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Upgrade Traditional KOH Catalyzed Ring-Opening Polymerization of Cyclosiloxanes to More Efficient Process by Adding Catalytic Phosphazenium Salt as Cocatalyst

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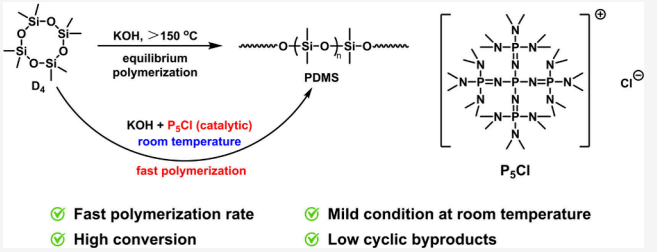
ABSTRACT: The development of efficient catalyst to overcome the limitation of equilibrium ring-opening polymerization (ROP) of cyclosiloxanes represents the most appealing solution to resolve the back-biting side reaction and high energy consumption during the traditional polysiloxane production. In this contribution, equilibrium polymerization of octamethylcyclotetrasiloxane (D_4) catalyzed by KOH at high temperature was shifted to more efficient polymerization at ambient conditions via fast kinetics and back-biting suppressing by adding a catalytic amount of phosphazenium salt as cocatalyst. Polydimethylsiloxanes (PDMSs) were synthesized in high conversion (≥90%) by bulky phosphazenium salt P_5Cl/KOH catalyzed ROP of D_4 at room temperature in THF solution. The ratio of P_5Cl could be lowered to 0.001 mol % of D_4, and the back-biting reactions were negligible as evaluated by *in situ* ^1H NMR characterization of the polymerization system. Kinetics investigations suggested that the fast and controlled manner of the ROP was promoted by the P_5Cl/KOH combination. Furthermore, bulk ROP of D_4 and octaphenylcyclotetrasiloxane (P_4) catalyzed by activated phosphazenium salt P_5OMe conveniently afforded PDMSs with different molecular weights (up to 1616 kg mol^{-1}) and poly(dimethylsiloxane-*co*-diphenylsiloxane) (PMPS) copolymers with different diphenylsiloxane contents (8.4−63.8 mol %) at 100 °C. The good random characteristic of PMPS copolymers were thoroughly verified by $^1H/^{29}Si$ NMR and thermodynamic measurements.



INTRODUCTION

The unique Si−O−Si backbone of polysiloxanes endows them with exceptional thermal stability, low-temperature flexibility, and remarkable radiation resistance, making them ideal candidates for a wide range of applications in extreme environments.[1−5] Ring-opening polymerization (ROP) of cyclosiloxanes represents a widely employed strategy for the synthesis of high molecular weight polysiloxanes with good controllability.[3,6−11] Many kinds of organic and inorganic catalysts have been proved effective for the ROP of cyclosiloxanes, such as metal hydroxides, acid catalysts,[12−17] metal silanolates, tetraalkylammonium hydroxide, phosphazene bases,[9,18−24] phosphonium ylides,[10,25] N-heterocyclic carbenes (NHC),[26,27] and guanidines.[7,8,28] As one of the earliest catalysts used for the ROP of cyclic siloxanes, potassium hydroxide (KOH) is still the most commonly used catalyst in industrial production of polysiloxanes. However, high temperature (>150 °C) is necessary for the polymerization to proceed and long polymerization time is needed to reach the equilibrium for high monomer conversion in the KOH catalyzed ROP of cyclosiloxanes.[2,29] High polymerization temperature then results in the unavoidable occurrence of back-biting reactions that lead to the undesirable byproducts of cyclic oligosiloxanes with different sizes. It is highly desirable to find more efficient catalysts balanced with synthesis conditions to prepare polysiloxane materials with less back-biting reactions.[6] Although it is impossible to overcome the thermodynamic limitation on equilibrium polymerization, a more efficient catalyst accompanied by benign polymerization conditions will certainly promote formation of polysiloxane with less or negligible back-biting side-reactions. Therefore, a fast and energy-efficient polymerization process with high monomer conversion and low volatile organic compounds (VOC) under mild conditions is also urgently needed to cut the costs. For the anionic ROP of cyclosiloxanes, the polymerization rate increases strongly with the size of the counterion: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim Et_4N^+ \sim Et_4P^+$.[18,29] The increased polymerization activities were derived from the less electrophilic bulky cations and weaker ion pairing, leading to the increased concentration of free anions in the polymerization system. Accordingly, phosphazene bases with

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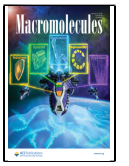

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Scheme 1. ROP of D_4 Catalyzed by P_5Cl/KOH at Room Temperature

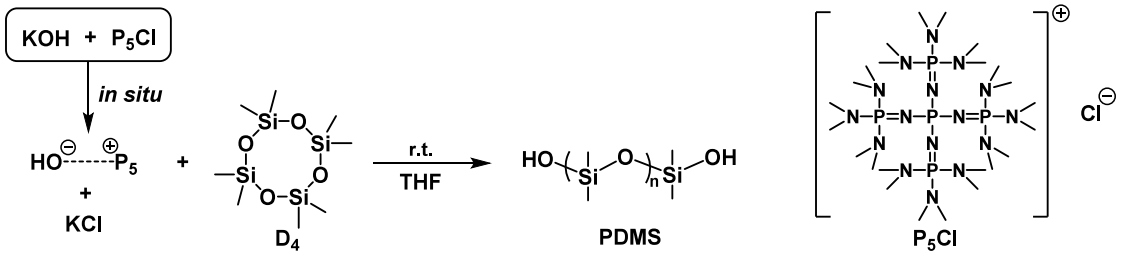

Table 1. ROP of D_4 Catalyzed by P_5Cl/base[a]

run	base	initiator	$[D_4]_0/[I]_0/[base]_0/[P_5Cl]_0$	conv (%)[b]	M_n^{theor} (kg mol^{-1})[c]	M_n^{GPC} (kg mol^{-1})[d]	$Đ$[d]
1	KOH		1000/0/1/0	0		nd	nd
2	KOMe		1000/0/1/0	0		nd	nd
3	*t*-BuOK		1000/0/1/0	0		nd	nd
4			1000/0/0/1	0		nd	nd
5		BnOH	1000/1/0/1	0		nd	nd
6	CH_3COONa		1000/1/1/1	0		nd	nd
7	KOH		1000/0/1/0.1	90	90.8	241.3	1.59
8[e]	KOH		1000/0/1/0.1	36	40.5	446.6	1.60
9	KOH		1000/0/1/0.01	90	90.8	299.3	1.63
10[f]	KOH		1000/0/0.1/0.01	91	163.6	1356.0	1.16
11	KOH	H_2O	1000/9/1/0.1	96	25.3	45.4	1.67
12	KOH	H_2O	1000/19/1/0.1	51	7.1	26.4	1.64
13[g]	KOH	H_2O	1000/19/1/0.1	92	13.2	82.9	1.48
14	*t*-BuOK		1000/0/1/0.1	92	92.8	163.2	1.76
15	KOMe		1000/0/1/0.1	93	93.8	153.4	1.64
16	KOMe		1000/0/1/0.01	90	90.8	289.6	1.87

[a]The polymerizations were carried out in THF for 60 min at 25 °C, $[D_4]_0$ = 2.8 mol·L^{-1}. [b]Determined by ^{1}H NMR. [c]Calculated from $M_n^{theor} = M_{D4}$ (296.6 g/mol) × ($[D_4]_0/[base+H_2O]_0$) × conversion + $M_{initiator}$. [d]Determined by GPC at 40 °C in THF using standard polystyrene as reference. [e]The polymerization was performed in bulk. [f]The polymerization was performed in toluene solution at 100 °C. [g]The polymerization was performed in toluene solution at 100 °C for 10 min.

largest molecular size exhibited highest catalytic activity toward the anionic ROP of cyclic siloxanes.[18,19,22]

As one type of important organocatalyst, phosphazene bases have proven efficient catalysts in the ROP of various kinds of cyclic monomers including cyclosiloxanes.[30−34] In 1995, Möller et al. reported the ROP of octamethylcyclotetrasiloxane (D_4) using the commercially available phosphazene base *t*-BuP_4 as catalyst and methanol as initiator.[18] The polymerization rate was much faster than the conventional alkali metal hydroxide catalysts and the equilibrium could be rapidly reached within 1 min in toluene solution at room temperature, giving polydimethylsiloxanes (PDMSs) with molecular weights up to 440 kg mol^{-1}.[18,19] However, due to the extensive occurrence of back-biting reaction, the product of the ROP was a mixture of high polymer (up to 80%), macrocyclics, and small rings. The *t*-BuP_4 also proved to be highly efficient for the ROP of tetraphenyltetramethylcyclotetrasiloxane (P_4^{Me}) at room temperature both in bulk and in toluene solution with a polymerization rate of up to 1.6 min^{-1}.[35] In the past few years, our group has made great efforts in the phosphazene catalyzed ROP of different cyclosiloxanes. Self-developed cyclic trimeric phosphazene base (CTPB) with bulky spherical structure and moderate basicity was highly efficient for the ROP of D_4 and hexaethylcyclotrisiloxane (E_3) at room temperature.[22,23] Furthermore, ring-opening copolymerization (ROCP) of D_4 with E_3, P_4^{Me}, ooctaphenylcyclotetrasiloxane (P_4), and 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane (V_4) could also be efficiently mediated by CTPB, yielding copolysiloxanes with polymer composition close to the monomer feeding ratio.[1,22,23,36,37] C_3N_3-Me-P_3, a cyclic phosphazene with a smaller size and lower basicity, could realize the ROP of hexamethylcyclotrisiloxane (D_3) at room temperature. The ROP proceeded in a fast and kinetically controlled manner, and the molecular weights and polymer structure of the resulted linear polymers were well-defined.[9] In addition to phosphazene bases, tetrakis[tris(dimethylamino)-phosphoranylidenamino]phosphazenium hydroxide ($P_5^+OH^-$) prepared from the precursor tetrakis[tris-(dimethylamino)phosphoranylidenamino]phosphazenium chloride (P_5Cl) by simple anion exchange could also catalyze the ROP of D_4 at high temperature (≥100 °C) within minutes to prepare PDMS polymers with M_n up to 51.2 kg mol^{-1}.[21] The $P_5^+OH^-$ was seen to exhibit sluggish behavior at low catalyst concentrations and low reaction temperatures, which may be a reflection of basicity differences with *t*-BuP_4. The tetrakis[tris(dimethylamino)phosphoranylidenamino]-phosphazenium cation (P_5^+) has the similar molecular size as the strongest phosphazene base *t*-BuP_4.[21] Apart from the ROP of cyclosiloxanes, phosphazenium salts have been used as catalyst in the polymerization of methacrylate,[38,39] propylene oxide (PO),[40−42] and epoxide copolymerization.[43−46]

Recently, Kato et al. reported a thermodynamically controlled ROP of D_4 without producing undesirable cyclic oligosiloxanes.[10] A well-designed phosphazenium cation prepared from phosphonium ylide was adopted as a self-quenching system in response to the loss of coordinating

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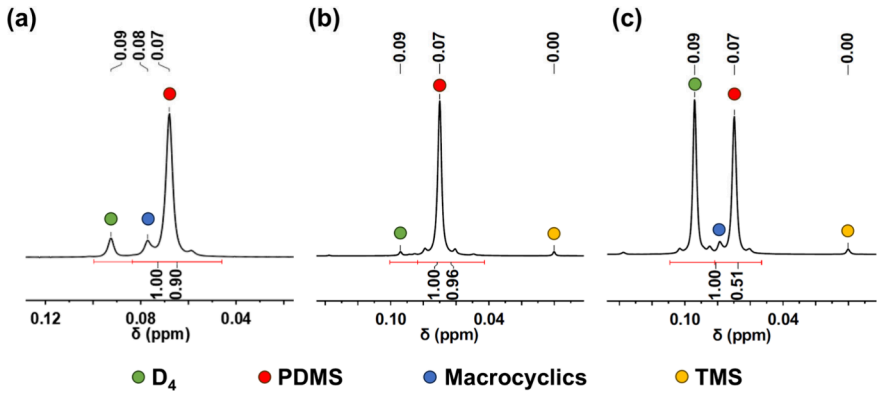

Figure 1. ^{1}H NMR spectra of the crude product in the ROP of D_4 taken after the addition of acetic acid in $CDCl_3$: (a) run 7; (b) run 11; (c) run 12 in Table 1.

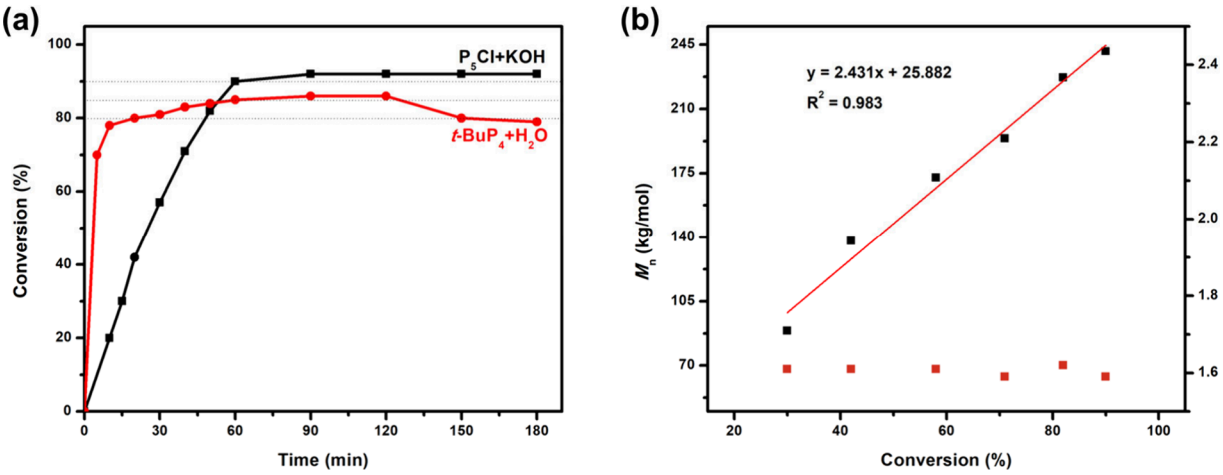

Figure 2. (a) First-order kinetics plots and (b) dependence of M_n resulting PDMS on the monomer conversion for ROP of D_4 (under the same condition as run 7 in Table 1; black squares represent M_n, and red squares represent $Đ$).

alcohols. Inspired by this pioneering work, we hypothesized that weaker coordination between bulky P_5^+ cation and the anionic silanolate chain end should increase steric hindrance around the nucleophilic site in the KOH catalyzed ROP of cyclosiloxanes to reduce the back-biting side reactions. Also, we speculated that the catalytic activity of KOH could be dramatically improved with the addition of P_5Cl due to the large size of the P_5^+ counterion. Herein, we reported the fast kinetically controlled ROP of D_4 mediated by the P_5Cl/KOH catalytic system at room temperature. PDMSs with different molecular weights and copolymers with different diphenylsiloxane contents were also successfully prepared via P_5OMe catalyzed polymerization.

RESULTS AND DISCUSSION

In order to improve the catalytic activity of the KOH, we first tried to change the cation from K^+ to P_5^+ by *in situ* exchange reaction of P_5Cl with K^+ to form P_5^+ and KCl in the polymerization system (Scheme 1). A series of experiments were conducted to investigate the catalytic performance of the P_5Cl/base mixture in the ROP of D_4 under various conditions. First, the ROP of D_4 using different bases, including KOH, KOMe, and *t*-BuOK, as catalyst was carried out in THF at room temperature without the addition of P_5Cl alone (Table 1, runs 1−3) for comparison. The results revealed that the activity of these bases was not sufficient to catalyze the ROP of D_4 at room temperature, as expected. Further attempts using P_5Cl as catalyst to initiate the ROP of D_4 in THF at room temperature also failed, even with BnOH as initiator (Table 1, runs 4 and 5). Control experiments adopting P_5Cl/CH_3COONa as catalyst could not convert D_4 to polymers at room temperature as expected (Table 1, run 6). Strong bases seemed to be essential for P_5Cl to initiate the ROP of D_4 at room temperature.

Then we attempted to perform the ROP of D_4 in the presence of catalytic amount of P_5Cl (0.1 equiv) relative to KOH (0.1 mol % versus D_4) in THF (Table 1, run 7) at room temperature. A high monomer conversion of 90% was observed as determined by the ^{1}H NMR spectrum for the crude product taken directly from the polymerization system after 60 min of polymerization as shown in Figure 1a and Figure S1 (full spectrum). The resonances at 0.09 ppm corresponded to methyl protons of the D_4 monomer, while the resonances at 0.07 ppm could be attributed to the methyl group in PDMS polymers. Surprisingly, the resonances at around 0.08 ppm (blue spot in Figure 1a), attributed to macrocyclics such as decamethylcyclopentasiloxane (D_5) and dodecamethylcyclohexasiloxane (D_6) formed by the back-biting side reactions during the ROP, were very low in the ^{1}H NMR spectrum of the crude product. Compared with the commonly presented 15% cyclic oligosiloxanes in the thermodynamically controlled reaction mixture of D_4 at higher

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temperature,[10] the back-biting side reactions were effectively suppressed by the bulky P_5^+ cations situated in the active anionic silanolate chain ends. This result strongly verified our hypothesis that weaker coordination between bulky P_5^+ cation and the anionic silanolate chain end could increase steric hindrance around the nucleophilic site in the KOH catalyzed ROP of cyclosiloxanes to reduce the back-biting side reactions. Furthermore, the polymerization at room temperature resulted in the slow back-biting side reactions. In combination with the highly increased polymerization rate, a controlled ROP was achieved with only small amounts of cyclic byproducts. The cyclosiloxanes generated via back-biting reactions would also be opened by the propagating chain ends to propagating to the chain ends, leading to the low contents of macrocyclics such as D_5 and D_6. Consequently, the back-biting products were very little in the P_5Cl/KOH catalyzed ROP of D_4 at room temperature. The dramatically improved catalytic activity may be derived from the *in situ* generated phosphazene base $P_5^+OH^-$, and the OH^- anion in the catalytic system could serve as an initiator for the ROP of cyclosiloxane.

A kinetics study was then performed under the same condition of $[D_4]_0/[KOH]_0/[P_5Cl]_0$ = 1000/1/0.1 for 180 min to further understand the ROP manner of D_4, and the results were shown in Figure 2 and Table 2. Different from typical kinetic curve for the thermodynamically controlled ROP of D_4, the kinetic curves for the ROP of D_4 catalyzed by P_5Cl/KOH were intermediate between conventional kinetically and thermodynamically controlled ROP. In the first stage of the polymerization (0−60 min), the chain propagation quickly proceeded, achieving high monomer conversion of 90% within 60 min. A linear relationship was observed in the first-order kinetics plot between the polymerization time and monomer conversion, demonstrating that the ROP of D_4 mediated by P_5Cl/KOH first proceeded like a kinetically controlled ROP. With the polymerization time increased to 180 min, the monomer conversion was maintained at 92%, which was much higher than the reported thermodynamically controlled ROP with 85% monomer conversion.[10] The back-biting reactions occurred at the polymer chain end was inhibited by the bulky phosphazenium cation. The propagation reaction dominated during the whole ROP, leading to a change of the thermodynamically controlled equilibrium. As shown in Figure 2b, the M_n of PDMSs determined by GPC (black squares) increased almost linearly with D_4 conversion and the molecular weight distribution ($Đ$) remained around 1.6 even in high D_4 conversion (red squares). Furthermore, the *in situ* ^{1}H NMR spectra of the crude product of polymerizations in Table 2 were exhibited in Figures S2−S12. Similar to the result in Figure 1a, the resonances attributed to macrocyclics (δ 0.08 ppm) formed by the back-biting side reactions were maintained at a very low level during the polymerization process. In the P_5Cl/KOH catalyzed polymerization system, linear polysiloxanes with high molecular weights were formed from the very beginning of the polymerization, while the cyclic oligosiloxanes were negligible from beginning to end. Consequently, the controlled manner of P_5Cl/KOH mediated ROP of D_4 in a THF solution was fully proved.

Table 2. Kinetic Study of the ROP of D_4 Catalyzed by P_5Cl and KOH[a]

run	time (min)	conv (%)[b]	M_n (kg mol^{-1})[c]	$Đ$[c]
1	10	20	nd	nd
2	15	30	88.9	1.61
3	20	42	138.1	1.61
4	30	58	172.7	1.61
5	40	71	194.0	1.59
6	50	82	227.1	1.62
7	60	90	241.3	1.59
8	90	92	256.6	1.68
9	120	92	257.6	1.66
10	150	92	279.8	1.89
11	180	92	282.7	1.91

[a]The polymerizations were carried out at room temperature. Catalyst and initiator were mixed first in THF; $[D_4]_0/[KOH]_0/[P_5Cl]_0$ = 1000/1/0.1; $[D_4]_0$ = 2.8 mol·L^{-1}. [b]Determined by ^{1}H NMR. [c]Determined by GPC at 40 °C in THF using standard polystyrene as a reference.

The kinetic study using *t*-BuP_4/H_2O catalytic system was also conducted to compare with the P_5Cl/KOH catalyst. The feeding molar ratio of D_4/*t*-BuP_4/H_2O was 1000/0.1/1, and the ROP was carried out in THF solution with $[D_4]_0$ = 2.8 mol·L^{-1}. As shown in Figure 2a and Table S1, the polymerization rate was much faster than the rate of P_5Cl/KOH catalyzed ROP. The highest conversion of 86% was achieved within 90 min but decreased to below 80% with prolonged polymerization time of 180 min. These results may be derived from the basicity differences between *t*-BuP_4 and $P_5^+OH^-$ that were generated *in situ* during the polymerization. Besides, different from the strong basic characteristic of *t*-BuP_4, P_5Cl was a phosphazenium salt. The exchange between P_5Cl and KOH with a low concentration in the polymerization system reduced the polymerization rate and made the chain propagation more controllable.

The polymerization of D_4 in bulk (Table 1, run 8) was then performed at room temperature. Low conversion of 36% was achieved within 60 min but gave PDMS with high molecular weight of 446.6 kg mol^{-1} and molecular weight distribution of 1.60. The uncontrolled molecular weight may be derived from the rapidly increased viscosity in bulk polymerization that limited the movement of the polymer chain. Furthermore, the chain transfer and condensation reactions might be increased in bulk polymerization, leading to the higher molecular weight of the resulting PDMS than that of solution polymerization (Table 1, run 7, M_n = 241.3 kg mol^{-1}). So, solution polymerization was adopted to further study the catalytic performance of the P_5Cl/KOH catalyst combination.

Reducing the amounts of P_5Cl to 0.01 equiv. relative to KOH (Table 1, run 9) also obtained 90% conversion of D_4 after 60 min in THF solution, giving PDMS polymers with high molecular weight of 299.3 kg mol^{-1}. The higher molecular weight than the PDMSs obtained from run 7 in Table 1 was accordingly due to the decreased amount of active OH^-. When the amount of KOH was further decreased to $[D_4]_0/[KOH]_0/[P_5Cl]_0$ = 1000/0.1/0.01 (Table 1, run 10), higher polymerization temperature of 100 °C was needed, at which 91% monomer conversion can be obtained within 60 min in toluene solution and high M_n of 1356.0 kg mol^{-1} was achieved with low $Đ$ of 1.16.

Based on these results, we tried to regulate the molecular weights of the resulting PDMS polymers by adding extra initiator in the P_5Cl/KOH catalytic system. With the feeding molar ratio of D_4/KOH/P_5Cl fixed at 1000/1/0.1, different amount of water was introduced to the polymerization system as initiator (Table 1, runs 11 and 12). A high monomer

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Table 3. ROP of D_4 Catalyzed by P_5OMe[a]

run	$[D_4]_0/[P_5OMe]_0$	T (°C)	time (min)	conv (%)[b]	M_n (kg mol^{-1})[c]	$Đ$[c]	product yield (%)[d]
1	20000/1	60	50	nd	586	1.36	82.7
2	20000/1	80	50	nd	611	1.45	81.1
3	20000/1	100	30	93	629	1.24	87.4
4	1000/1	100	1	72	nd	nd	nd
5	1000/1	100	5	92	nd	nd	nd
6	1000/1	100	10	92	297	1.37	74.9
1	1000/1	100	10	92	297	1.37	74.9
2	10000/1	100	30	92	574	1.34	80.4
3	20000/1	100	30	93	629	1.24	87.4
4	30000/1	100	30	92	789	1.26	nd
5	40000/1	100	30	92	982	1.18	nd
6	80000/1	100	30	92	1,565	1.11	nd
7	130000/1	100	30	90	1,616	1.11	nd

[a]Conditions: the polymerizations were carried out in bulk. [b]Determined by ^{1}H NMR. [c]Determined by GPC at 40 °C in THF using standard polystyrene as reference. [d]Determined by gravimetric method of purified polymers.

conversion of 96% could be obtained after 1 h with a 1000/9/1/0.1 feeding ratio of $D_4/H_2O/KOH/P_5Cl$ in THF solution (Table 1, run 11). The ^{1}H NMR spectrum of the crude product (Figure 1b) revealed that there were almost no D_5 and D_6 in the polymerization system. The monomer conversion decreased to 51% when the amount of water was increased to 19 equiv relative to KOH in THF solution (Table 1, run 12). Fortunately, there was still trace amount of cyclic oligosiloxanes resulting from back-biting reactions in the polymerization system (Figure 1c). The growing number of H_2O initiators led to the greater exchanges of P_5^+ cation between the active terminal silanol anion and inactive silicon hydroxyl terminated polymer chain during the ROP. Therefore, the polymerization rate decreased with the increased amount of initiator. Accordingly, with the increased feeding ratio of water, the molecular weights of the resulting PDMSs decreased from 241.3 kg mol^{-1} to 45.4 kg mol^{-1} and 26.4 kg mol^{-1}, respectively. It is worth noting that high monomer conversion of 92% could be achieved within 10 min at 100 °C with $[D_4]_0/[H_2O]_0/[KOH]_0/[P_5Cl]_0$ of 1000/19/1/0.1 in toluene solution (Table 1, run 13).

To explore the catalytic performances of different P_5Cl/base catalytic system toward the ROP of D_4, KOMe and *t*-BuOK were examined as an alternative to KOH. The P_5Cl/*t*-BuOK and P_5Cl/KOMe catalytic system exhibited similar catalytic activity with P_5Cl/KOH in THF solution (Table 1, runs 14 and 15). High monomer conversion above 90% could be achieved within 60 min at room temperature with 1000/1/0.01 feeding molar ratio of D_4/base/P_5Cl, giving PDMS with high molecular weights of 163.2 and 153.4 kg mol^{-1}, respectively. When the amount of P_5Cl was reduced to 0.01 equiv relative to KOMe, 90% monomer could be converted to PDMS after polymerization for 60 min in THF solution (Table 1, run 16). Therefore, P_5Cl/KOMe was also a good candidate to mediate the fast ROP of D_4 in THF at room temperature.

However, the M_n values of the resulting PDMS were smaller than the theoretical value calculated with the initiator/D_4 ratio and the monomer conversion. Even with careful purification, there was still H_2O in the polymerization system that behaved as an initiator. Determined by Karl Fischer titration, the H_2O contents in D_4, THF, and toluene were all about 100 ppm. The H_2O contents and the amount of H_2O used as initiator (I) in the polymerization system of runs 7−16 in Table 1 were listed in Table S2. Accordingly, the theoretical M_n values were calculated by adopting H_2O and OH^- (*t*-BuO^- or MeO^-) as the initiator. Based on these calculations, the M_n^{GPC} values were all higher than their M_n^{theor} values, resulting from the partial nonuse of the initiator during polymerization.

As discussed above, P_5Cl/base catalytic systems were efficient for the ROP of D_4 in THF at room temperature. However, a high temperature was needed to prepare PDMS with higher molecular weights to improve the fluidity of the polymer during the polymerization. P_5OMe, prepared by the simple replacement of P_5Cl by KOMe in THF, was adopted as the substituent of P_5Cl/KOMe to achieve the precise control of the initiator (OMe^-).

The ROP of D_4 in bulk at elevated temperatures was then evaluated using P_5OMe as catalyst to prepare ultrahigh molecular weight linear polysiloxanes. First, the optimal reaction temperature for D_4 homopolymerization was screened using a D_4/P_5OMe molar ratio of 20000/1 (Table 3, runs 1−3). During the polymerization process, the viscosity of the system increased slowly at 60 and 80 °C, affording PDMSs after 50 min with product yield of 82.7% and 81.1%, respectively. Nevertheless, the P_5OMe demonstrated remarkable catalytic activity toward the ROP of D_4 at 100 °C (Table 3, run 3). The polymerization system rapidly became gum within a few seconds, resulting in PDMSs with a higher molecular weight (M_n = 629 kg mol^{-1}) and a narrow molecular weight distribution ($Đ$ = 1.24) in higher yields (87.4%). So, the following polymerizations of D_4 were carried out at 100 °C. The conversion of D_4 under different polymerization time was examined as well using a D_4/P_5OMe molar ratio of 1000/1 (Table 3, runs 4−6) at 100 °C. As the viscosity increased rapidly at the beginning of the ROP, a conversion of 72% was attained within just 1 min (Table 3, run 4). The monomer conversion reached 92% after 5 min and then remained unchanged until 10 min (Table 3, runs 5 and 6). These results verified the exceptional catalytic activity of P_5OMe, leading to the attainment of equilibrium within a mere 5 min at 100 °C. More importantly, the equilibrium did not move to cyclic oligosiloxanes with the prolonged polymerization time. As shown in Figure S13, the ratio of macrocyclics generated by back-biting reactions in the crude product of run 6 in Table 3 was as low as 2%. Compared with the common polymer/cyclic oligomer mixture in a thermodynamically controlled ratio of about 85/15, the back-biting side reactions were successfully suppressed by the bulky phosphazenium cation P_5^+ in the

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chain ends. The ROP of D_4 was highly effective, and the equilibrium linear polymer/cyclic oligomer ratio was greatly increased from 85/15 to 92/8.

PDMSs with different molecular weights were then prepared by changing the feeding molar ratio of D_4/P_5OMe from 1000/1 to 130000/1 in the bulk ROP of D_4 at 100 °C (Table 3, runs 6−12). High monomer conversions over 90% could be reached within 30 min for all of the experiments. With the monomer/initiator ratio increased from 1000/1 to 130000/1, the molecular weight of the resulting polymers grew gradually from 297 kg mol^{-1} to 1616 kg mol^{-1}. Significantly, the molecular weight distribution of the obtained polymers became narrower with the increase of the M_n ($Đ$ values decreased from 1.37 to 1.11) and the GPC curves of the polymers were all exhibited as a unimodal distribution (Figure 3). It is noteworthy that the monomer conversions of these

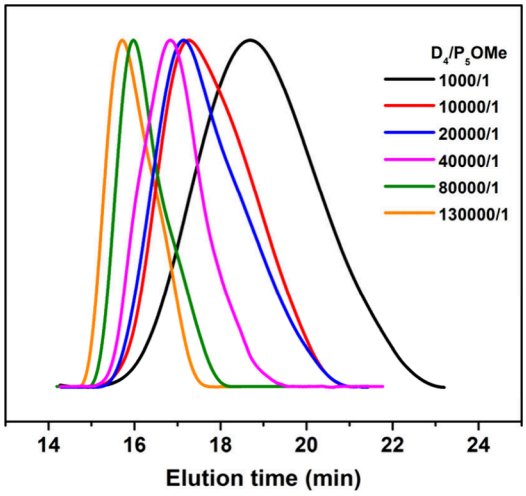

Figure 3. GPC traces of PDMS homopolymers prepared with different $[D_4]_0/[P_5OMe]_0$ ratios (Table 3, runs 6−8 and 10−12).

ROPs catalyzed by P_5OMe were between 90% and 93% (Table 3, runs 6−12), which were much higher than that of KOH catalyzed ROPs (~85%).[2] These findings also verified that the existence of P_5^+ cation in the polymerization system of D_4 could effectively accelerate the polymerization and inhibit the side reactions such as chain transfer or back-biting, leading to the higher monomer conversions to linear polymers.

Preparation of perfect high molecular weight linear diphenylsiloxane containing polysiloxanes was challenging due to the large activity gap of D_4 and P_4, poor solubility of the poly(dimethylsiloxane-*co*-diphenylsiloxane) (PMPS) copolymers, and the unexpected branches formed during the ROCP of phenylcyclosiloxane monomers.[22,37,47−49] The copolymerization behavior of D_4 and P_4 in bulk at 100 °C was then evaluated using highly active P_5OMe as catalyst (Scheme 2). At first, a Schlenk tube was used to investigate the reaction conditions for the ROCP of D_4 and P_4. The feeding molar ratio of D_4/P_4 monomers was fixed at 7/3, and the molar ratio of P_5OMe was changed from 2/10000 to 1/10000 of the total cyclosiloxane monomers (Table 4, runs 1 and 2). The molecular weight of the resultant PMPS copolymers was increased from 314 kg mol^{-1} to 397 kg mol^{-1} with the decrease of the amount of P_5OMe. However, the diphenylsiloxane contents of the resulting polymers, determined by ^1H NMR spectra of the purified PMPS copolymers, decreased from 26.0 to 23.2 mol % with the reduction of the P_5OMe amount. The large deviation of diphenylsiloxane contents with the theoretical value was probably attributed to the nonuniform stirring of the P_4 monomer in the polymerization system. The diphenylsiloxane contents of the PMPSs with 8/2 feeding molar ratio of D_4/P_4 were also lower than the theoretical value, even with the prolonged polymerization time of 60 min (Table 4, runs 3 and 4).

Autoclave with mechanical agitation was then adopted to accomplish better mixing of P_4 with polymer during the ROCP process. P_5OMe was added to the premixed monomers with specific molar ratio of D_4 and P_4 at 100 °C and then stirred intensely for 30 min in bulk. We fixed the P_5OMe loading at 0.01 mol % and tried to prepare PMPS copolymers with different diphenylsiloxane contents by changing the feeding molar ratio of D_4/P_4 monomers from 9/1 to 3/7 (Table 4, runs 5−10). The diphenylsiloxane contents in the resulting polymers increased from 8.4 to 63.8 mol % accordingly (Figures S14−S19). Compared with the polymerization in the Schlenk tube (Table 4, runs 2 and 3), the diphenylsiloxane contents in the copolymer agreed better with the feeding molar ratio of the P_4 monomer. When the feeding molar ratio of D_4/

Scheme 2. (a) ROP of D_4 and (b) ROCP of P_4 and D_4 Catalyzed by P_5OMe

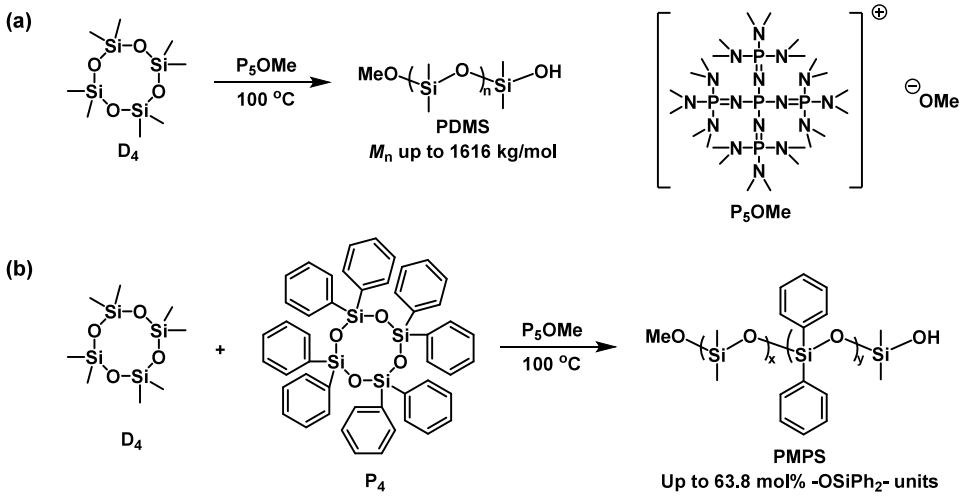

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Table 4. Copolymerization of D_4 and P_4 Catalyzed by P_5OMe[a]

run	$[D_4]_0/[P_4]_0/[P_5OMe]_0$	time (min)	P/(D + P) (mol %)[b]	M_n (kg mol^{-1})[c]	$Đ$[c]	product yield (%)[d]
1[e]	7000/3000/2	30	26.0	314	1.86	58.5
2[e]	7000/3000/1	30	23.2	397	1.77	65.4
3[e]	8000/2000/1	30	16.0	383	1.65	70.2
4[e]	8000/2000/1	60	15.3	376	1.62	69.3
5	9000/1000/1	30	8.4	756.8	1.59	62.3
6	8500/1500/1	30	14.8	551.6	1.62	67.4
7	8000/2000/1	30	18.8	436.7	1.98	61.7
8	7000/3000/1	30	27.5	334.0	2.04	76.0
9	5000/5000/1	30	46.0	182.9	1.98	83.6
10	3000/7000/1	30	63.8	96.7	1.62	61.3

[a]Conditions: the polymerizations were carried out in bulk in autoclave at 100 °C for 30 min. [b]Determined by ^{1}H NMR. [c]Determined by GPC at 40 °C in THF using standard polystyrene as reference. [d]Determined by gravimetric method of purified polymers. [e]The polymerizations were carried out in Schlenk tube.

P_4/P_5OMe was 9000/1000/1 (Table 4, run 5), PMPS with a high molecular weight of 756.8 kg mol^{-1} could be prepared. The GPC trace of this polymer exhibited bimodal distribution (Figure 4, black curve), which should be attributed to the

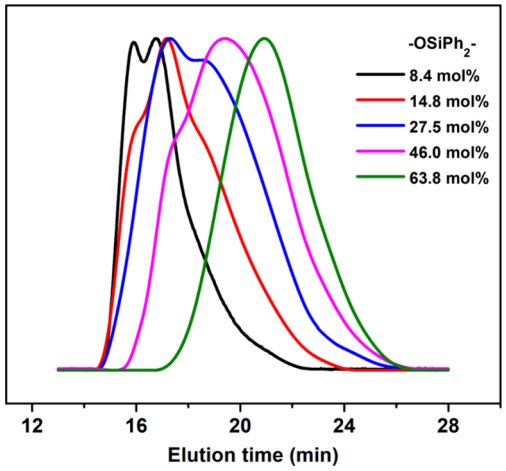

Figure 4. GPC traces of PMPS comopolymers with different diphenylsiloxane contents (Table 4, runs 5, 6, 8–10).

formation of branched polymer products.[47] With the feeding molar ratio of D_4/P_4 increased from 9/1 to 3/7 (Table 4, runs 5–10), the molecular weights of the obtained polymers decreased from 756.8 kg mol^{-1} to 96.7 kg mol^{-1} gradually (Figure 4), which was in accordance with our previous results.[22] We assumed that the gradually decreased molecular weight might be caused by the low solubility of solid P_4 in D_4. Given the relative reactivity of P_4 and D_4, D-P-D-P-D multiblocks of diphenylsiloxane units (P) and dimethysiloxane units (D) tended to be first formed and final PMPS copolymers were obtained via redistribution of the former multiblocks.[48] Therefore, the synthesis of copolymers with higher P contents needed more chain exchange, leading to the lowered molecular weights.

^{29}Si NMR analysis of the PMPS copolymers with different diphenylsiloxane contents was performed to study their microstructure (Figure 5b). The resonances between −18.5 and −22 ppm were attributed to the D units, and the resonances between −46 to −48.5 ppm were ascribed to the P units.[22,47] The quantitative analysis results of the sequence distributions of D and P units in the PMPS copolymers via the integration of different signals in ^{29}Si NMR spectra were shown

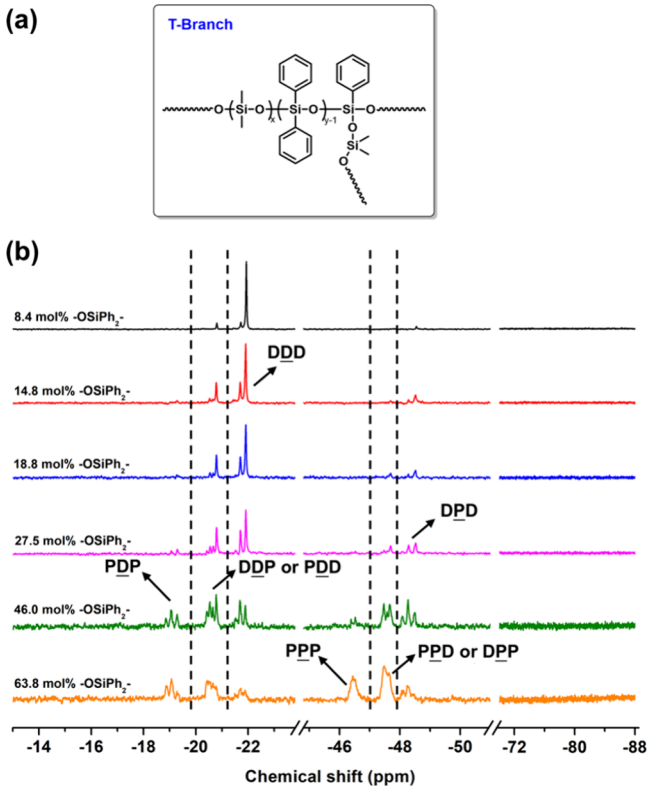

Figure 5. (a) T-branch in PMPS copolymers and (b) ^{29}Si NMR spectra of PMPSs with different diphenylsiloxane contents (Table 4, runs 5–10).

in Table 5. It can be seen that the molar ratios of the P/D units in the resulting copolymers calculated from ^{29}Si NMR (Table 5) were almost the same with the corresponding ratios calculated from ^{1}H NMR (Table 4). With the increase of feeding ratio of P_4 from 10 to 70 mol %, the dominant sequences gradually changed from DDD to DDP to PPD, verifying the random microstructures of the PMPS copolymers.

It has been reported that Si−C_{phenyl} bonds are quite prone to desilylation because of the presence of ionic substances.[47,50] Accordingly, unexpected nonfunctional and freely dangling chain branching (trisiloxy, T-branch) usually occurs in the ROP of phenylsiloxane containing cyclosiloxanes catalyzed by a base catalyst as shown in Figure 5a.[22,47] Although bimodal GPC curves indicated the existence of chain branching, no

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Table 5. Sequence Distribution of D and P Units in PMPS Copolymers with Different Contents of Diphenylsiloxane Group

			D and P sequence distributions (%)					
run	$[D_4]_0/[P_4]_0$	P/(D + P) (mol %)[a]	DDD	DDP	PDP	PPP	PPD	DPD
1	9000/1000	5.1	88.3	6.6	0	0	0	5.1
2	8500/1500	13.8	63.8	22.4	0	0	2.6	11.2
3	8000/2000	17.1	58.9	24.0	0	0	6.3	10.8
4	7000/3000	27.2	46.1	25.8	0.9	0	8.8	18.5
5	5000/5000	48.5	17.6	25.8	8.2	3.7	22.7	22.1
6	3000/7000	64.4	0	21.6	14.0	17.2	34.3	12.9

[a]Determined by ^{29}Si NMR.

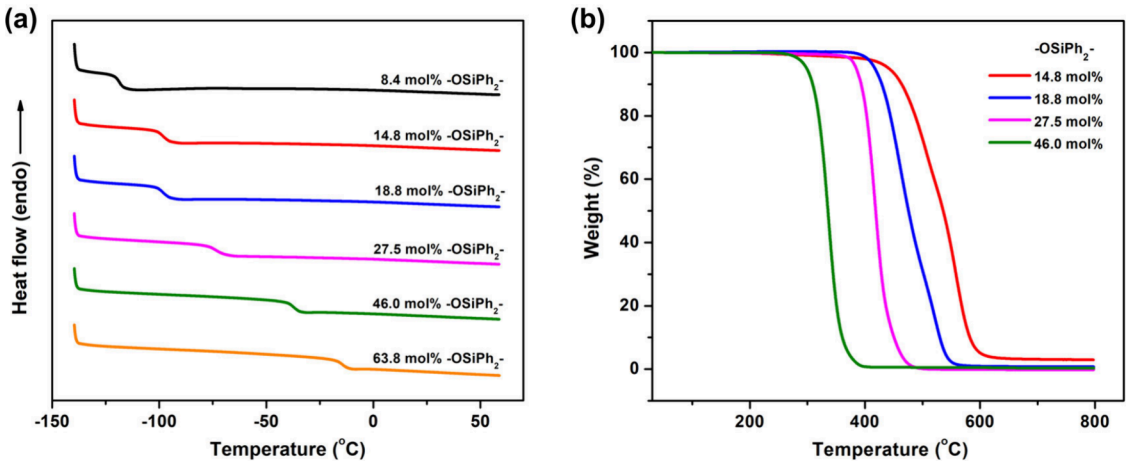

Figure 6. (a) DSC thermograms of the second heating run of the PMPS copolymers with different diphenylsiloxane contents (Table 4, runs 5−10) and (b) TGA curves of the PMPS copolymers with different diphenylsiloxane contents (Table 4, runs 6−9).

signal at around −80 ppm was observed in the ^{29}Si NMR spectrum of PMPS copolymers with different P units (Figure 5b). The low intensity of signals for Si atoms assigned to the trisiloxy (T-branch) was due to the high molecular weight of these PMPS copolymers that led to the low concentration of trisiloxy.

DSC and TGA measurements were then conducted (Figure 6) to investigate the thermal properties of the PMPS copolymers, and the results were summarized in Table S3. As shown in Figure 6a, the increase of diphenylsiloxane contents in PMPS copolymers resulted in the apparent increase of the glass-transition temperature (T_g). With the molar ratio of diphenylsiloxane unit increased from 8.4 to 63.8 mol %, T_g increased from −118.6 to −19.9 °C gradually. There was no low temperature crystallization in the PMPS copolymers, and the experimental single T_g values agreed well with the reported value,[51] indicating the random structure of the PMPS copolymers.

Thermal stability of PMPSs with different diphenylsiloxane contents was evaluated by TGA measurement in N_2 (Figure 6b), and the onset degradation temperature ($T_{d,5\%}$) and the maximum degradation temperature ($T_{d,max}$) were given in Table S5. As shown in Figure 6b, the TGA curves of PMPSs exhibited a one-step degradation. Among them, PMPS with 14.8 mol % diphenylsiloxane units exhibited best thermal stability with $T_{d,5\%}$ of 441.3 °C and a $T_{d,max}$ of 630.2 °C. The $T_{d,5\%}$ was much higher than the value of polydiphenylsiloxane-polydimethylsiloxane-polydiphenylsiloxane triblock copolymers and PMPS with similar P contents reported before, demonstrating the excellent random distribution of D and P units in the polymer chain.[22,52] Although the $T_{d,5\%}$ and $T_{d,max}$ decreased gradually with the increase of diphenylsiloxane contents, the $T_{d,5\%}$ values of PMPS copolymers were all higher than 300 °C. These results suggested the random characteristic and good heat resistance of PMPS copolymers obtained from the ROP catalyzed by P_5OMe.

CONCLUSIONS

In summary, the fast ROP of D_4 in a THF solution was successfully achieved using a P_5Cl/KOH binary catalytic system at room temperature. The catalytic efficiency of KOH could be greatly improved via the addition of a catalytic amount of bulky phosphazenium salt P_5Cl. With a 1000/1/0.01 feeding molar ratio of D_4/KOH/P_5Cl, PDMS with molecular weight of 228.5 kg mol^{-1} was conveniently obtained in high monomer conversion of 90% within 60 min. The *in situ* ^{1}H NMR spectrum showed that the strength of signals attributed to macrocyclics formed by the back-biting side reactions during the ROP was very low and verified that weaker coordination between bulky P_5^+ cation and the anionic silanolate chain end could increase steric hindrance around the nucleophilic site in the KOH catalyzed ROP of cyclosiloxanes to reduce the back-biting side reactions. Kinetics investigations indicated that the ROP of D_4 catalyzed by P_5Cl/KOH proceeded in a fast, controlled manner. Furthermore, the activated phosphazenium salt P_5OMe proved highly effective toward the bulk ROP of D_4. Changing the feeding ratio of D_4/P_5OMe from 1000/1 to 130000/1 gradually, PDMS with a high molecular weight from 297 kg mol^{-1} to 1616 kg mol^{-1} could be synthesized in high conversion (≥90%) at 100 °C. PMPS copolymers with different diphenylsiloxane contents (8.4−63.8 mol %) could also be easily prepared by P_5OMe

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catalyzed bulk ROCP of D_4 and P_4. The random characteristics of obtained PMPSs were collaboratively characterized with ^1H and ^{29}Si NMR and DSC measurements. TGA analyses indicated the good thermal stability of obtained PMPS copolysiloxanes. This study provides a convenient and efficient method to prepare high molecular weight PDMS and PMPS copolymers with minimum back-biting reaction under mild conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02388.

Experimental details, additional polymerization data, and NMR spectra of polysiloxanes (PDF)

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Notes

The authors declare no competing financial interest.

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