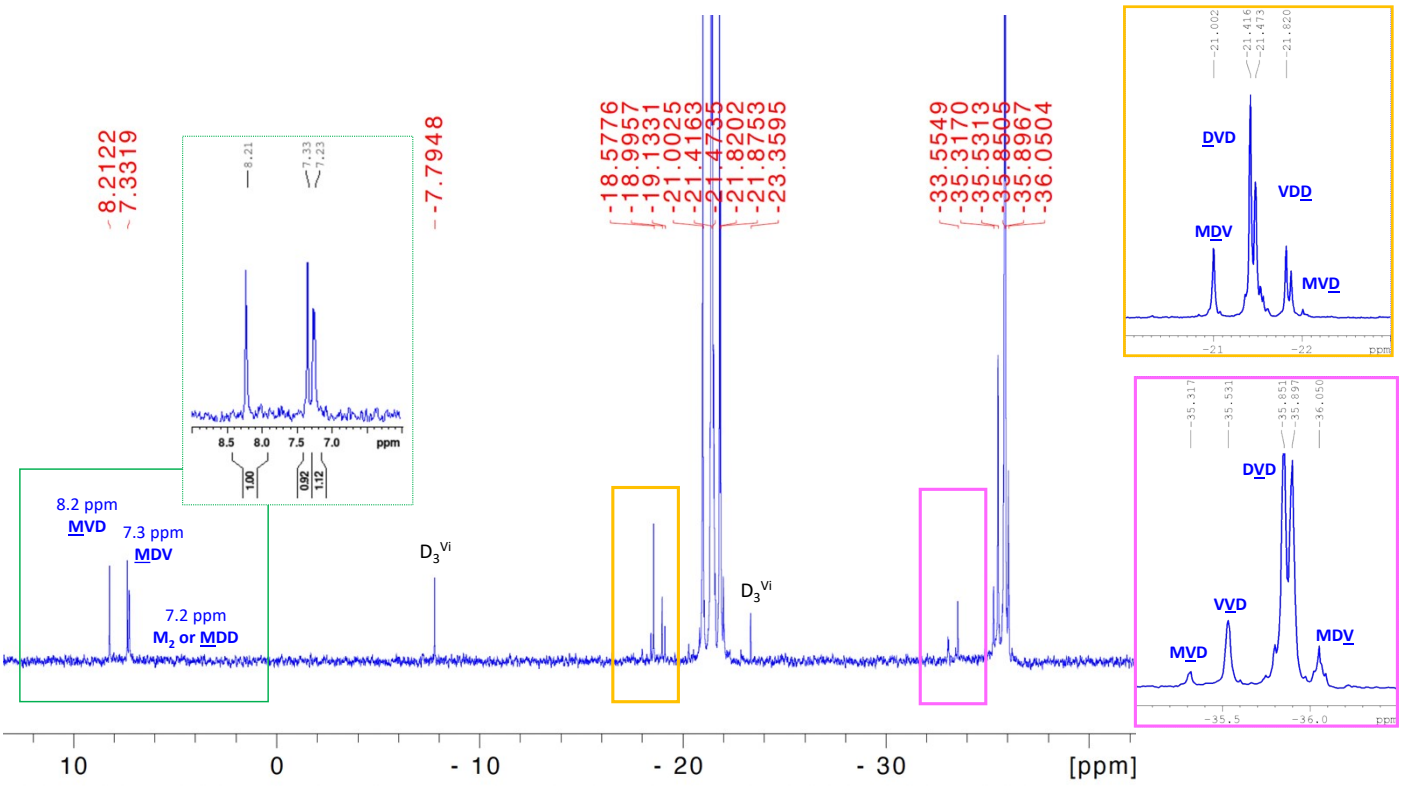


Figure S8. ^{29}Si NMR spectra (in $CDCl_3$) of [BMIMSO$_3$H]NTf$_2$-catalyzed copolymerization of D_3^{Vi} in bulk at 90°C using $[D_3^{Vi3}]_0/[M_2]_0/[BAIL]_0$ = 21/1/0.01 (t = 1h) (Table 4, entry 15)

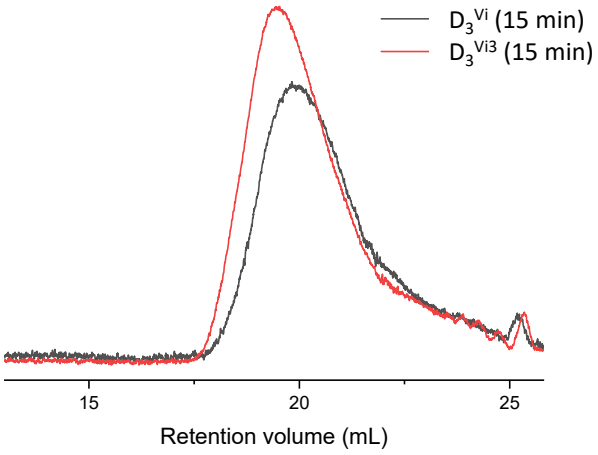


Figure S9. SEC traces (RI detector) of polymers synthesized from [BMIMSO$_3$H]NTf$_2$-catalyzed polymerization of D$_n^F$ in bulk at 90°C using M$_2$ as chain regulator (Table 4, entries 13-14).

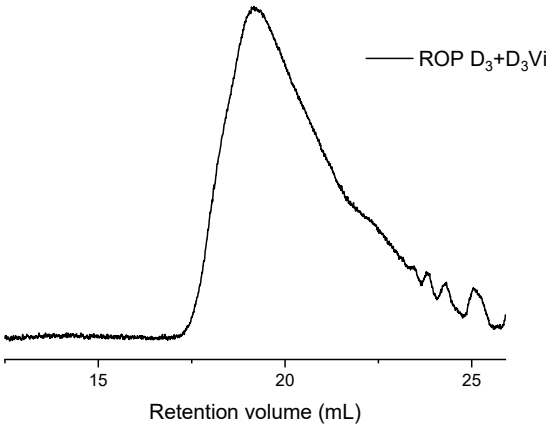


Figure S10. SEC-RI traces of polymer obtained after copolymerization of D$_3$ with D$_3$Vi (Table 4, entry 16)

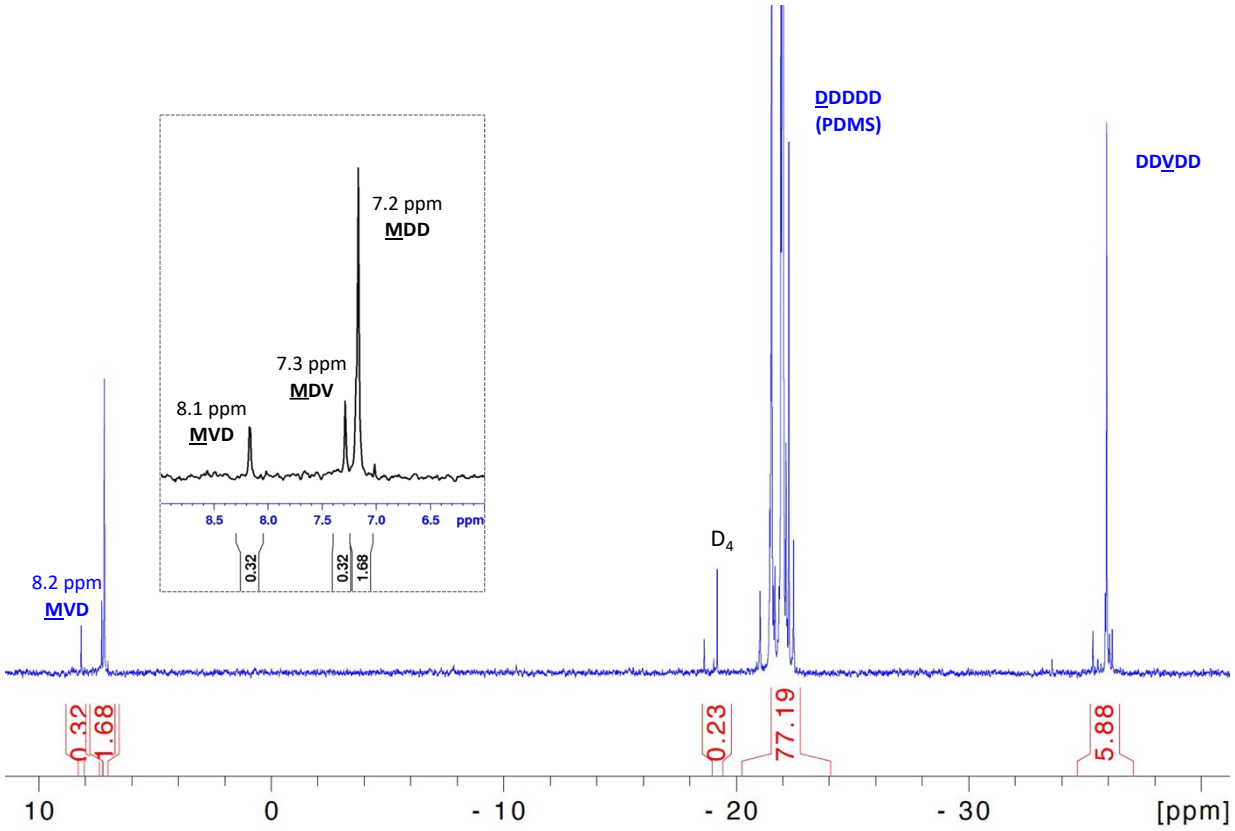
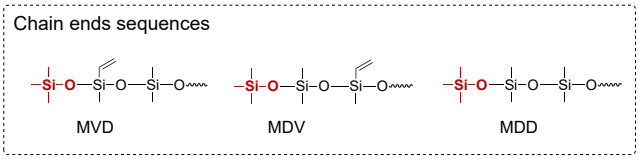


Figure S11.^{29}Si NMR (in $CDCl_3$) of $[BMIMSO_3H]NTf_2$-catalyzed copolymerization of D_3/D_3^{Vi} (80/20) in bulk at 90°C using $[D_3+D_3^{Vi3}]_0/[M_2]_0/[BAIL]_0$ = 20/1/0.01 (t = 1h) (Table 4, entry 15).

Table S5. Microstructure of copolymer obtained by $[BMIMSO_3H]NTf_2$-catalyzed copolymerization of D_3/D_3^{Vi} (80/20) in bulk at 90°C using $[D_3+D_3^{Vi3}]_0/[M_2]_0/[BAIL]_0$ = 20/1/0.01 (t = 1h)



	D units						V units				
	Chain-ends (%)			Triads (%)			Chain-ends (%)		Triads (%)		
	D-OH	MDV	MDD	VDV	DDV	DDD	V-OH	MVD	VVV	VVD	DVD
$D_3 + D_3^{Vi}$	0	13.9	72.3	0.7	14.7	78.2	0	13.8	0	0.3	6.1

■ Discussion on polymerization mechanismeInfluence of catalyst structure => Polymerization mechanism

Table S6: Polymerization of D_3 using various catalytic systems in bulk at 90°C.

				SEC composition[b] (% wt)			M_n (kg.mol^{-1})	
Entry	Catalyst	$[D_n]_0/[M_2]_0$/ catalyst	Time	D_3	$D_4 + D_5 + D_6$	PDMS	Theo[a]	SEC ($Đ$)[b]
S22	$[BMIM]NTf_2$	21/1/0.02	15min	100	0	0	No polymer[c]	
			4h	100	0	0	No polymer[c]	
S23	C5-SO_3H	21/1/0.03	15min	0.32	36.9	62.7	4.9	4.1 (2.3)
			1h	0.13	38.4	61.5	4.9	3.5 (2.8)
			2h	0.38	38.2	61.4	4.9	4.6 (2.4)
			4h	0.40	35.9	63.7	4.9	11.9 (1.7)
S24	$[BMIM]NTf_2$ + C5-SO_3H	21/1/0.02/0.03	15min	0.28	34.4	65.3	4.9	4.4 (2.3)
			1h	0.27	34.0	65.7	4.9	4.8 (2.4)
			2h	0.24	34.5	65.2	4.9	4.7 (2.4)
			4h	0.11	32.7	67.2	4.9	4.7 (2.7)

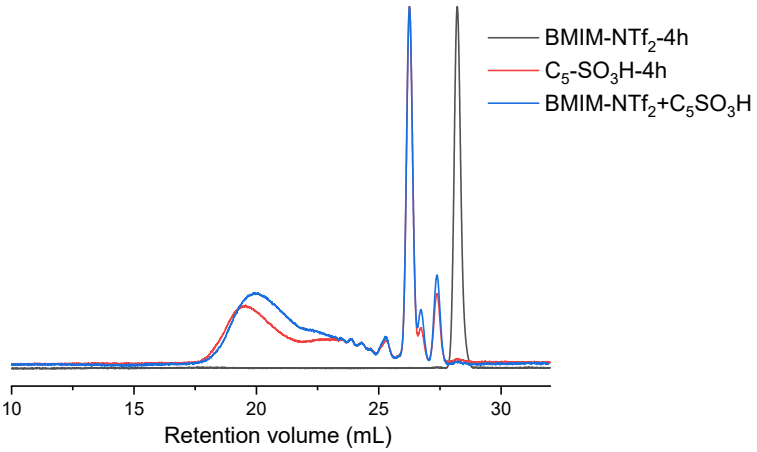


Figure S12. SEC traces (RI detector) of reaction mixture of polymerization of D_3 using various catalytic systems in bulk at 90°C using $[D_3]_0/[M_2]_0$/catalyst = 21/1/0.003 (Table S6, entries 22-24).