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supporting information

Synthesis of guanidinophosphazene superbase for the facile preparation of high molecular weight polysiloxane under mild conditions

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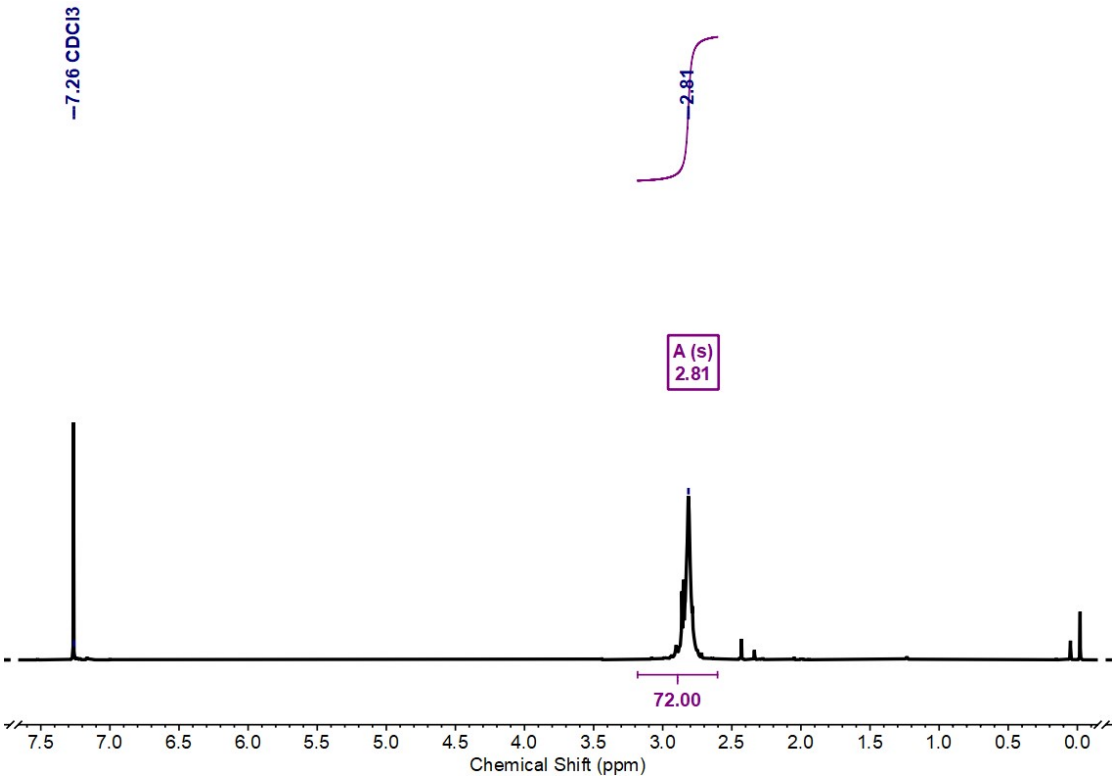

Fig. S1 ^{1}H-NMR spectrum of HTGCP in $CDCl_3$.

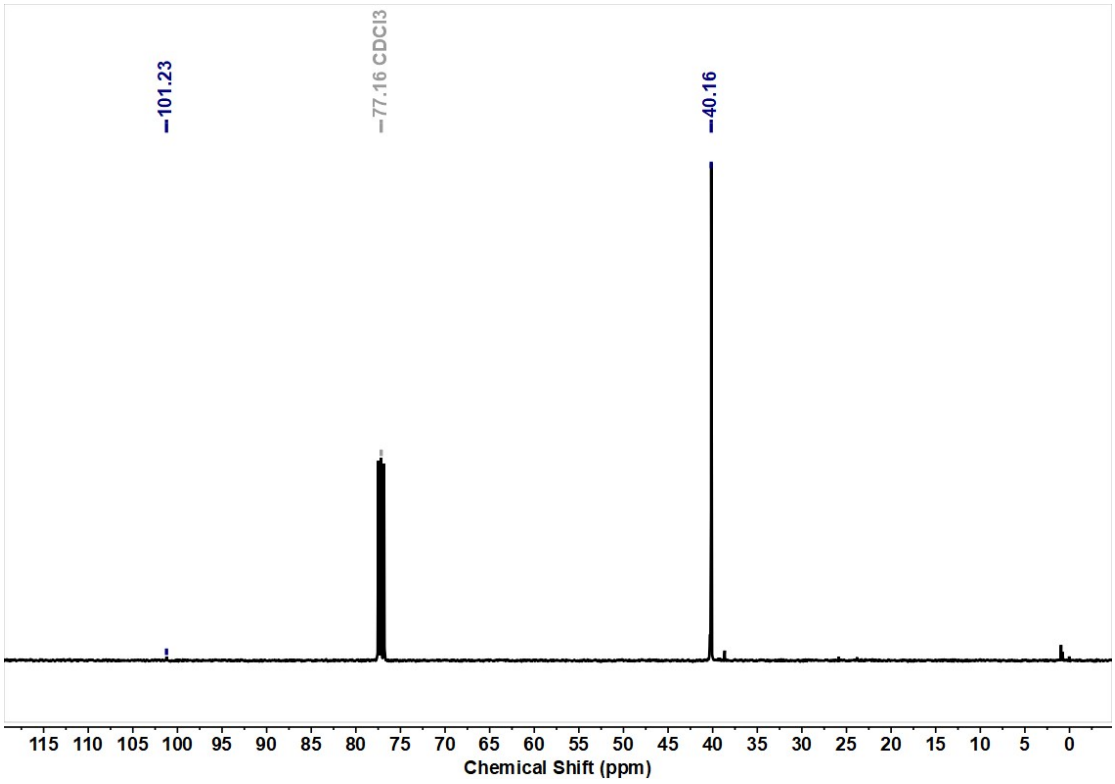

Fig. S2 ^{13}C-NMR spectrum of HTGCP in $CDCl_3$.

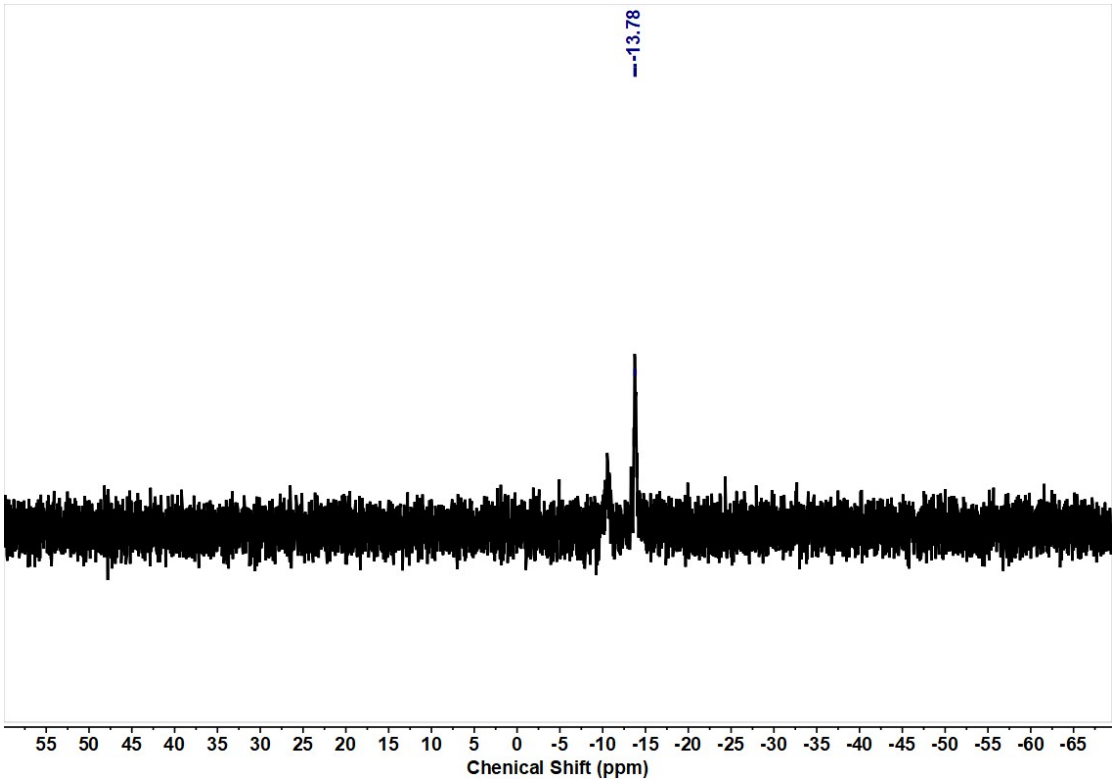

Fig. S3 ^{31}P-NMR spectrum of HTGCP in $CDCl_3$.

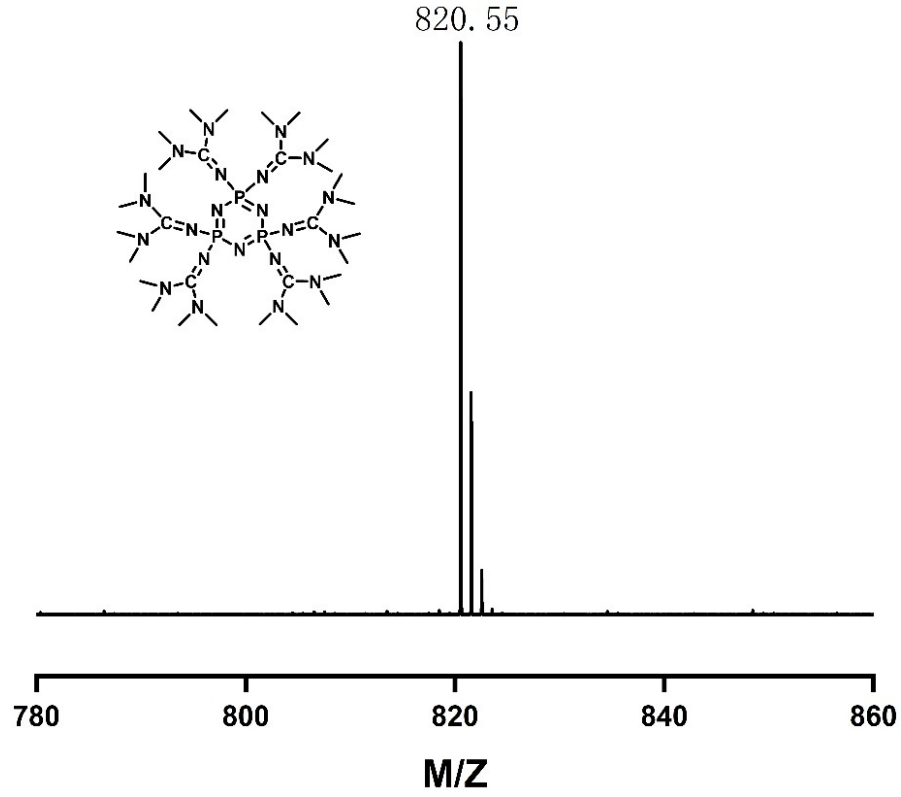

Fig. S4 ESI-MS spectrum of HTGCP.

NMR p*K*a Measurements and Determination. The p*K*a of **HTGCP** was

measured in CD_3CN using NMR method according to previous literature. The ^{13}C NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer at 101 MHz. The desired drug was prepared as a solution (approximately 0.1 mol/L) and placed in the NMR tubes. The pK_a values of phosphazenes were determined using an approximately equimolar mixture of phosphazene and indicator in CD_3CN. TBD with a known pK_a value of 26.0 was used as an indicator in this work. There is a fast (on the NMR time scale) exchange between phosphazene and the indicator base and their acid forms (equation (S1)), leading to the coalescence of NMR lines in the ^{13}C NMR spectra. Correspondingly, the chemical shifts of these forms were determined separately from the single component CD_3CN solutions of these species. The calculation of the ΔpK_a value of the phosphazene relative to the used indicator compound pK_a was performed on the basis of equations (S2). For the phosphazene, the calculation was performed according to equation (S3), while for the indicator the calculation was performed according to equation (S4).

$$PH^+ + TBD \rightleftharpoons P + TBDH^+ \qquad (S1)$$

$$\Delta pKa = lg([PH][TBD]/[P][TBDH]) \qquad (S2)$$

$$[P]/[PH] = [\delta - \delta_{PH}]/[\delta_P - \delta] \qquad (S3)$$

$$[TBD]/[TBDH] = [\delta - \delta_{TBD}]/[\delta_{TBDH} - \delta] \qquad (S4)$$

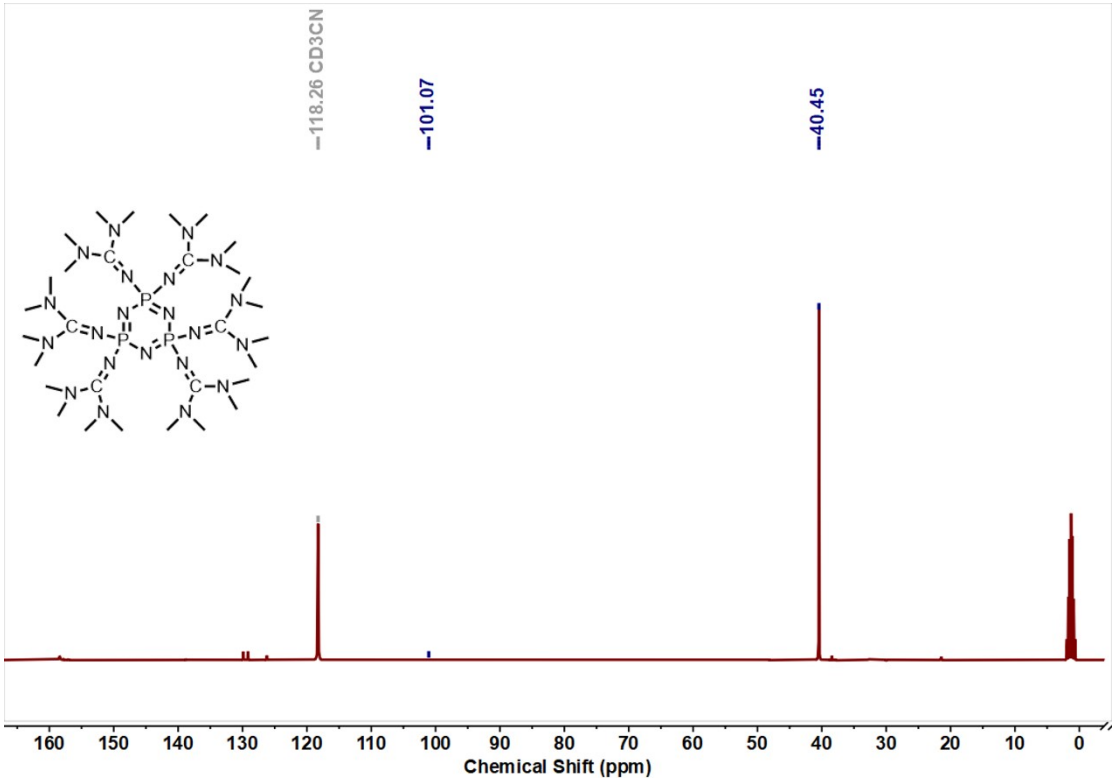

Fig. S5 ^{13}C-NMR spectrum of HTGCP in CD_3CN.

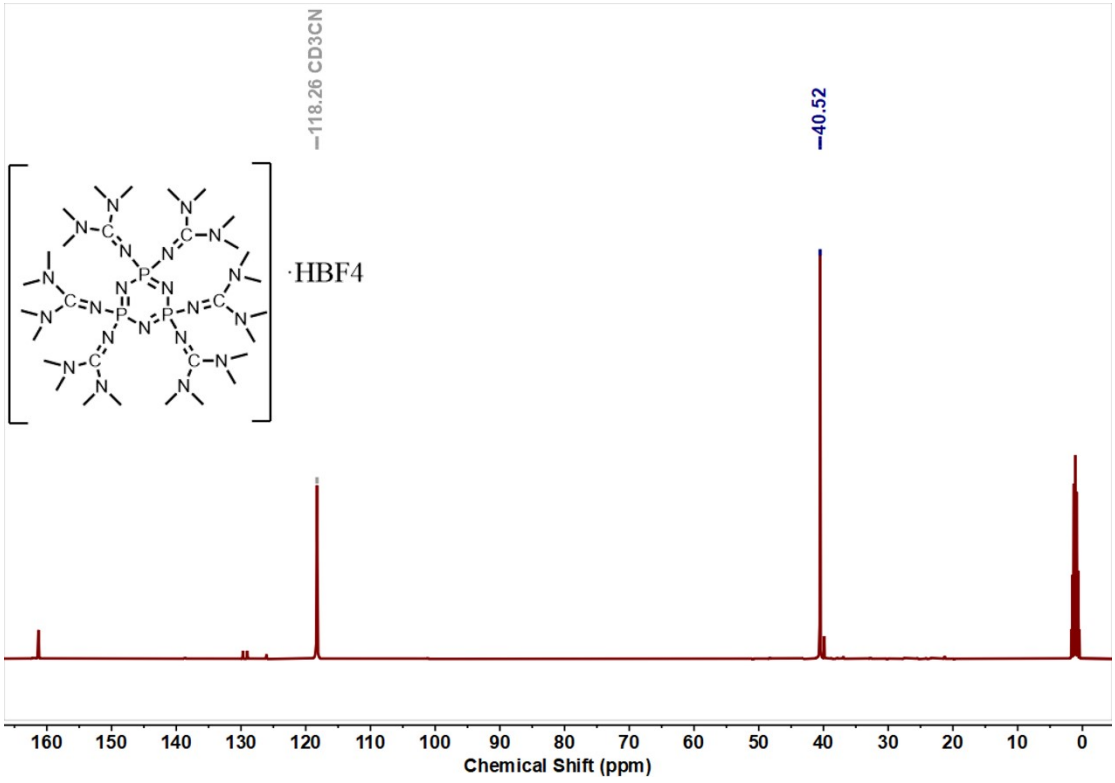

Fig. S6 ^{13}C-NMR spectrum of HTGCP + HBF_4 in CD_3CN.

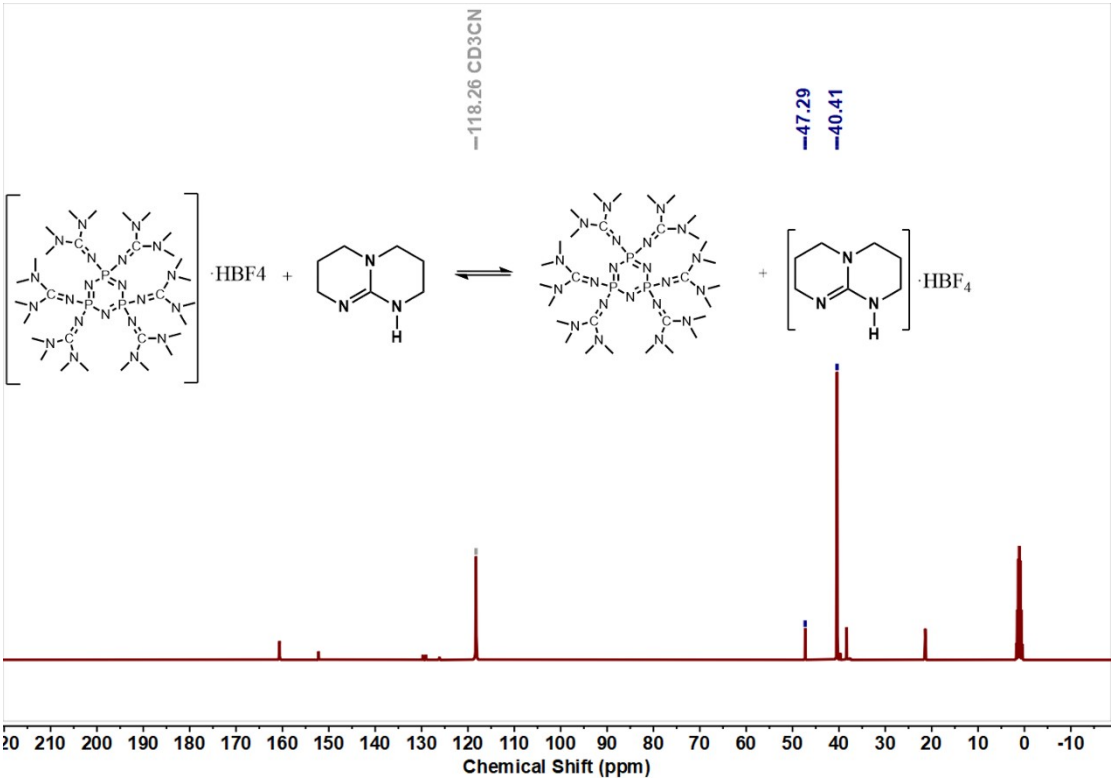

Fig. S7 ^{13}C-NMR spectrum of HTGCP+ HBF_4 + TBD in CD_3CN.

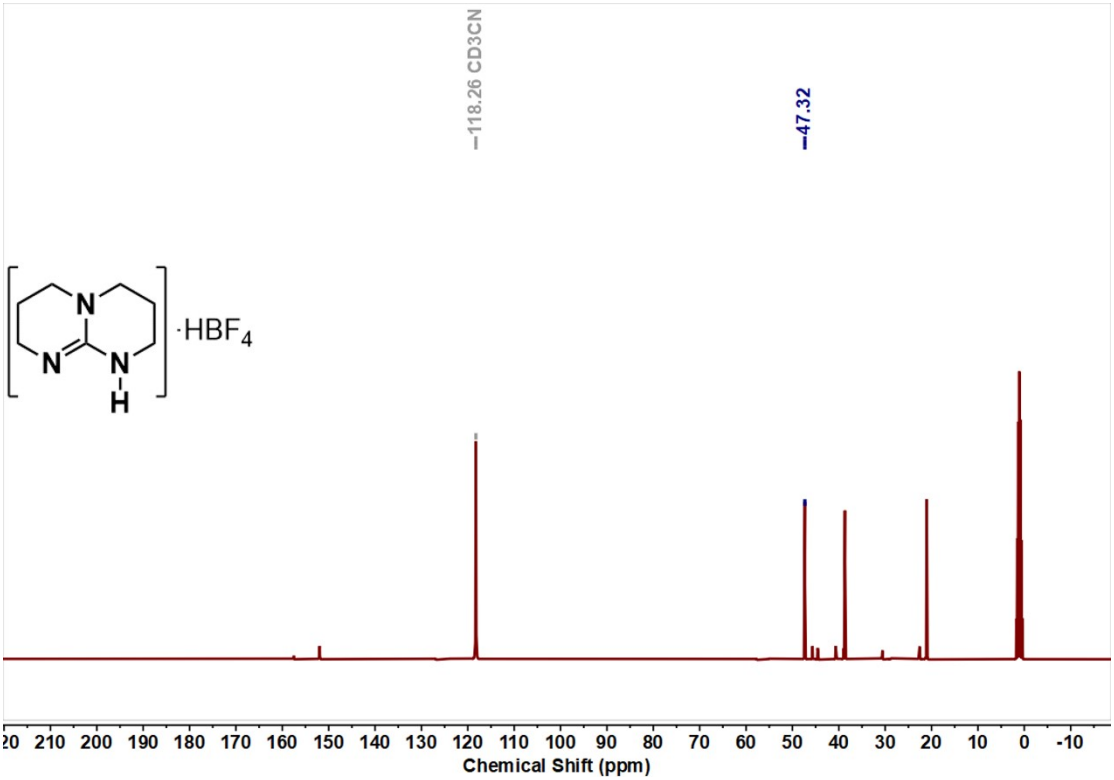

Fig. S8 ^{13}C-NMR spectrum of TBD + HBF_4 in CD_3CN.

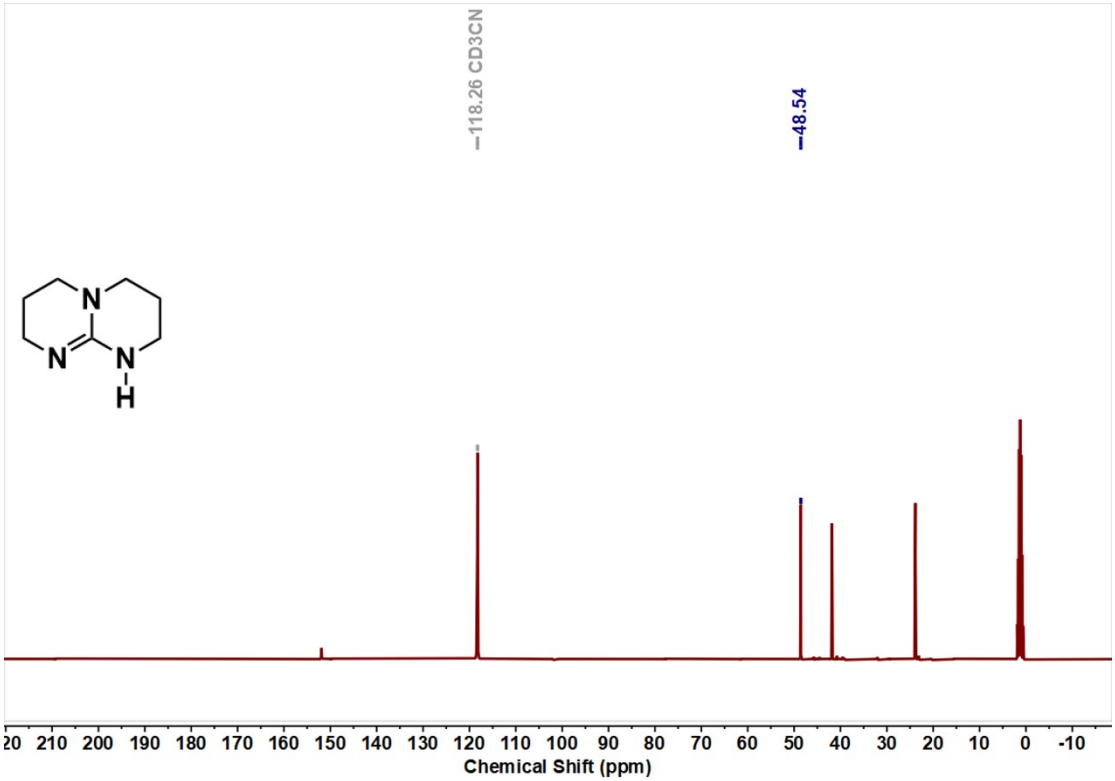

Fig. S9 ^{13}C-NMR spectrum of TBD in CD_3CN.

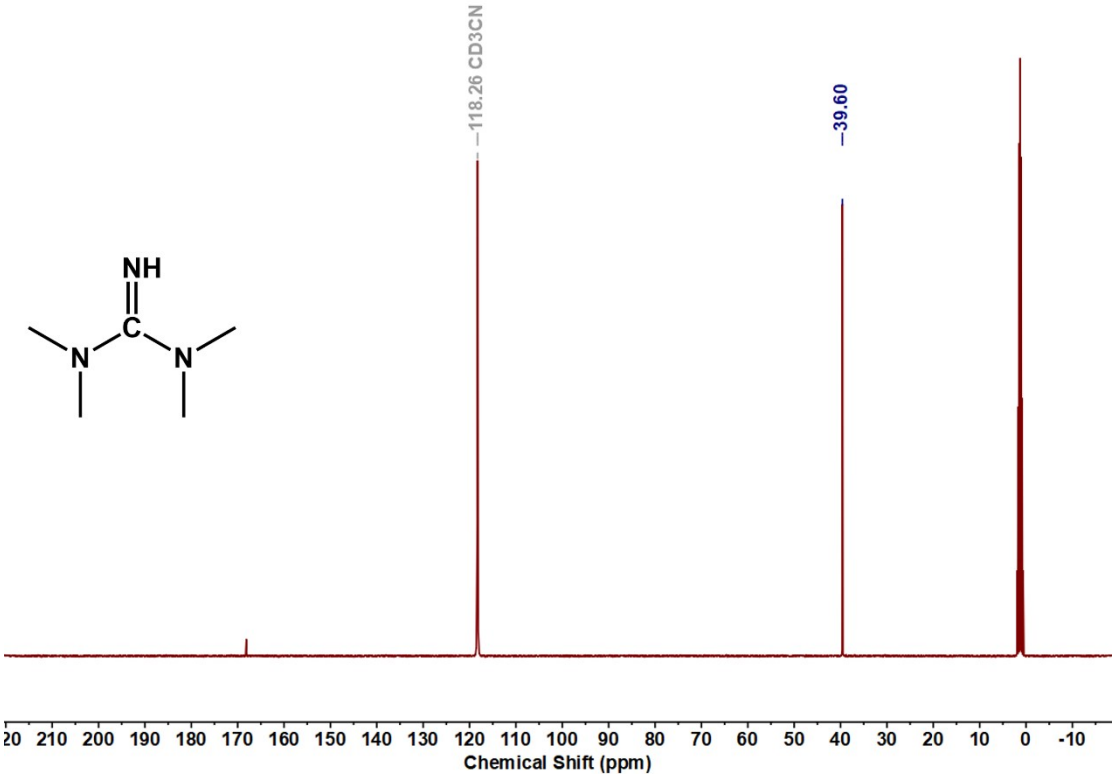

Fig. S10 ^{13}C-NMR spectrum of TMG in CD_3CN.

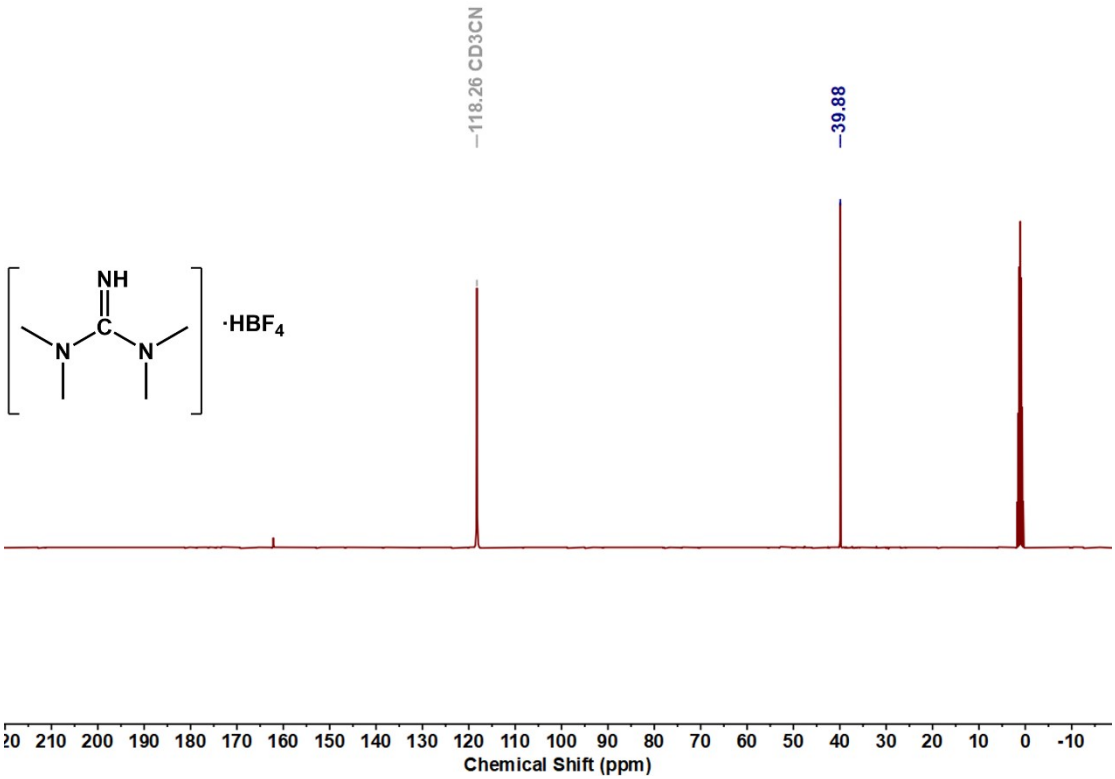

Fig. S11 ^{13}C-NMR spectrum of TMG + HBF_4 in CD_3CN.

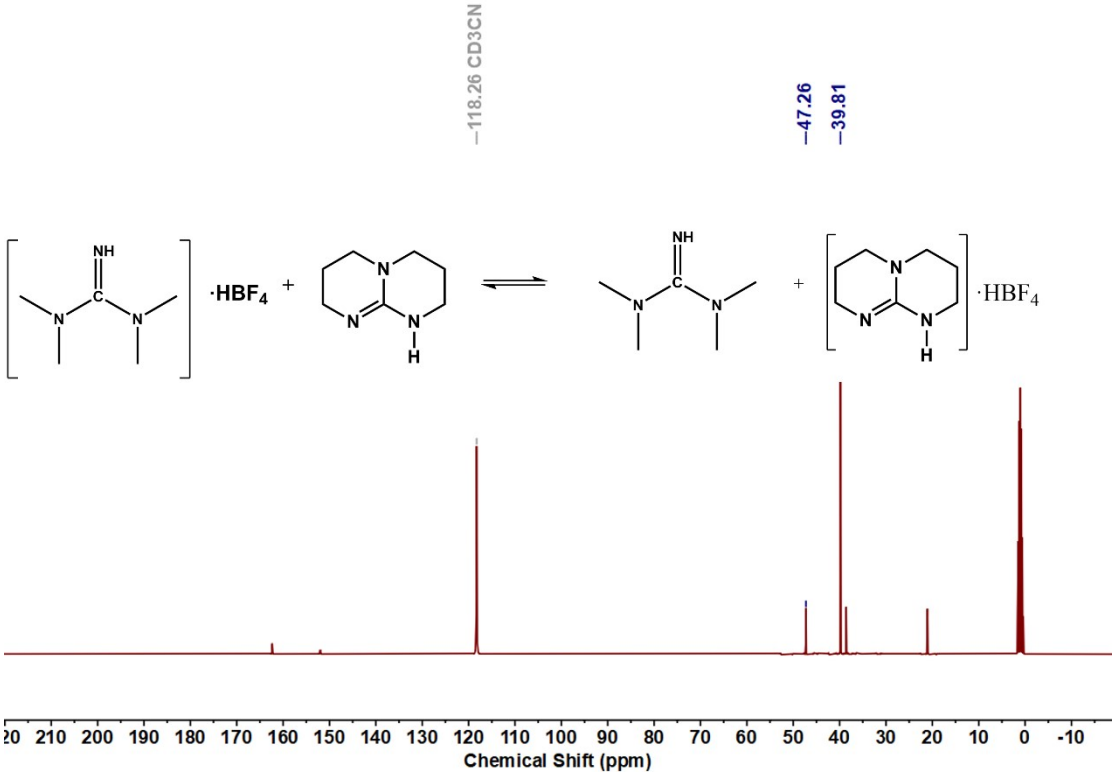

Fig. S12 ^{13}C-NMR spectrum of TMG+ HBF_4 + TBD in CD_3CN.

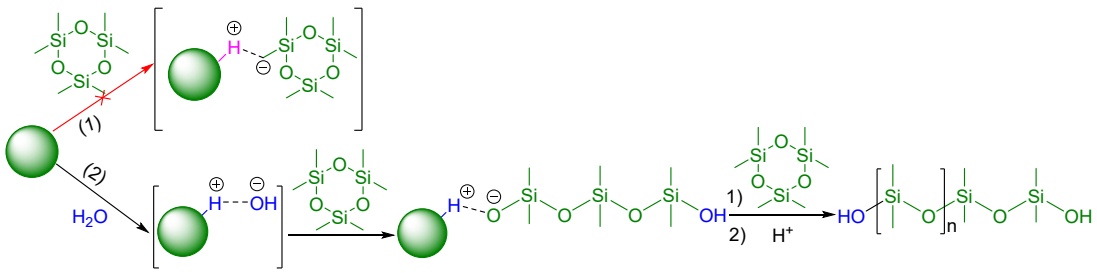

Fig. S13 Mechanism in the ROP of D_3 without initiator.

Two mechanisms have been proposed for this phenomenon: 1) the catalyst directly attacks the monomer to react shown in Figure 1 (1), 2) the interaction between trace water and catalyst forms the intermediate as shown in Figure 1 (2). Once this intermediate is formed, it acts as the active center to initiate the ROP of the monomer.

To elucidate the mechanism (1), HTGCP was mixed with 1 equivalent of D_3 in C_6D_6 at room temperature, and their chemical shifts were revealed in Figure S14. The respective peaks in the mixture remain independent without any change, indicating that there was no interaction between them, therefore, the ionic intermediates between the monomer and the catalyst do not form. It means that methyl deprotonation does not occur. As a result, mechanism (1) is not feasible.

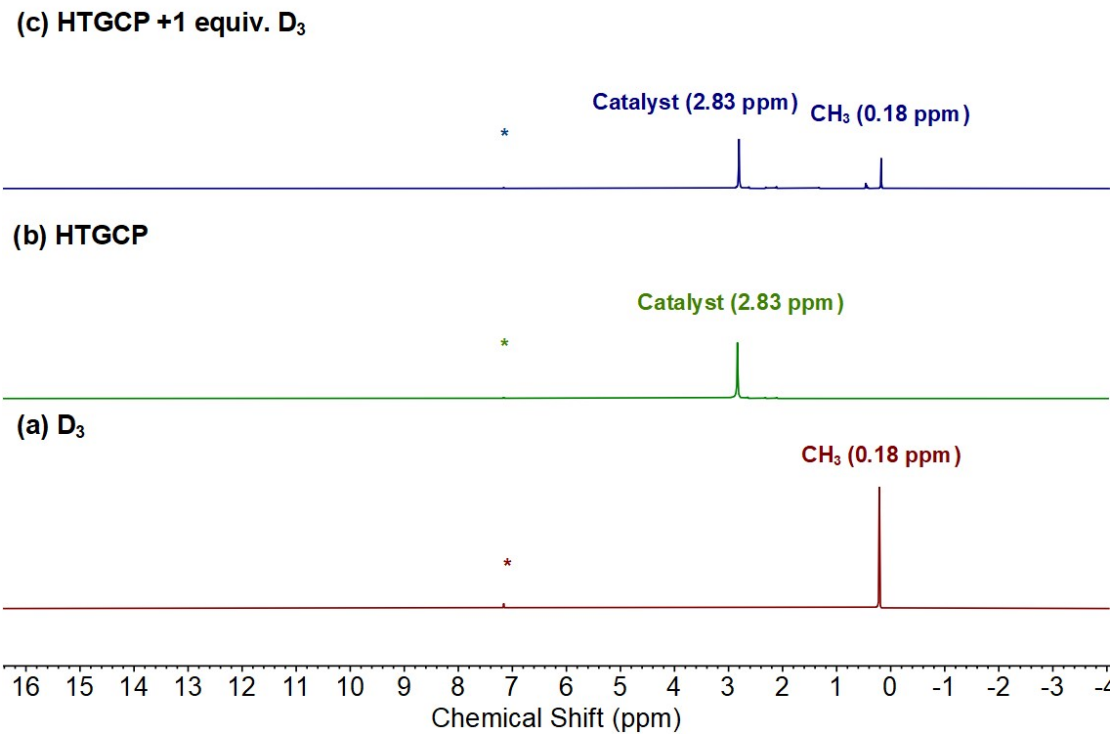

Fig. S14 ^{1}H-NMR spectra of D_3 (a) catalyst HTGCP (b) and their equimolar mixture (c) in C_6D_6.

The ^{1}H-NMR spectra of PDMS in the absence of an initiator as shown in Figure S15, discover that its structure was consistent with that of the product obtained with water as initiator. Since the trace water is hard to be removed completely, the resulting polymer may contain the HO-PDMS-OH more or less. The Figure S16 of MALDI-TOF MS spectra also proves this phenomenon (Table 1, run 15). In this characterization, a set of molecular ion peaks were found to be consistent with the molecular weight of HO-PDMS-OH by the relationship (M_n = 74.2 n + 18.0 (H_2O) + 107.9 (Ag^+)), confirming that trace water may act as the initiator in the reaction. Consequently, it can be presumed that mechanism (2) is feasible.

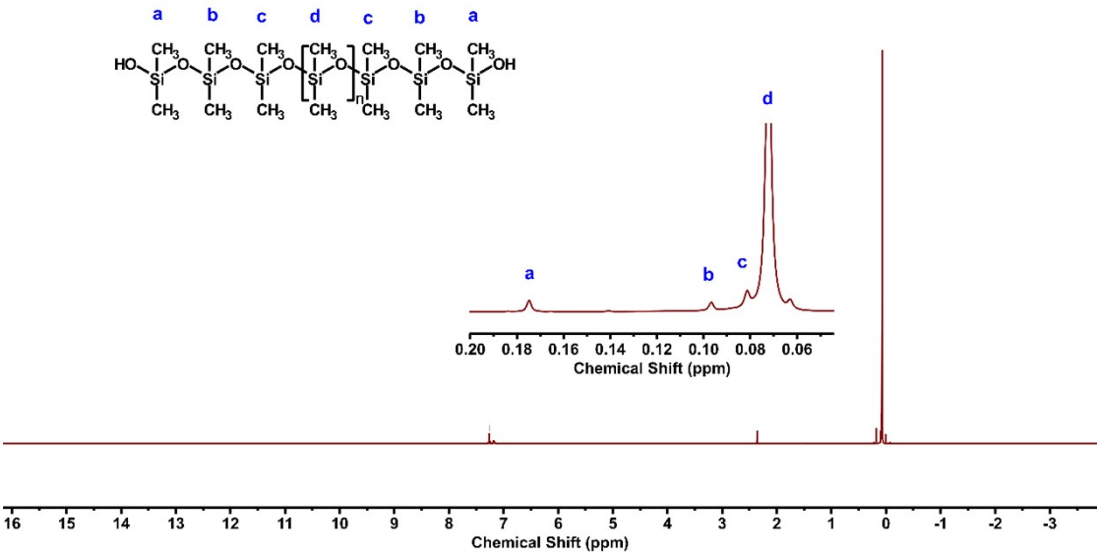

Fig. S15 ^{1}H-NMR spectra of the synthesized PDMS([*M*]/[*I*]/[*C*]=100/0/1,Table1,run 1）

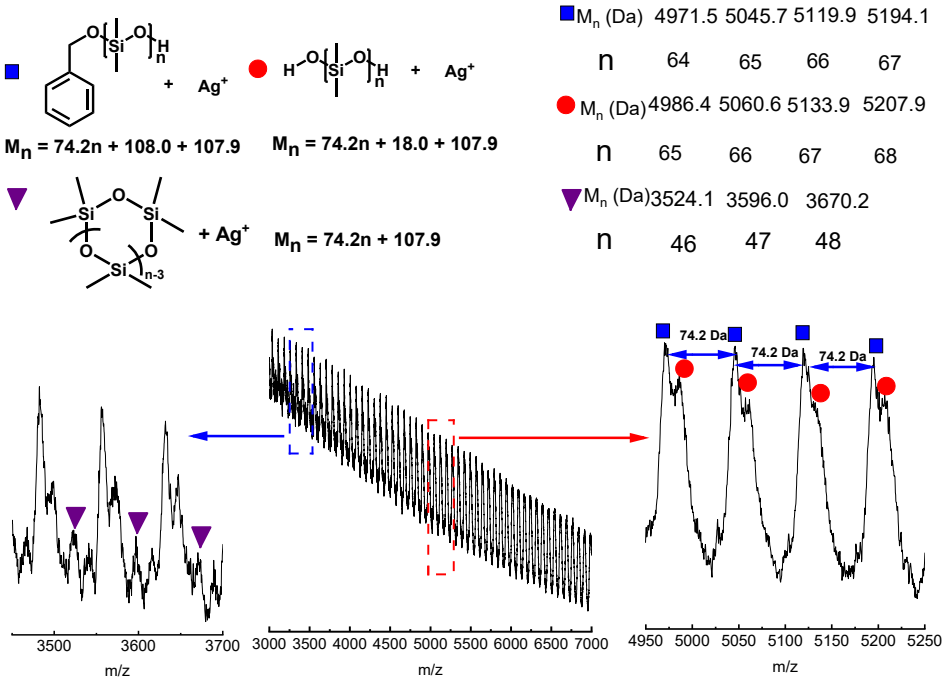

Fig. S16 MALDI-TOF MS spectrum of the synthesized PDMS (Table 1, run 15).

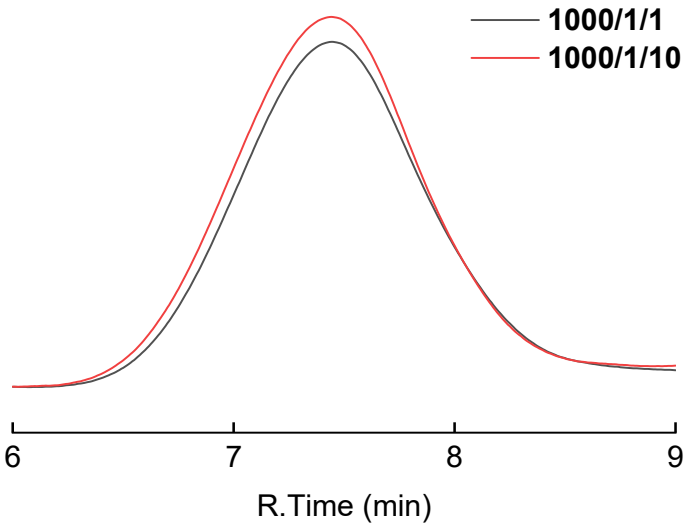

Fig. S17 Overlay of GPC curves at different catalyst dosage (Table 1, runs 9 ~ 10).

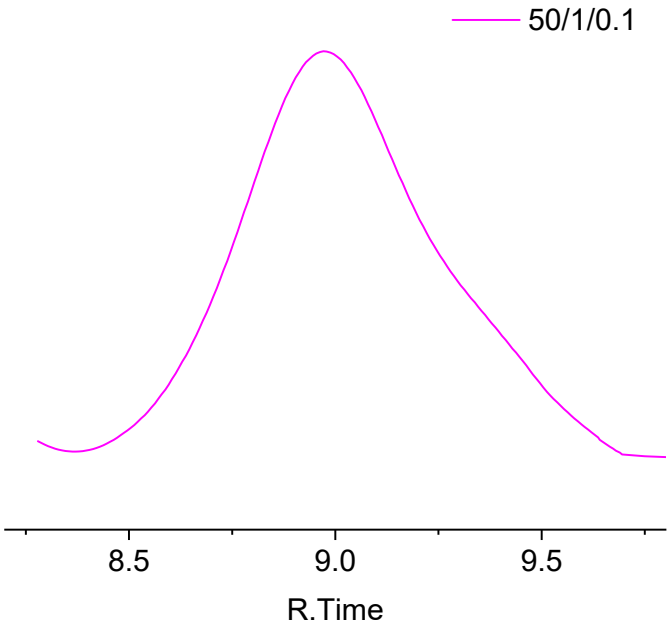

Fig. S18 GPC operating curve at [*M*]/[*I*]/[*C*] = 50/1/0.1 (Table 1, run 15).

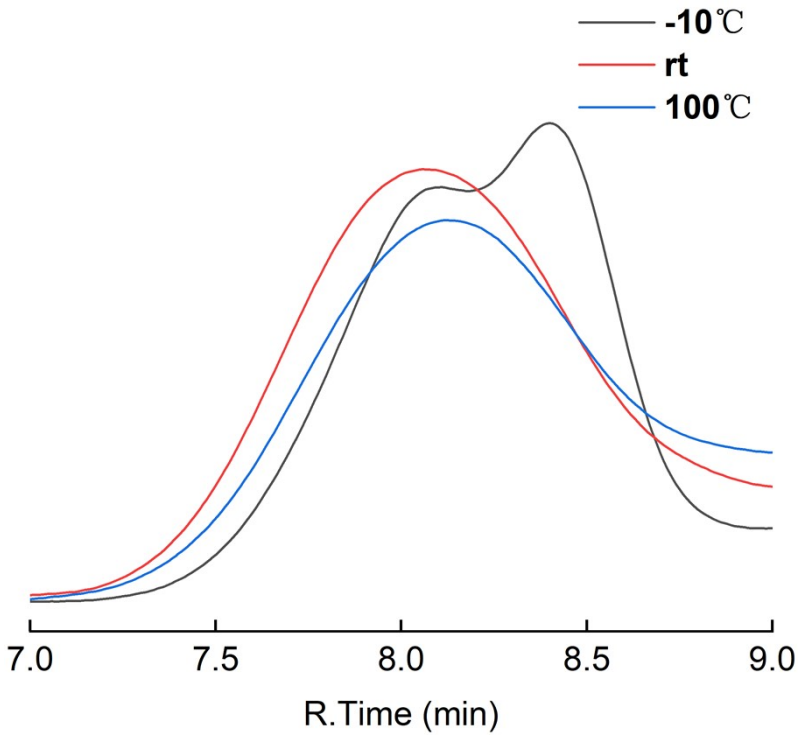

Fig. S19 Overlay of GPC curves at different temperatures(Table 1, runs 7,13 and 14).

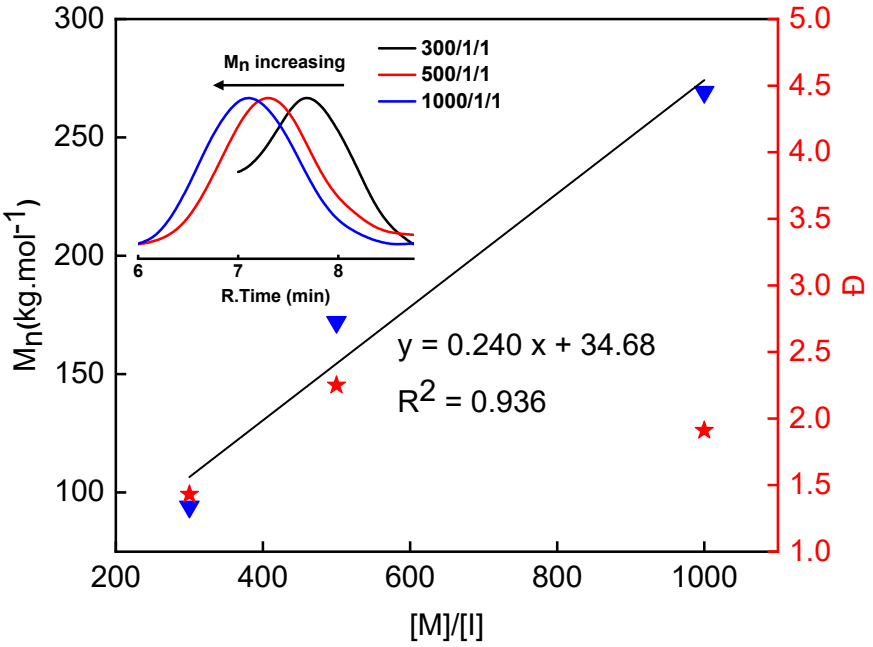

Fig. S20 Evolutions of Mn and Đ as a function of [*M*]/[*I*] ratio(Table 2, runs 1 ~ 3).Insert: Overlay of GPC curves at different [*M*]/[*I*]/[*C*] ratios.

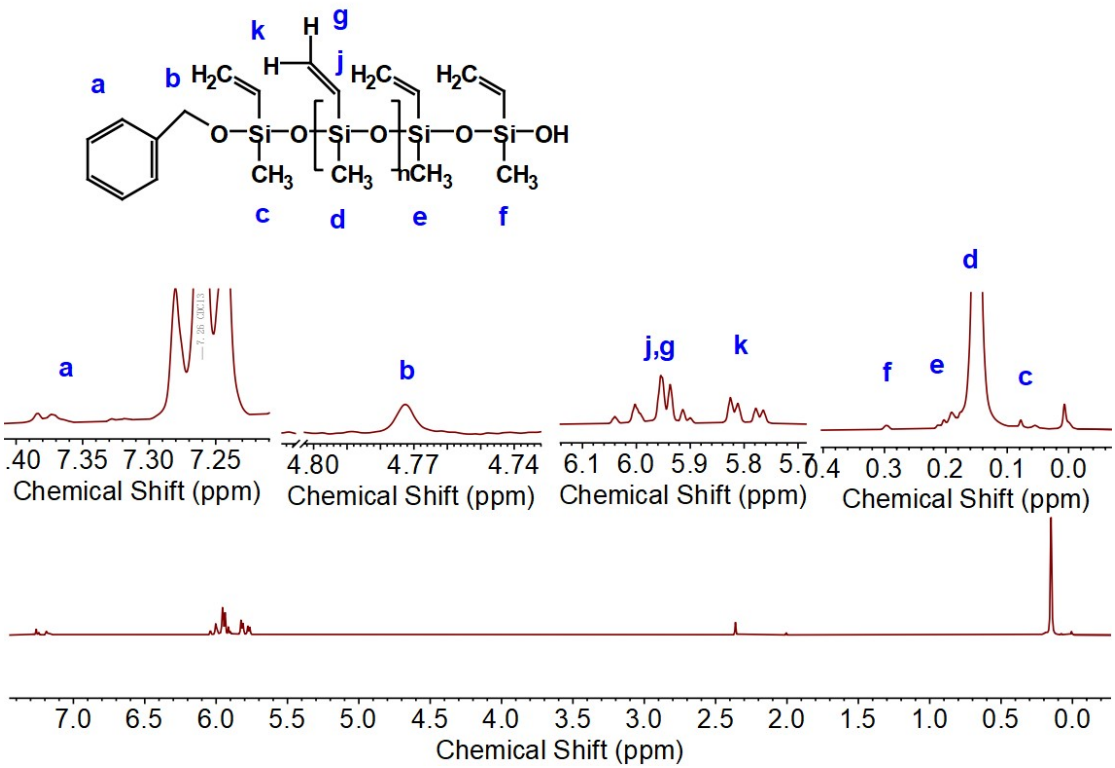

Fig. S21 ^{1}H-NMR spectra of the PMVS sample (Table 1, Run 23) in $CDCl_3$.

Table S1. ROP of V_4 using HTGCP as catalyst at different temperatures [a]

Run	[*M*]/[*I*]/[*C*]	T (℃)	Time (min)	*Conv.*[b] (%)	$M_{n,theory}$[c] (kg/mol)	$M_{n,GPC}$[d] (kg/mol)	Đ[d]
1	500:1:1	0	120	17	29.4	39.3	1.53
2	500:1:1	25	30	92	153.5	112.3	1.90
3	500:1:1	40	7	93	160.4	148.2	1.84
4	500:1:1	70	3	89	153.5	107.9	1.96
5	500:1:1	100	1	92	158.7	124.3	2.03

[a] Conditions: [D_3] = 2.5 mol/L in toluene, HTGCP 0.05 mmol, [*M*]/[*I*]/[*C*] = Monomer/Initiator/Catalyst.

[b] Determined by ^{1}H NMR.

[c] $M_{n,theory}$= [*M*]/[*I*] × *Conv.* × (M_W. of V_4=344) + (M_W. of terminal structures).

[d] Determined by GPC at 40 ℃ in THF relative to polystyrene standards.

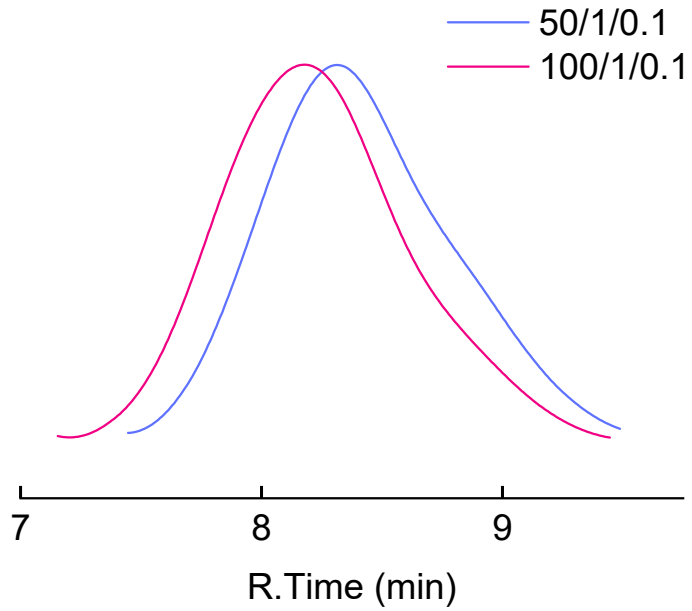

Fig. S22 Overlay of GPC curves at different [*M*]/[*I*]/[*C*] ratios(Table 2, runs 12 ~ 13).

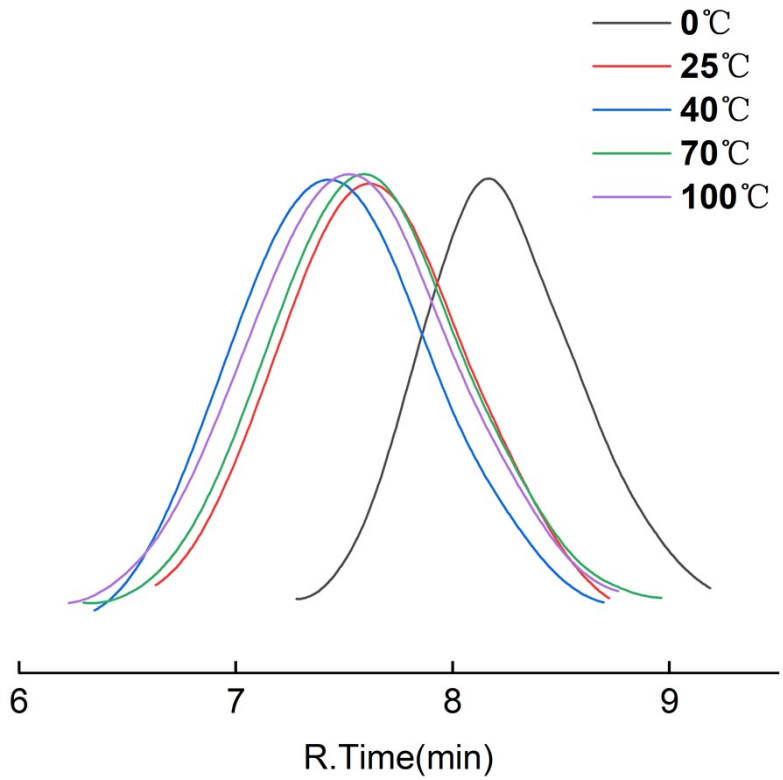

Fig. S23 Overlay of GPC curves at at different temperatures(Table S1, runs 1~5)

Table S2. Kinetic study of the ROP of D_3 using HTGCP.

[*M*]/[*I*]/[*C*]	Time (min)	*Conv.*[a] (%)	M_n[b] (kg·mol^{-1})	Đ[b]	$K_{p,app}$ (min^{-1})	k_p (L·mol^{-1}·min^{-1})
250:1:1	30	>99	55.5	1.35	0.19	19

250:1:0.75	30	94	50.4	1.36	0.096	9.6
250:1:0.5	40	84	47.0	1.40	0.041	4.1
250:1:0.25	45	73	40.7	1.35	0.027	2.7

[a] Determined by ^{1}H NMR.

[b] Determined by GPC at 40 ℃ in THF relative to polystyrene standards.

Table S3. Kinetic study of the ROP D_3 in the [*M*]/[*I*]/[*C*]=250:1:1.

Time(min)	*Conv.*(%)[a]	M_n(kg·mol^{-1})[b]	Đ[b]
2	43	21.0	1.35
5	56	29.7	1.31
10	83	43.6	1.42
20	96	51.2	1.42
30	>99	55.5	1.35

[a] Determined by ^{1}H NMR.

[b] Determined by GPC at 40 ℃ in THF relative to polystyrene standards.

Table S4. Kinetic study of the ROP D_3 in the [*M*]/[*I*]/[*C*]=250:1:0.75.

Time(min)	*Conv.*(%)[a]	M_n(kg·mol^{-1})[b]	Đ[b]
5	41	20.5	1.20
10	57	31.7	1.27
15	71	38.9	1.33
20	88	48.0	1.34
30	94	50.4	1.36

[a] Determined by ^{1}H NMR.

[b] Determined by GPC at 40 ℃ in THF relative to polystyrene standards.

Table S5. Kinetic study of the ROP D_3 in the [*M*]/[*I*]/[*C*]=250:1:0.5.

Time(min)	*Conv.*(%)[a]	M_n(kg·mol^{-1})[b]	Đ[b]
5	38	13.1	1.21
10	47	22.8	1.26
20	67	34.2	1.37
30	79	41.9	1.36
40	84	47.0	1.40

[a] Determined by ^{1}H NMR.

[b] Determined by GPC at 40 ℃ in THF relative to polystyrene standards.

Table S6. Kinetic study of the ROP D_3 in the [*M*]/[*I*]/[*C*]=250:1:0.25.

Time(min)	*Conv.*(%)[a]	M_n(kg·mol^{-1})[b]	Đ[b]
5	18	7.3	1.05
10	29	11.9	1.15
25	51	27.0	1.25
35	63	36.7	1.29
45	73	40.7	1.35

[a] Determined by ^{1}H NMR.

[b] Determined by GPC at 40 °C in THF relative to polystyrene standards.

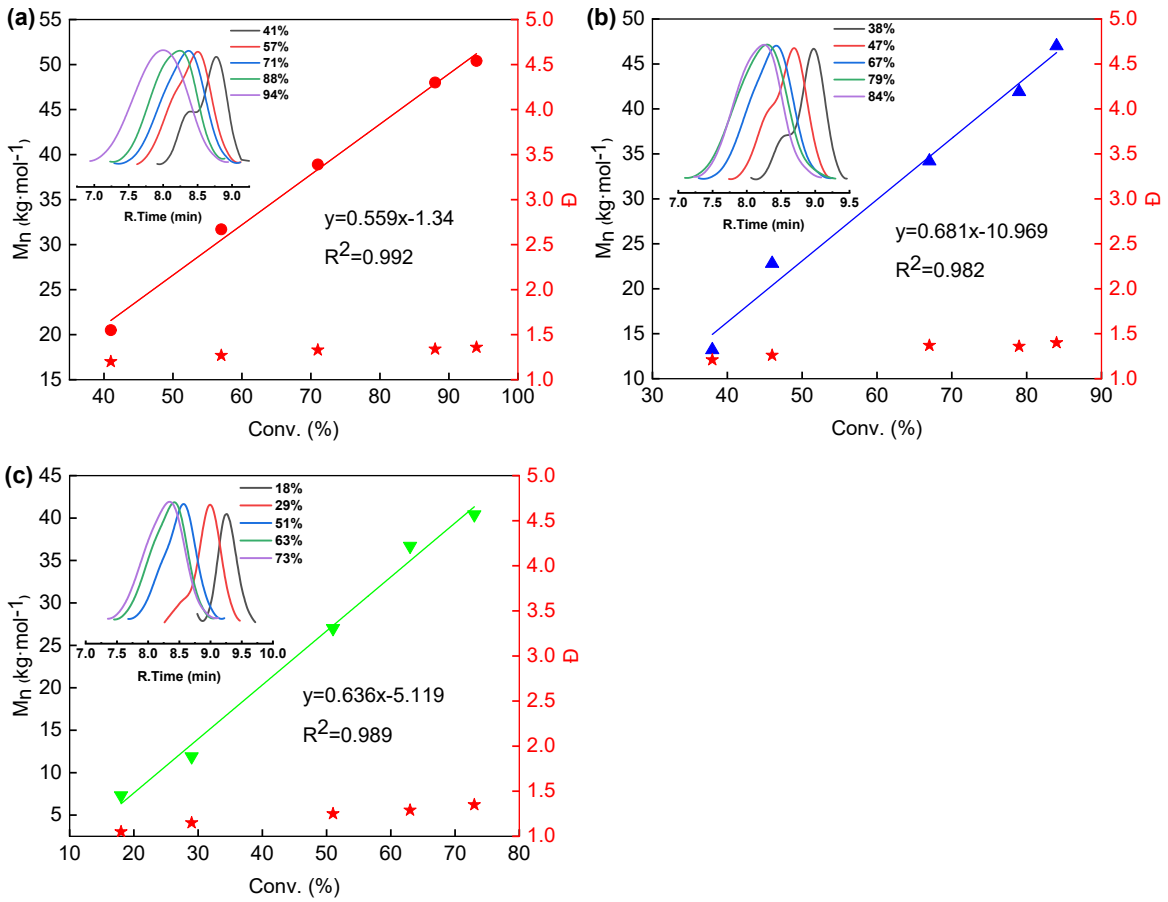

Fig. S24 Plots of Mn and Đ as a function of monomer conversion at a [*M*]/[*I*]/[*C*] ratio of 250:1:(0.75 ~ 0.25) (a) ~ (c). Inset: Overlay of GPC curves at different monomer conversions.

Table S7. ROP of D_3 using TMG as the catalyst at room temperature [a]

Run	[*M*]/[*I*]/[*C*]	T (°C)	Time (min)	*Conv.*[b] (%)	$M_{n,theory}$[c] (kg·mol^{-1})	$M_{n,GPC}$[d] (kg·mol^{-1})	Đ[d]
1	100/1/1	rt	10	16.0	3.67	n.d.	n.d.[e]
2	100/1/1	rt	60	18.7	4.27	n.d.	n.d.
3	200/1/1	rt	180	10.7	4.87	n.d.	n.d.
4	100/1/6	rt	10	19.4	4.42	n.d.	n.d.

[a] [*M*]/[*I*]/[*C*] = Monomer/Initiator/Catalyst.

[b] Determined by ^{1}H NMR.

[c] $M_{n,theory}$= [*M*]/[*I*] × *Conv.* × (M_W. of monomer) + (M_W. of terminal structures).

[d] Determined by GPC relative to polystyrene standards.

[e] Not determined.

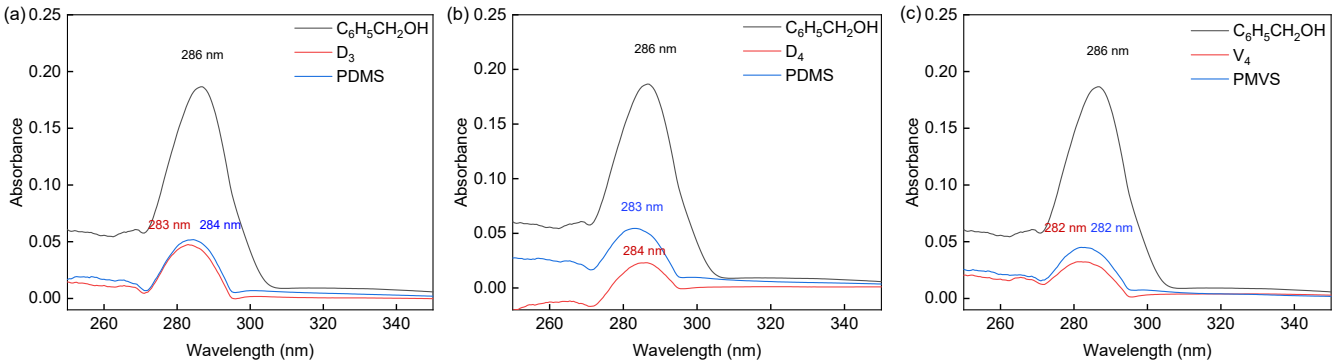

Fig. S25 Comparison of UV absorption spectra of reaction materials ($C_6H_5CH_2OH$, D_3, D_4, V_4) and polymers (PDMS, PMVS) (a) ~ (c).

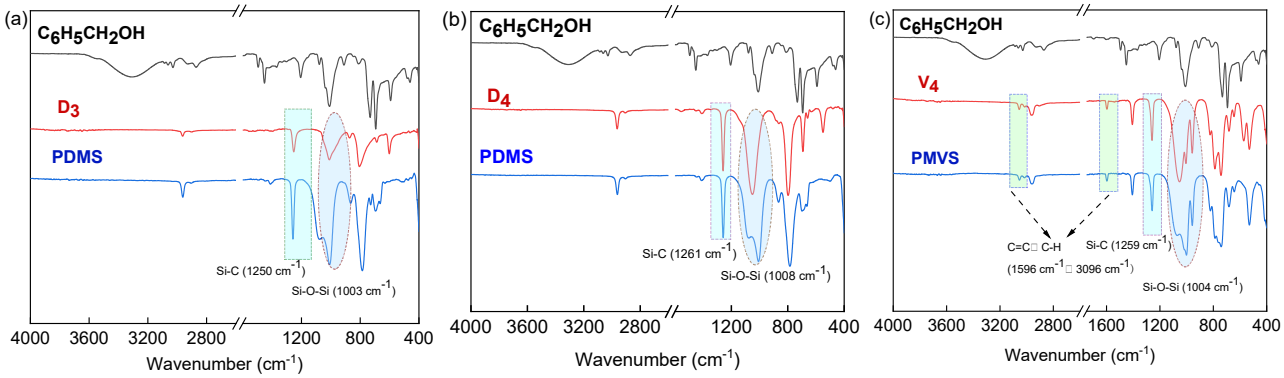

Fig. S26 Comparison of FT-IR spectra of reaction materials ($C_6H_5CH_2OH$, D_3, D_4, V_4) and polymers (PDMS, PMVS) (a) ~ (c).