

# Synthesis of Well-Defined Difunctional Polydimethylsiloxane with an Efficient Dianionic Initiator for ABA Triblock Copolymer

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**ABSTRACT:** A new efficient dianionic initiator dipotassium diphenylsilanediolate ( $\text{Ph}_2\text{Si}(\text{OK})_2$ ) was synthesized by reacting diphenylsilanediol with potassium in the mixture of THF and benzene. The anionic ring-opening polymerization of octamethylcyclotetrasiloxane ( $\text{D}_4$ ) or tetramethyltetravinylcyclotetrasiloxane ( $\text{D}_4^{\text{Vi}}$ ) initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  was systematically investigated. A number of factors including the nature of initiators, promoters, and monomers, the molar ratio of promoter to initiator ( $C_p/C_i$  ratio) and monomer to initiator ( $C_m/C_i$  ratio) affect the polymerization remarkably. Using *N*-methyl-2-pyrrolidinone as the promoter, a series of

well-defined difunctional H—Si-terminated polydimethylsiloxanes (PDMSs) were prepared with high monomer conversion (> 90%) and relatively low polydispersity (< 1.6) at 30°C. By hydrosilation of the synthesized PDMS with allyl end-capped poly(ethylene oxide) (PEO), amphiphilic PEO-*b*-PDMS-*b*-PEO triblock copolymers with low polydispersities and high block purities were obtained. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 153–159, 2007

**Key words:** anionic polymerization; cyclotetrasiloxane; polydimethylsiloxane; hydrosilation; block copolymer

## INTRODUCTION

Well-defined block copolymers have attracted considerable attention for their widespread applications such as in the formation of various nanosized aggregates in solution,<sup>1–3</sup> and in the preparation of thin films with nanostructured surfaces.<sup>4–6</sup> Both of the above-mentioned applications require the precise control of the block copolymer including not only its molecular weight and polydispersity but also its composition and structure. Among the variety of block copolymers, the amphiphilic triblock copolymer with polydimethylsiloxane (PDMS) as hydrophobic block and poly(ethylene oxide) (PEO) as hydrophilic block is of interest due to its highly asymmetric characteristic and excellent biocompatibility. One of the most important synthetic methods to obtain the above-mentioned copolymer is by hydrosilation reaction of difunctional H—Si-terminated PDMS with allyl end-capped PEO.<sup>7</sup> Nevertheless, the synthesis of well-defined difunctional PDMS is not an easy task.<sup>8</sup> A general route to synthesize difunctional H—Si-terminated PDMS is by acid-catalyzed polymerization of octamethylcyclotetrasiloxane ( $\text{D}_4$ ) with tetramethyldisiloxane as the end captor.<sup>7,9–11</sup> However, this route cannot supply high-

quality difunctional PDMS because of the broad polydispersity of the resulting polymer. Recently, more interests have been attracted on the synthesis of such PDMS by nonequilibrium polymerization.<sup>12</sup> When compared with the nonequilibrium polymerization of hexamethylcyclotrisiloxane ( $\text{D}_3$ ),<sup>8,13,14</sup> only very limited attention<sup>15</sup> was paid on  $\text{D}_4$  because of its lower ring-opening tendency.<sup>16</sup> But, the easier commercial availability of  $\text{D}_4$  and the demand to work on a larger scale make it promising in developing the nonequilibrium polymerization of  $\text{D}_4$ .

To our best knowledge, the synthesis of difunctional PDMS by anionic ring-opening polymerization of  $\text{D}_4$  initiated by dipotassium siloxanolate has not been reported. In this work, a new efficient dianionic initiator dipotassium diphenylsilanediolate ( $\text{Ph}_2\text{Si}(\text{OK})_2$ ) was synthesized and used for the synthesis of difunctional H—Si-terminated PDMS by anionic ring-opening polymerization of  $\text{D}_4$ . Then well-defined ABA PEO-*b*-PDMS-*b*-PEO triblock copolymers were obtained by hydrosilation reaction of the synthesized PDMS with the commercially available PEO.

## EXPERIMENTAL

### Materials

Diphenylsilanediol ( $\text{Ph}_2\text{Si}(\text{OH})_2$ ) was prepared according to the literature.<sup>17</sup> Benzene and THF were dried from refluxing with sodium and distilled prior

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to use. Dilithium diphenylsilanediolate ( $\text{Ph}_2\text{Si}(\text{OLi})_2$ ) was synthesized according to the literature.<sup>18</sup> *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and diglyme were dried over sodium and collected by trap-to-trap distillation under reduced pressure. Potassium is cut into small pieces under nitrogen prior to use.  $\text{D}_4$  and tetramethyltetravinylcyclotetrasiloxane ( $\text{D}_4^{\text{Vi}}$ ) was dried over  $\text{CaH}_2$ , and distilled under nitrogen. Dimethylchlorosilane and trimethylchlorosilane was distilled under nitrogen. Poly(ethylene oxide) (PEO) (Nanjing JLPC Tenside Chemical and Technical, JiangSu) was dried at  $30^\circ\text{C}$  in vacuum oven overnight prior to use.

### Synthesis of dipotassium diphenylsilanediolate

To a mixture of (12.8 g, 0.33 mol) potassium and benzene (60 mL), a THF (60 mL) solution of diphenylsilanediol (32.0 g, 0.15 mol) was added dropwise for 6 h at room temperature under nitrogen. After stirred overnight, the solution turned into homogeneous milky emulsion. Removed from the unreacted potassium, the emulsion was stored under nitrogen. The titration of the resulting emulsion with HCl gave the concentration of 1.190M.

### Polymerizations of cyclotetrasiloxanes

To the flask charged with  $\text{D}_4$  (or  $\text{D}_4^{\text{Vi}}$ ), an initiator was added using a syringe. When the promoter was injected into the flask, the system turned clear immediately. After stirred for designed time, the reaction mixture was quenched with an excess amount of dimethylchlorosilane (or trimethylchlorosilane). Then, the solution was washed with deionized water for three times, and the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  overnight, filtered, and submitted to  $^{29}\text{Si}$  NMR and gel permeation chromatography (GPC) measurements.

### Synthesis of ABA triblock copolymer

To the flask charged with PEO and PDMS, toluene was injected. The catalyst ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) solution (1.0% g/mL) in isopropanol was added into the mixture at  $90^\circ\text{C}$ , and then the solution was heated to  $110^\circ\text{C}$  and stirred for 5 h. After adsorption of catalyst by active carbon and removal of toluene by distillation

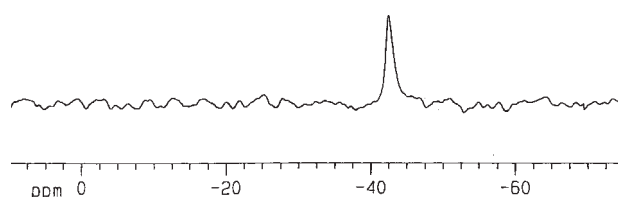


Figure 1  $^{29}\text{Si}$  NMR spectrum of  $\text{Ph}_2\text{Si}(\text{OK})_2$  in  $\text{CD}_3\text{COCD}_3$ .

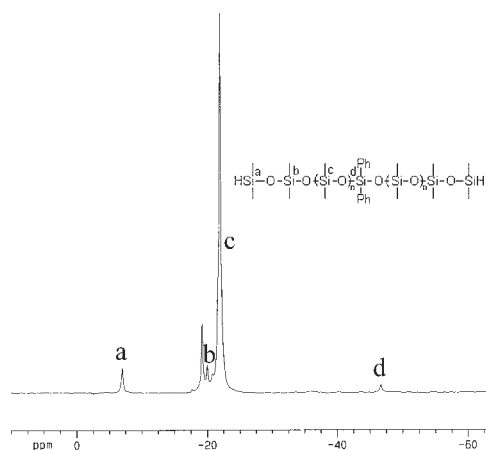


Figure 2  $^{29}\text{Si}$  NMR spectrum of difunctional H-Si-terminated PDMS in  $\text{CDCl}_3$ .

under reduced pressure, the product was measured by  $^1\text{H}$  NMR and GPC.

### Measurements

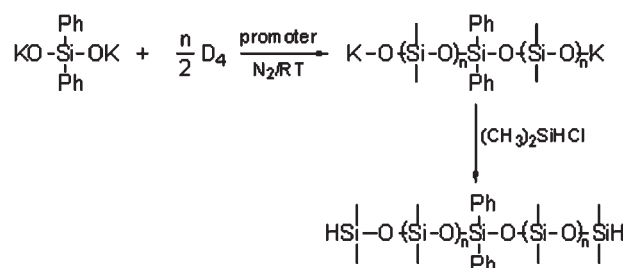
$^{29}\text{Si}$  NMR and  $^1\text{H}$  NMR:  $^{29}\text{Si}$  NMR and  $^1\text{H}$  NMR spectra were recorded on a Bruker AV600 instrument operating at 119 MHz for  $^{29}\text{Si}$  and 600 MHz for  $^1\text{H}$ , respectively.

Gel permeation chromatography (GPC): GPC measurements in toluene were performed with a Water's system including a 515 high-pressure liquid chromatography pump, a 2410 differential refractive-index detector, and Styragel columns (HR) at  $40^\circ\text{C}$  at a rate of 1.0 mL/min with linear polystyrene standards.

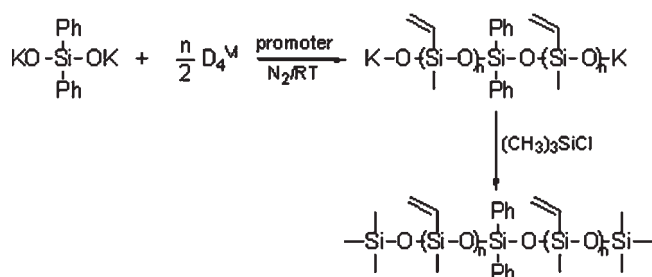
## RESULTS AND DISCUSSION

### Synthesis of dipotassium diphenylsilanediolate

$\text{Ph}_2\text{Si}(\text{OLi})_2$  has been used in the nonequilibrium polymerization of  $\text{D}_3$ ,<sup>13</sup> while for the anionic ring-opening polymerization of  $\text{D}_4$ , it is firstly used as the initiator. Unfortunately, the polymerization of  $\text{D}_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OLi})_2$  cannot proceed successfully at room temperature (see the next section). Considering, the polymerization rate is directly related to the size of the cation and increases strongly in the series:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ ,



Scheme 1



Scheme 2

a new efficient dianionic initiator,  $\text{Ph}_2\text{Si}(\text{OK})_2$ , was synthesized by reacting diphenylsilanediol with potassium in the mixture of THF and benzene. The reaction mixture was stirred in high purity nitrogen overnight at room temperature, and then sampled and submitted to  $^{29}\text{Si}$  NMR measurement (Fig. 1). The disappearance of the peak at  $-37.09$  ppm ( $\text{Ph}_2\text{Si}(\text{OH})_2$ ) and the exclusive occurrence of the peak at  $-42.90$  ppm ( $\text{Ph}_2\text{Si}(\text{OK})_2$ ) indicated that diphenylsilanediol has been completely converted into dipotassium diphenylsilanediolate, and a high purity of the product was obtained.

#### Preparation of difunctional H—Si-terminated PDMS and polymethylvinylsiloxane initiated by $\text{Ph}_2\text{Si}(\text{OK})_2$

The precursor PDMS was prepared by anionic ring-opening polymerization of  $\text{D}_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  followed by end-capsulation of the polymer chain with dimethylchlorosilane. Figure 2 shows that the well-defined difunctional H—Si-terminated PDMS was synthesized successfully. The integration area ratio of the two peaks at  $-7.05$  ppm ( $\text{HMe}_2\text{Si}^-$ ) and  $-46.70$  ppm ( $\text{Ph}_2\text{Si}^-$ ) is  $\sim 2.0$ , which suggests that the whole process including initiation, propagation, and termination proceeded at both ends of the initiator. It

simultaneously testifies our desired reaction process, as shown in Scheme 1. By comparing the peak at  $-22.06$  ppm ( $-\text{Si}-\text{O}-$  repeat unit) to the peak at  $-19.29$  ppm (the unreacted  $\text{D}_4$ ), the monomer conversion can be calculated accordingly. The peak at  $-20.05$  ppm represents for the  $\text{Me}_2\text{SiO}^-$  next to the chain end. The shift ( $\sim 2$  ppm) to lower field was probably related to the induction effect of  $\text{HMe}_2\text{Si}^-$  end on the adjacent  $\text{Me}_2\text{SiO}^-$  repeat unit. The same result was obtained in the acid-catalyzed polymerization of  $\text{D}_4$  with tetramethyldisiloxane as the end-captor.

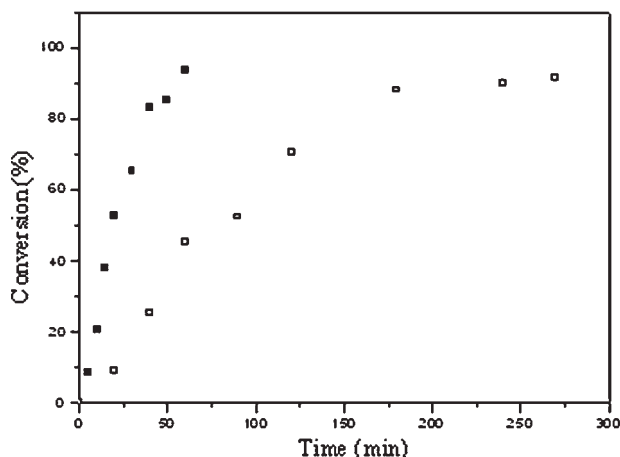
Similarly, the polymethylvinylsiloxane (PMVS) was obtained by polymerization of  $\text{D}_4^{\text{Vi}}$  with the same initiator followed by end-capsulation of the polymer chain with trimethylchlorosilane. The reaction process shown by Scheme 2, analogous to that of PDMS, was also supported by the successful synthesis of well-defined PMVS.

Monomer conversions and polymer polydispersities for various polymerizations were listed in Table I. Because of the smaller ring strain in  $\text{D}_4$ , the polymerization initiated by  $\text{Ph}_2\text{Si}(\text{OLi})_2$  (No. 2 in Table I) cannot proceed successfully at  $30^\circ\text{C}$ . When the reaction temperature is increased to  $80^\circ\text{C}$ , the polymerization (No. 3 in Table I) achieved a high monomer conversion. Comparing Nos. 9 to 3, the polymerization initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  reached a similar monomer conversion within much shorter time as well as at lower temperature. All of these indicate that  $\text{Ph}_2\text{Si}(\text{OK})_2$  is a much more efficient initiator than  $\text{Ph}_2\text{Si}(\text{OLi})_2$ , and the anionic ring-opening polymerization of  $\text{D}_4$  initiated by the former shows great superiority to that initiated by the latter. Likewise, Figure 3 clearly shows that the polymerization of  $\text{D}_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  at  $30^\circ\text{C}$  proceeds much faster than that initiated by  $\text{Ph}_2\text{Si}(\text{OLi})_2$  at  $80^\circ\text{C}$ , in agreement with the above-mentioned results.

TABLE I  
Monomer Conversions and Polymer Polydispersities for the Polymerization of  $\text{D}_4$  and  $\text{D}_4^{\text{Vi}}$  Initiated by Two Different Initiators

No.	Monomer (mol/L)	Initiator ( $C_m/C_i$ )	Promoter ( $C_p/C_i$ )	$T$ ( $^\circ\text{C}$ )	$t$ (min)	Conversion (wt %)	PD ( $M_w/M_n$ )
1	$\text{D}_4$ (2.82)	$\text{Ph}_2\text{Si}(\text{OLi})_2$ (25)	NMP (3.0)	80	150	92.9	1.58
2	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OLi})_2$ (34)	NMP (3.0)	30	270	<5.0	—
3	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OLi})_2$ (34)	NMP (3.0)	80	270	91.3	1.68
4	$\text{D}_4$ (2.54)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (13)	NMP (3.0)	30	25	94.8	1.32
5	$\text{D}_4$ (2.82)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (25)	NMP (3.0)	30	40	93.0	1.44
6	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	Diglyme (3.0)	30	300	37.1	1.71
7	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	DMF (3.0)	30	60	37.2	1.68
8	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	NMP (3.0)	30	15	38.2	1.29
9	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	NMP (3.0)	30	60	93.5	1.57
10	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	NMP (5.0)	30	30	92.1	1.55
11	$\text{D}_4$ (2.91)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (34)	NMP (6.0)	30	25	91.7	1.60
12	$\text{D}_4^{\text{Vi}}$ (1.43)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (3.2)	NMP (3.0)	30	10	96.8	1.28
13	$\text{D}_4^{\text{Vi}}$ (2.54)	$\text{Ph}_2\text{Si}(\text{OK})_2$ (13)	NMP (3.0)	30	17	94.5	1.36

<sup>a</sup> The terminator is  $(\text{CH}_3)_2\text{HSiCl}$  in the polymerization of  $\text{D}_4$ , while  $(\text{CH}_3)_3\text{SiCl}$  in the polymerization of  $\text{D}_4^{\text{Vi}}$ .



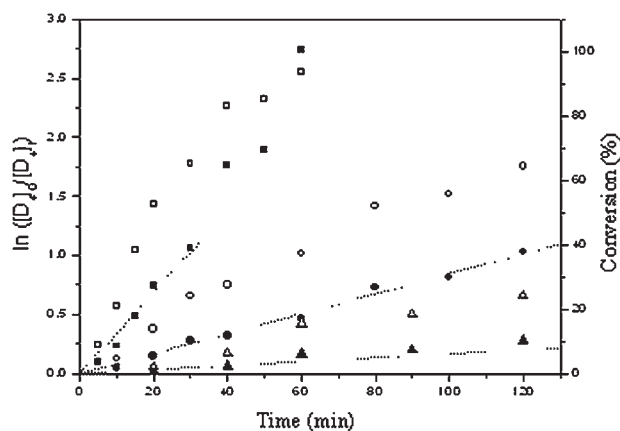
**Figure 3** Comparison of monomer conversions versus reaction time for the anionic ring-opening polymerization of  $D_4$  initiated by (■)  $\text{Ph}_2\text{Si}(\text{OK})_2$  at  $30^\circ\text{C}$  and (□)  $\text{Ph}_2\text{Si}(\text{OLi})_2$  at  $80^\circ\text{C}$  with NMP as a promoter.  $[\text{D}_4]_0/[\text{I}]_0/[\text{P}]_0 = 34/1.0/3.0$ .

The nature of the promoters affects the polymerization remarkably. Figure 4 shows the comparison of kinetic plots for the anionic ring-opening polymerization of  $D_4$  with various promoters. It reveals that for each of the promoters, the polymerization has initially a high level of control (first-order kinetics) shown by the linear dependence of  $\ln([\text{D}_4]_0/[\text{D}_4]_t)$  with increasing reaction time, which indicates the nonequilibrium property of the polymerization. The polymerization rate constants during the initial stage of polymerization were calculated to be 0.032, 0.008, and 0.002  $\text{min}^{-1}$  for the polymerizations accelerated by NMP, DMF, and diglyme, respectively. Evidently, the polymerization rate accelerated by promoters decreases in the order: NMP > DMF > diglyme. However, for the polymerization with NMP as the promoter, after  $\sim 30$  min, there is a remarkable curvature in the kinetic plot, which means that the first-order kinetics were disturbed by the establishment of an equilibrium reaction, in which the rate constant of propagation becomes smaller than that of the side reaction by backbiting of the chain end. The conversion plot also supported the interpretation. Although the monomer conversion increases very quickly during the initial stage of polymerization, after 30 min, the curve dramatically flattens, revealing the above-mentioned formation of equilibrium. The  $\text{Ph}_2\text{Si}(\text{OK})_2/\text{DMF}$  or  $\text{Ph}_2\text{Si}(\text{OK})_2/\text{diglyme}$  polymerization shows first-order kinetics at the whole designed time until a curvature occurs in the plot at higher conversion (not shown). On the other hand, by the comparison of Nos. 6–8 in Table I, the polymerization accelerated by NMP shows the largest polymerization rate, in agreement with the results from Figure 4, and the polysiloxane has much lower polydispersity (1.29) than the other two polymerizations at similar conversion. Both of

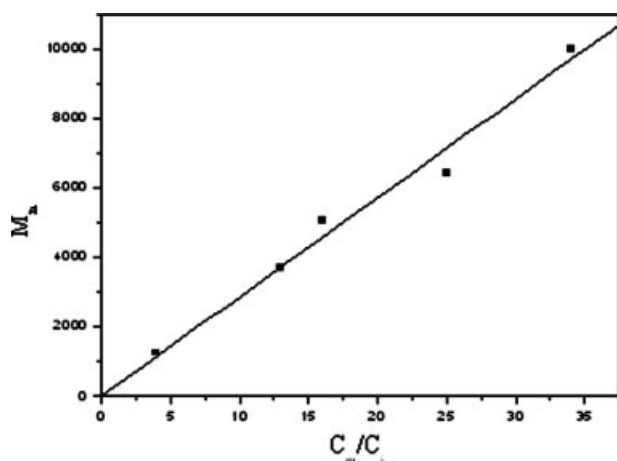
these mean that NMP is the best one among the three promoters, which may relate to the extremely great complexing capability of NMP with the cation of the initiator. Furthermore, using NMP as the promoter, the polydispersity of the polysiloxane remains relatively narrow ( $< 1.6$ ) even at high conversion ( $> 90\%$ ) (Nos. 4–5 and 9–13 in Table I), which favors the industrial application of the  $\text{Ph}_2\text{Si}(\text{OK})_2/\text{NMP}$  polymerization of  $D_4$ .

Not only the nature of promoters but also the  $C_p/C_i$  ratio influences the polymerization of  $D_4$ . When the  $C_p/C_i$  ratio increases from 3.0 to 5.0 and to 6.0 (Nos. 9–11 in Table I), the polymerization achieved similar monomer conversion within 60, 30, and 25 min, respectively, while the polysiloxane has nearly equivalent polydispersity. It indicates that the increasing of the  $C_p/C_i$  ratio can accelerate the polymerization of  $D_4$  but has no significant effect on the polydispersity of polysiloxane.

The polymerization is also affected by the nature of monomers and the  $C_m/C_i$  ratio. From Table I, comparing Nos. 13 with 4, the polymerization rate of  $D_4^{\text{VI}}$  is larger than that of  $D_4$ , while the polydispersity is nearly equivalent to each other, which reveals that the induction effect of vinyl affects the polymerization of  $D_4^{\text{VI}}$  greater than the steric effect, as the polymerization is accelerated by the former but hindered by the latter. It is noteworthy that in bulk polymerization of  $D_4$  (Nos. 4, 5, and 9 in Table I) or  $D_4^{\text{VI}}$  (Nos. 12 and 13 in Table I), when the  $C_m/C_i$  ratio increases, the polymerization rate decreases and the polydispersity of the polymer becomes broader at nearly the same monomer conversion. The evolution of the molecular weight of the polysiloxane on the  $C_m/C_i$  ratio at monomer conversion of 93% was shown in Figure 5. The linear dependence of  $M_n$  on the  $C_m/C_i$  ratio,

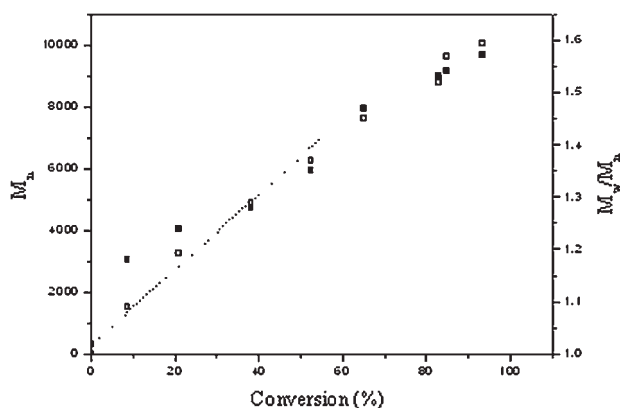


**Figure 4** Comparison of kinetic plots for the anionic ring-opening polymerization of  $D_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  at  $30^\circ\text{C}$  with NMP ((■) kinetic plot; (□) conversion), DMF ((●) kinetic plot; (○) conversion), and diglyme ((▲) kinetic plot; (△) conversion) as promoter.  $[\text{D}_4]_0/[\text{I}]_0/[\text{P}]_0 = 34/1.0/3.0$ .

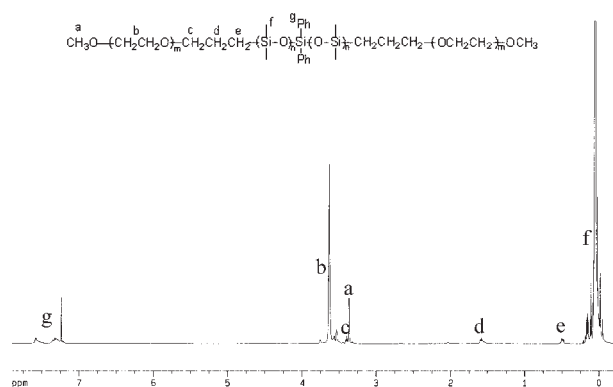


**Figure 5** Evolution of the molecular weight on the  $C_m/C_i$  ratio at monomer conversion of 93% for the anionic ring-opening polymerization of  $D_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  at  $30^\circ\text{C}$  with NMP as a promoter.  $[\text{P}]_0/[\text{I}]_0 = 3.0$ .

which is one of the nonequilibrium characteristics, reveals that for the anionic ring-opening polymerization of  $D_4$ , the molecular weights of the polysiloxanes were well controlled by the  $C_m/C_i$  ratio at the same monomer conversion. On the other hand, Figure 6 shows the evolution of molecular weights and polydispersities in the polymerization of  $D_4$  with increasing conversion at  $C_m/C_i$  ratio equal to 34. The molecular weight of the polymer evolves nearly with a linear dependence up to 50% conversion, showing another nonequilibrium characteristic, which suggests that during the initial stage of polymerization, the consumed monomer was completely converted into the polysiloxane chain. The polydispersities of the polymer also increases with the monomer conversion, but not in linear dependence. Similar results were obtained at other  $C_m/C_i$  ratios.



**Figure 6** Evolution of the ( $\square$ ) molecular weight and ( $\blacksquare$ ) molecular weight distribution ( $M_w/M_n$ ) on monomer conversion for the anionic ring-opening polymerization of  $D_4$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  at  $30^\circ\text{C}$  with NMP as a promoter.  $[\text{D}_4]_0/[\text{I}]_0/[\text{P}]_0 = 34/1.0/3.0$ .

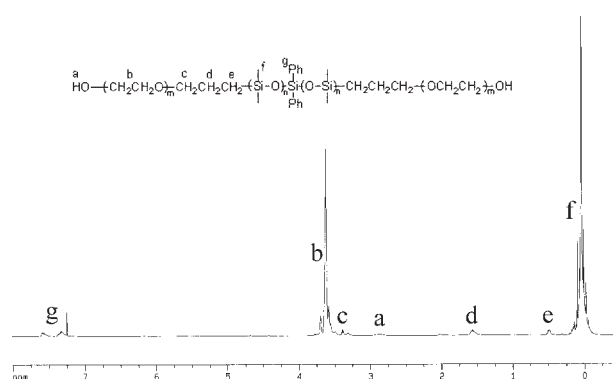


**Figure 7**  $^1\text{H}$  NMR spectrum of dimethoxy end-capped ABA triblock copolymer containing PDMS and PEO in  $\text{CDCl}_3$ .

Considering all the above-mentioned results, the polymerization was determined by a number of factors such as the nature of initiators, promoters, and monomers, the  $C_p/C_i$  ratio, and the  $C_m/C_i$  ratio. More importantly, a series of H—Si-terminated PDMS or PMVS chains with relative narrow polydispersity ( $< 1.6$ ) and high conversion ( $> 90\%$ ) were prepared by polymerization of  $D_4$  or  $D_4^{\text{VI}}$  initiated by  $\text{Ph}_2\text{Si}(\text{OK})_2$  under mild conditions.

#### Synthesis of well-defined ABA triblock copolymer containing PDMS and PEO

On the basis of synthesized difunctional H—Si-terminated PDMS, a series of PEO-*b*-PDMS-*b*-PEO triblock copolymers were synthesized by hydrosilylation reaction of PDMS with the allyl end-capped PEO. For PEO with methoxy group at one end, the hydrosilylation reaction can be conducted directly. Figure 7 shows that the well-defined copolymer was synthesized. The peak at 7.24 ppm is the characteristic peak of  $\text{CDCl}_3$ . The two groups of peaks at 7.32 ppm and 7.59 ppm represent  $\text{Ph}_2\text{Si}^-$ . The peaks near 3.63 ppm represent the repeat ( $-\text{CH}_2\text{CH}_2\text{O}-$ ) units of PEO block, and the peaks near 0 ppm represent the repeat



**Figure 8**  $^1\text{H}$  NMR spectrum of dihydroxy end-capped ABA triblock copolymer containing PDMS and PEO in  $\text{CDCl}_3$ .

TABLE II  
The Molecular Weights and Polydispersities of Homopolymers  
and the Resulting Copolymers

No.	PDMS			PEO			Copolymer		
	$M_n^a$	$M_n^b$	$M_w/M_n$	$M_n^a$	$M_n^b$	$M_w/M_n$	$M_n^c$	$M_n^b$	$M_w/M_n$
1	10420	10050	1.57	900	910	1.06	11870	12070	1.60
2	6980	6400	1.44	430	470	1.02	7340	7160	1.52
3 <sup>d</sup>	5360	5030	1.39	1080	940	1.04	6910	7190	1.39
4 <sup>d</sup>	3670	3780	1.32	700	760	1.02	5300	5270	1.29

<sup>a</sup> The molecular weights were obtained by <sup>1</sup>H NMR.

<sup>b</sup> The molecular weights were obtained by GPC.

<sup>c</sup> The molecular weight was calculated according to the formula:  $M_n(\text{co}) = M_n^c(\text{PDMS}) + 2 M_n^c(\text{PEO})$ .

<sup>d</sup> PEO with hydroxyl end group was used in the preparation of copolymer.

(Me<sub>2</sub>SiO<sup>-</sup>) units of PDMS block. The peak at 3.36 ppm represents for the CH<sub>3</sub>O<sup>-</sup> end group. From Figure 7, it can be seen that the peak at 4.70 ppm (H—Si—) and the three group peaks at 5.77–5.82, 5.05–5.18, and 3.90–3.92 ppm (allyl group) disappeared completely, while another three group peaks at 3.39, 1.55, and 0.43 ppm (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si—) occurred instead, which means that the hydrosilation reaction was performed perfectly. The integration area ratio of —OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si— peak to Ph<sub>2</sub>Si<sup>-</sup> peak is about 1.2, indicating that the hydrosilation reaction proceeded at both ends of PDMS and the resulting copolymer was ABA triblock copolymer.

As for PEO with hydroxy end group, the hydrosilation reaction cannot proceed directly because of the side reaction between the hydroxy end group and the H—Si end group of PDMS. By protecting the hydroxy group with trimethylsilyl group,<sup>19</sup> the hydrosilation reaction can be performed successfully. After hydrolysis of the protecting group, the well-defined dihydroxy end-capped triblock copolymer was obtained (Fig. 8). The peak at 2.85 ppm represents the hydroxy group.

Table II shows the molecular weights and polydispersities of homopolymers and the synthesized copolymers. The molecular weights of PDMS and PEO were determined by <sup>1</sup>H NMR and GPC, respectively. Due to the monodispersity of PEO, the resulting copolymer has similar polydispersity to that of PDMS. The molecular weight of copolymer measured by GPC is nearly equal to the calculated one, which is also indicating that the copolymer is ABA triblock copolymer. The GPC traces of both the PDMS precursor and the prepared copolymer for No. 1 in Table II were shown in Figure 9. The monomodal peak clearly demonstrates the well-defined structures of the resulting triblock copolymer. Similar results were obtained from the other cases in Table II.

On the basis of the already synthesized PDMS and the commercially available PEO, a series of well-defined PEO-*b*-PDMS-*b*-PEO triblock copolymers were synthesized successfully. Aside from the controllable molecular weights and relatively low polydispersities, the obtained copolymers also have specific compositions and structures, even special functionalities.

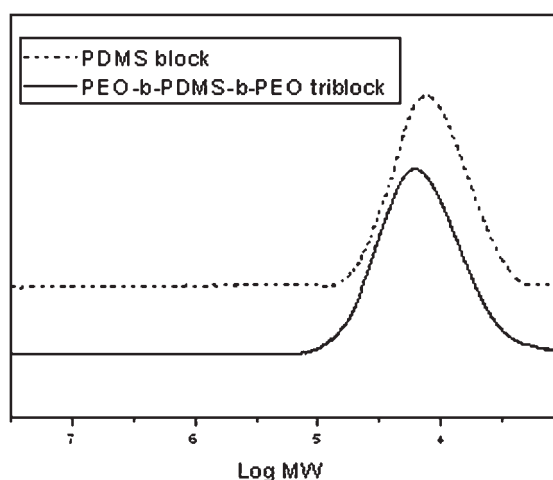


Figure 9 GPC traces of both the PDMS precursor and the prepared copolymer for No. 1 in Table II.

## CONCLUSIONS

A new efficient dianionic initiator Ph<sub>2</sub>Si(OK)<sub>2</sub> was synthesized by reacting diphenylsilanediol with potassium in the mixture of THF and benzene. With this initiator, the anionic ring-opening polymerization of D<sub>4</sub> and D<sub>4</sub><sup>Vi</sup> proceeded successfully at room temperature. Using NMP as the promoter, not only the molecular weight and polydispersity but also the component, structure, and functionality of polymer obtained better control than using other promoters. Further, the typical nonequilibrium characteristics were also shown in the anionic ring-opening polymerization of cyclotetrasiloxanes. The Ph<sub>2</sub>Si(OK)<sub>2</sub>/NMP polymerization of D<sub>4</sub> produced a series of well-defined difunctional H—Si-terminated PDMS with relatively narrow polydispersity (< 1.6) and high monomer conversion (> 90%). By hydrosilation reaction of the synthesized

PDMS and the commercially available PEO, amphiphilic PEO-*b*-PDMS-*b*-PEO triblock copolymer with methoxy or hydroxy end group and high block purities were synthesized.

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