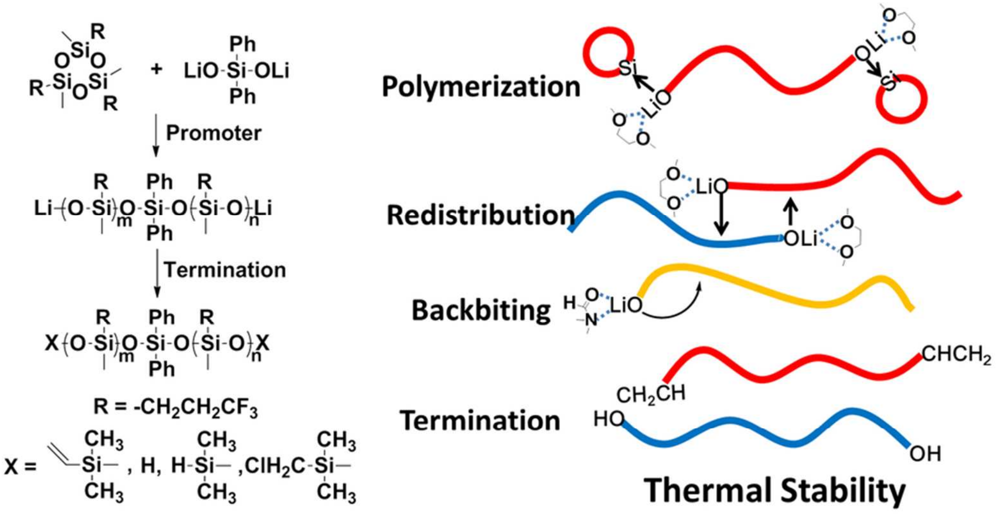
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances



Controlled polymerization method to synthesize poly[methyl(3,3,3-trifluoropropyl)siloxane] with narrow molar mass distribution, broad "termination window", selective end groups and quantitative transformation.
40x21mm (600 x 600 DPI)

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Controlled Synthesis and Characterization of Poly[methyl(3,3,3-trifluoropropyl)siloxane] with Selective End Groups

Hua-Feng Fei[a,b], Wenchun Xie[a], Qian Wang[a], Xiyin Gao[a,b], Tao Hu[a,b], Zhijie Zhang*[a] and Zemin Xie[a]

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

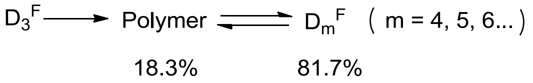
www.rsc.org/

Anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane in bulk was studied using dilithium diphenylsilanediolate as an initiator (I); and N,N-dimethylformamide (DMF), bis(2-methoxyethyl)ether (Diglyme), and 1,2-dimethoxyethane (DME) as promoters (P). A detailed study on kinetics of polymerization with different molar ratio of promoter to initiator ([P]/[I]) that were equal to 2.0, 4.0, and 6.0 revealed that the yield of linear polymers was the highest when [P]/[I] = 2.0 for all the promoters, among which DME was the most efficient promoter for suppressing the backbiting reactions. The reaction promoted by DME had a very broad "termination window" with the highest yield of linear polymer and very narrow molar mass distribution. The results of the matrix-assisted laser desorption/ionization time of flight mass spectrometry indicated that the intermolecular redistribution occurred during the process of polymerization. PMTFPS with end groups such as vinyl, hydroxyl, hydrogen and chloromethyl were prepared and characterized by ^{1}H NMR, ^{29}Si NMR and FT-IR. Polymers having vinyl end groups displayed higher thermo stability than those having hydroxyl end groups under nitrogen.

Introduction

Poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) has a wide range of commercial applications due to superior properties, such as high thermal stability[1-6], low temperature flexibility[7-9], radiation resistance[10], low surface energy[11], and outstanding fuel and chemical resistance because it is capable of introducing fluorine atoms into the polymer structure[12-15]. Traditionally, PMTFPS is synthesized by anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (D_3^F) in bulk initiated by sodium hydroxide (NaOH), potassium hydroxide (KOH) or tetramethylammonium hydroxide (TMAOH), which is an equilibrium reaction that has a significant tendency to form the cyclic compounds, D_m^F, (m = 4, 5, 6…)[12, 15-20]. Therefore, the reaction residue contains considerable amount of cyclic products and the yield of the resulting linear polymer is only about 18.3% (Scheme 1)[15-17, 21], and the molar mass distribution is broad.

Scheme 1 Equilibrium between Linear Polymer and Cyclic Products in Bulk or Solution Polymerization of D_3^F.



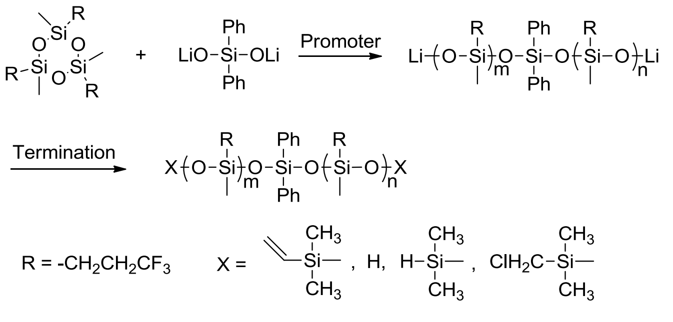
$$\underset{}{D_3^F} \longrightarrow \underset{18.3\%}{\text{Polymer}} \rightleftharpoons \underset{81.7\%}{D_m^F} \quad (\text{m} = 4, 5, 6...)$$

To overcome the shortcomings of the equilibrium polymerization, many efforts have been put to study the non-equilibrium polymerization[16,18, 22-30]. Yuzhelevskii and coworkers[22-25] studied the effect of promoters like aprotic and polar solvents including dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and organic phosphates on D_3^F polymerization and found that the polymerization rate could be increased by at least two orders of magnitude by promoting the dissociation of ion pairs between SiO^- and Li^+. Veith et al.[16] investigated the effect of the DMSO/butyllithium (BuLi), promoter–initiator (P–I) combination on the polymerization of D_3^F at 40 °C indicating that the initiator containing lithium ion instead of sodium ion could remarkably reduce the rate of backbiting reaction. Besides, according to their kinetic model, they predicted that the highest yield of polymer was 90%. Barrère et al.[17] polymerized D_3^F by the miniemulsion technique using didodecyldimethylammonium bromide as an emulsifier and NaOH as an initiator. PMTFPS with hydroxyl as end group was prepared and they reported that the maximum yield of the polymerization was almost quantitative and analyzed the by-products formed due to intermolecular redistribution by matrix-assisted laser desorption/ionization time of flight (MALDI–TOF) mass spectrometry. The limitation of miniemulsion technique is that the number-average molar mass and molar mass distribution is difficult to be controlled and the polymerization cannot attain polymer with other end groups such as vinyl, hydrogen or chloromethyl. Therefore, it is important to explore a polymerization method to synthesize PMTFPS with narrow molar mass distribution, selective end groups and high yield.

Moreover, earlier, the researchers focused on the thermal stability of polydimethylsiloxane[2-5, 31, 32]. For example, Thomas and Kendrick[31, 32] proposed the random depolymerization mechanism based on uncatalyzed siloxane bond cleavage. Budden[5] put forward the unzipping depolymerization and bond exchange mechanism during thermal degradation. Their studies suggested that cleavage of backbone by moisture was the principal mode at lower temperature in the range of 120 to 275 °C. However, the thermal degradation and thermo-oxidative degradation mechanisms of PMTFPS have rarely been studied. Thomas[4] investigated the thermal stability of end hydroxyl fluorosilicone vulcanisates. They found that fluorosilicones was more susceptible to oxidative attack than methyl silicones because of their high content of methylene groups.

Herein, we investigated the mechanism of non-equilibrium polymerization of D_3^F using dilithium diphenylsilanediolate ($Ph_2Si(OLi)_2$) as an initiator (I); *N*,*N*-dimethylformamide (DMF), bis(2-methoxyethyl)ether (Diglyme), and 1,2-dimethoxyethane (DME) as promoters (P), and achieved the polymerization with high yield, selective end groups, well controlled molar mass and molar mass distribution, and broad "termination window". PMTFPS with end groups such as α, ω-vinyl, hydroxyl, hydrogen and chloromethyl were attained nearly quantitatively by using chlorodimethylvinylsilane, acetic acid, dimethylchlorosilane and chloromethyldimethylchlorosilane as termination reagent, respectively (Scheme 2). The α, ω-vinyl and hydroxyl PMTFPS are very important addition type and condensation type fluorosilicone rubber, respectively; α, ω-hydrogen PMTFPS is always used as chain extender; and α, ω- chloromethyl PMTFPS can derive out other functional end groups. Besides, –Ph_2SiO– units from $Ph_2Si(OLi)_2$ were used as markers in MALDI–TOF analysis. Subsequently, the microstructure of the polymer was determined. Furthermore, we investigated the thermal stability of PMTFPS with hydroxyl and vinyl end groups by TGA analysis under nitrogen and air, respectively.

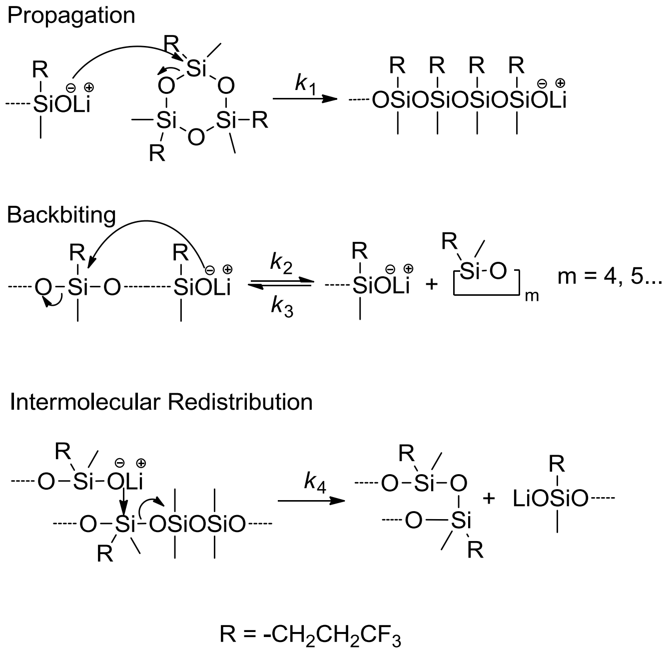
Scheme 2 Synthetic routes of PMTFPS with different end groups.



Results and Discussion

Theory. The backbiting reactions and intermolecular redistribution (Scheme 3) are both observed during the course of polymerization initiated by $Ph_2Si(OLi)_2$ using different promoters in bulk. The backbiting reaction can lead to the decrease of the molar mass; however, the redistribution leads to the increase of the molar mass and the molar mass distribution of the polymer[16, 17].

Scheme 3 Possible Reactions Occurring during Polymerization of D_3^F in Bulk.



The kinetics of propagation and side reactions can be expressed as equations (1) and (2), respectively:

$$\frac{dM}{dt} = -k_1[D_3^F][SiO^-] \quad (1)$$

$$\frac{dPoly}{dt} = \{-(k_2 + k_4)[Poly] + k_3[D_m^F]\}[SiO^-] \quad (2)$$

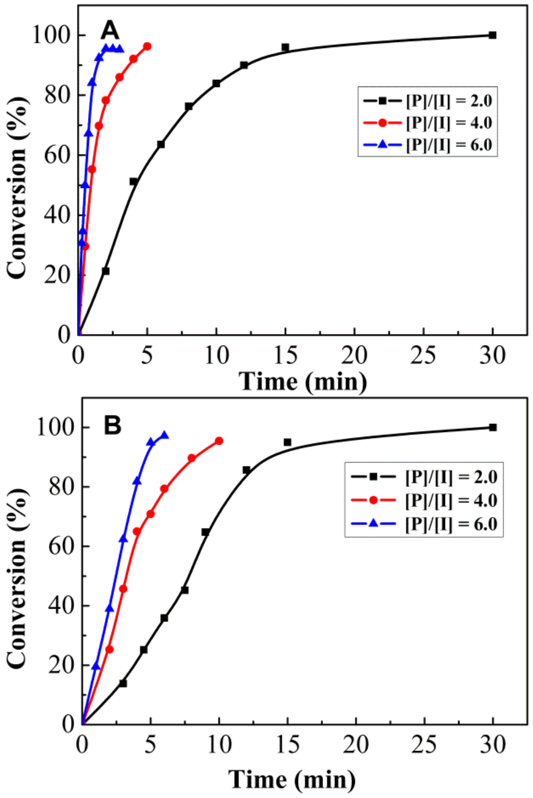
The rates of propagation and side reactions are dependent on $[SiO^-]$. Based on the assumption that $k_1 >> k_2$, k_3, and k_4, decreasing $[SiO^-]$ significantly suppresses the side reactions; and the rate of propagation slows down simultaneously. Furthermore, $[SiO^-]$ shows square root dependence on [I] and [P] (Eq. 3)[16].

$$[SiO^-] = C[I]^{1/2}[P]^{1/2} \quad (3)$$

C is a variable that depends on types of promoters and reaction temperature, indicating that when [I] is kept constant, lowing [P] or decreasing the values of C by varying the promoters can decrease $[SiO^-]$, and therefore, the side reactions can be suppressed.

Kinetics of polymerization. To monitor the progress of the polymerization, the conversion of the monomer (D_3^F) was calculated from the ^{29}Si NMR spectra of the reaction products based on the ratios of peak areas of silicon atoms in linear polymer (δ –22.3 ppm) to the total peaks areas of silicon atoms in D_3^F (δ –9.6 ppm), D_4^F (δ –19.5 ppm), and linear polymer (δ –22.3 ppm): Conversion of monomer = Area(polymer)/[Area(D_3^F) + Area(D_4^F) + Area(polymer)][18, 26]. We could not observe any peaks for the silicon atoms of D_5^F and D_6^F in the ^{29}Si NMR spectra indicating that the amounts of D_5^F and D_6^F in the reaction products were very little. Therefore, they were not included in the calculation. Theoretically, when the value of [P]/[I] is less than 2.0, only some of the initiators will be associated with the promoters. Therefore, the rate of the polymerization will be slow and the molar mass of polymers will be large. Therefore, too achieve the reasonable reaction time and well controlled molar mass of the resulting polymers, we only chose the [P]/[I] = 2.0, 4.0, and 6.0.

In our study, DMF, Diglyme, and DME were used as promoters in the polymerization of D_3^F. The consumption of D_3^F was very rapid after promoters were introduced into the reactor due to the fact that the ion-dipole interactions between Li^+ and promoters made $–SiO^-Li^+$ a loose ion pair. Thus, SiO^- became to be a more active species when performing propagation and other side reactions[16]. The kinetics of D_3^F polymerization is shown in Figure 1. The propagation rate increases rapidly with the increase in the value of [P]/[I]. Almost all the monomers are consumed in 2, 5, and 15 min when DMF is used as the promoter and [P]/[I] is equal to 2.0, 4.0, and 6.0, respectively (Figure 1(A)).



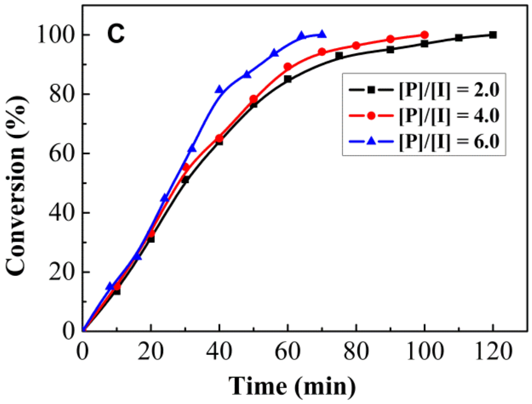


Figure 1 Kinetics of D_3^F polymerization at 40 ℃ in bulk initiated by $Ph_2Si(OLi)_2$ with (A) DMF, (B) Diglyme, and (C) DME as promoters.

Table 1 The propagation constants, *k** and linear polymer yields at different conditions.

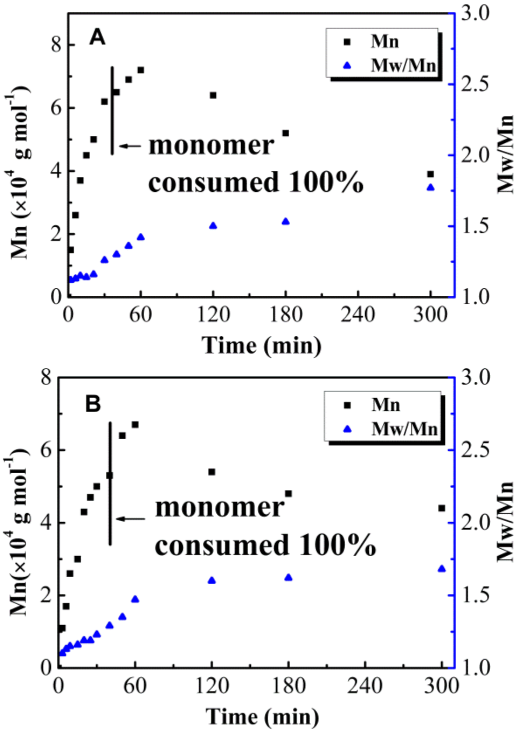
Promoter	[P]/[I]	k^* (cm^{-1})	Polymerization Time (h)	Linear Polymer Yields (%)[a]	D_4^F (%)[b]
DMF	2.0	0.170	5	94.4	5.6
DMF	4.0	0.850	5	91.3	8.7
DMF	6.0	1.210	5	89.6	10.4
Diglyme	2.0	0.100	5	95.4	4.6
Diglyme	4.0	0.380	5	93.9	6.1
Diglyme	6.0	0.740	5	90.6	9.4
DME	2.0	0.033	10	Cyclic products were not detected	
DME	4.0	0.041	5	Cyclic products were not detected	
DME	6.0	0.052	5	99.0	1.0

[a, b] The yields were measured by ^{29}Si NMR after polymerizing for 5 or 10 h.

When Diglyme is used, the propagation rates slow down insignificantly (Figure 1(B)); however, the propagation rates slow down significantly when DME is used as the promoter (Figure 1(C)), revealing the following order of the effect of promoting polymerization, DMF > Diglyme > DME. This is because the electron donating ability of nitrogen atoms is stronger than that of oxygen atoms resulting in greater ion-dipole interactions between Li^+ and nitrogen atoms. The related propagation constants, *k** calculated based on the equation: $k^* = \ln([D_3^F]_0 / [D_3^F]_t) / t$ [26], are listed in Table 1. *k** increases as the value of [P]/[I] grows for the same promoter, and for the same value of [P]/[I], a higher *k** indicate a stronger promoter.

However, the rapid rate of propagation is not always advantageous. Table 1 shows that for the weakest promoter, DME, almost no by-product, D_4^F is obtained in the reaction products; however, for DMF and Diglyme, little amount of D_4^F is obtained in the reaction products and the yields of D_4^F increase as the values of [P]/[I] increase. Therefore, the results indicate that when either stronger promoters or higher concentration of promoters are used in the reactions, –SiO$^-$ not only attacks cyclic trimer silicon, but also Si–O bond in the same polymer chain resulting in the backbiting reactions. Therefore, although lowering the values of [P]/[I] slows down the propagation rate, simultaneously the backbiting reactions are suppressed. We further investigated the evolution of the molar mass during the process of polymerization with each of the three promoters when [P]/[I] = 2.0. For reactions facilitated by DMF and Diglyme, and terminated by chlorodimethylvinylsilane (Figures 2A and B), although the monomer conversion reaches almost 100% in 30–40 min, subsequently, the number average molar mass (M_n) keeps on increasing, which is possibly because the intermolecular redistribution is dominant in 30–60 min. The M_n starts decreasing after 60 min because of the backbiting reactions.

The ^{29}Si NMR spectra and GPC chromatograms of the above mentioned reactions after 5 h (Figures 3A (1) - (2) and Figures 3B (1) - (2)) clearly show the appearance of D_4^F in the products due to the backbiting reactions[18]. However, when DME was used as the promoter and [P]/[I] = 2.0, the monomer is consumed in about 2 h, and later, the M_n does not show significant change for almost 8 h (Figure 2C). D_4^F is not observed in the ^{29}Si NMR spectrum and GPC chromatogram of the polymerization after 10 h (Figures 3A(3) and 3B(3)), indicating the absence of backbiting reactions. Furthermore, the resulting polymer has narrower molar mass distribution compared to those from reactions in which DMF and Diglyme were used as promoters (Figure 2). Therefore, when DME was used as the promoter, the reaction had a broad “termination windows” with high polymer yields and a narrow molar mass distribution. This is mainly because DME is a weak promoter, and backbiting side reactions and intermolecular redistributions can be considerably suppressed.



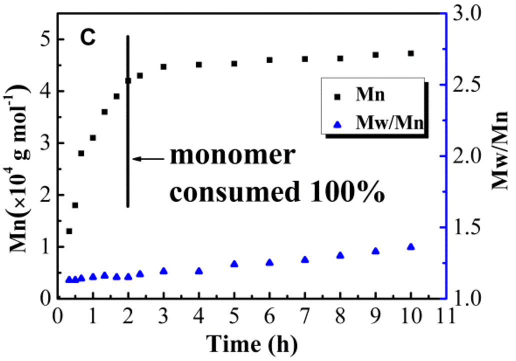


Figure 2 Kinetics of D_3^F polymerization at 40 ℃ in bulk initiated by $Ph_2Si(OLi)_2$ with (A) DMF, (B) Diglyme, and (C) DME as promoters; [P]/[I] = 2.0 in all the cases.

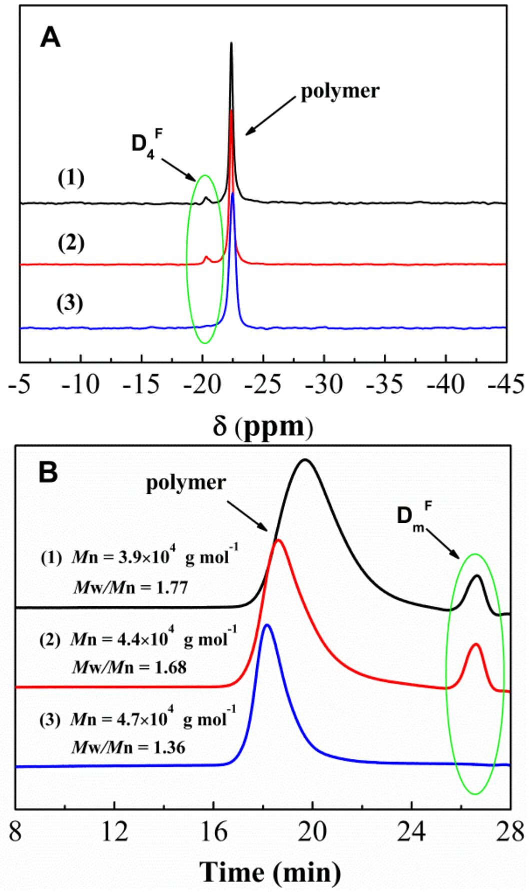


Figure 3 ^{29}Si NMR spectra (A) and GPC trace (B) of resulting polymers from reactions (1) DMF as the promoter, [P]/[I] = 2.0, polymerization for 5 h, (2) Diglyme as the promoter, [P]/[I] = 2.0, polymerization for 5 h, and (3) DME as the promoter, [P]/[I] = 2.0, polymerization for 10 h.

Intermolecular redistributions analyzed by MALDI–TOF–MS. To investigate the intermolecular redistributions during the polymerization, the resulting polymer of the reaction in which DME was used as promoter and [P]/[I] = 2.0 was analyzed by MALDI–TOF–MS. The reaction was quenched by addition of acetic acid before the crude product was characterized by

MALDI–TOF. The mass spectrum of the reaction product (Figure 4) shows four groups of peaks: A, B, C, and D. The m/z values of peaks A1, A2, A3, and A4 correspond to molecules containing one –$SiO(C_6H_5)_2$ unit (P) and 18, 19, 20, 21 –$SiOCH_3CH_2CH_2CF_3$ units (F) with a sodium ion, respectively (H-PF_{18}-OH+Na^+: $[M+Na]^+/z$ = 3047.2; H-PF_{19}-OH+Na^+: $[M+Na]^+/z$ = 3230.1; H-PF_{20}-OH+Na^+: $[M+Na]^+/z$ = 3358.9; H-PF_{21}-OH+Na^+: $[M+Na]^+/z$ = 3515.2). The A series only has one P unit, which indicates the absence of intermolecular redistribution in these polymers. The m/z values of peaks B1, B2, B3, and B4 correspond to H-P_2F_{17}-OH+Na^+ ($[M+Na]^+/z$ = 3088.3), H-P_2F_{18}-OH+Na^+ ($[M+Na]^+/z$ = 3245.1), H-P_2F_{19}-OH+Na^+ ($[M+Na]^+/z$ = 3401.1), and H-P_2F_{20}-OH+Na^+ ($[M+Na]^+/z$ = 3557.3), respectively. There are two P units presented in B series; therefore, this group of molecules must have undergone intermolecular redistribution at least once (Scheme 4 (1)). The m/z values of peaks C1, C2, C3, and C4 correspond to H-P_3F_{16}-OH+Na^+ ($[M+Na]^+/z$ = 3131.0), H-P_3F_{17}-OH+Na^+ ($[M+Na]^+/z$ = 3286.7), H-P_3F_{18}-OH+Na^+ ($[M+Na]^+/z$ = 3443.0), and H-P_3F_{19}-OH+Na^+ ($[M+Na]^+/z$ = 3599.1), respectively. The three P units indicate that the intermolecular redistribution occurs in this C series at least twice (Scheme 4 (2)). The m/z values of peaks D1, D2, D3, and D4 correspond to H-F_{20}-OH+Na^+ ($[M+Na]^+/z$ = 3161.2), H-F_{21}-OH+Na^+ ($[M+Na]^+/z$ = 3316.8), H-F_{22}-OH+Na^+ ($[M+Na]^+/z$ = 3473.1), and H-F_{23}-OH+Na^+ ($[M+Na]^+/z$ = 3628.9), respectively. The D series also displays products of intermolecular redistribution (Schemes 4 (1) and (2)). The MALDI-TOF analysis suggests that although DME was a weak promoter, the intermolecular redistribution cannot be absolutely suppressed during the process of polymerization.

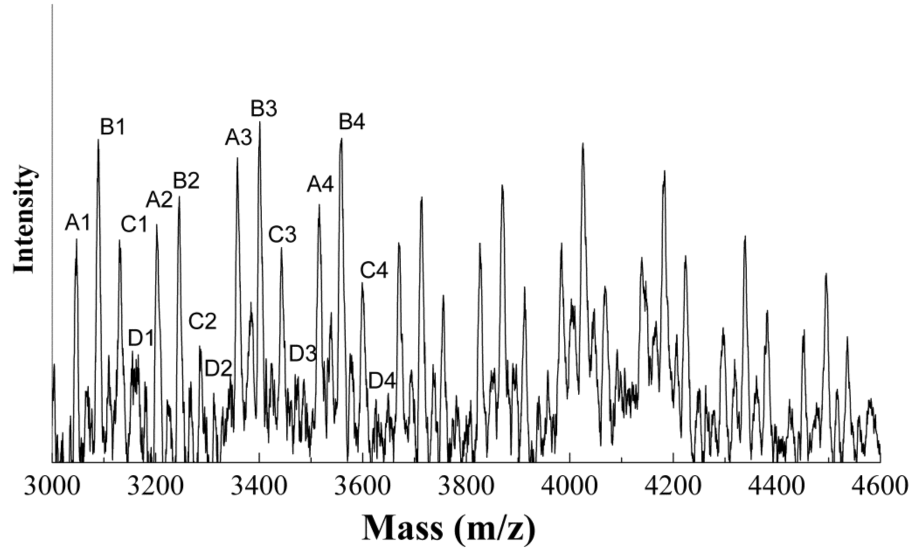
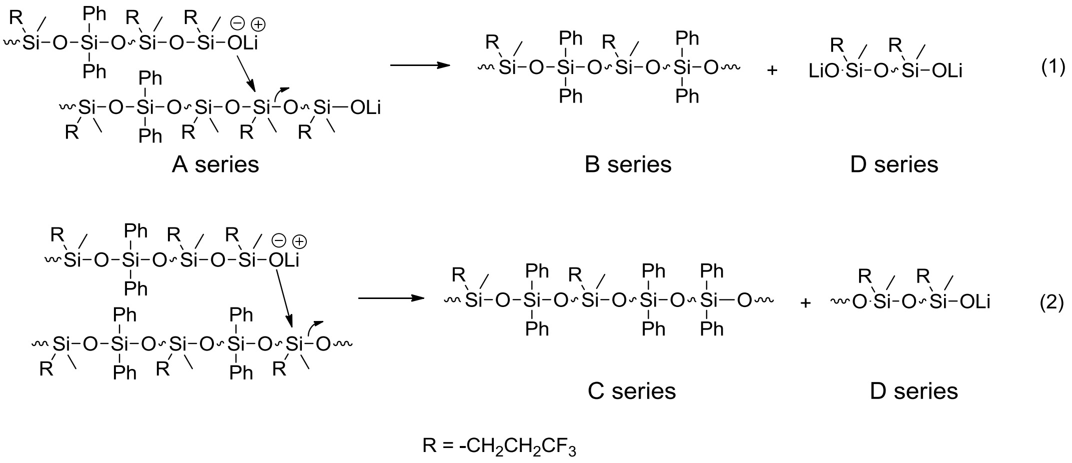


Figure 4 MALDI–TOF mass spectrum of resulting polymer obtained by polymerization initiated by $Ph_2Si(OLi)_2$ and using DME as the promoter, [P]/[I] = 2.0, polymerization for 2 h, terminated by equivalent amount of acetic acid.

Scheme 4 Possible Intermolecular Redistributions Occurred during the Process of Polymerization.



Chracterization of PMTFPS.

^{1}H NMR analysis. The ^{1}H NMR spectra of PMTFPS with end groups such as vinyl (P1), hydroxyl (P2), hydrogen (P3) and chloromethyl (P4) are shown in Figure 5A and 5B. Peak 1 (Figure 5A) (δ 0.30 ppm) corresponds to $-CH_3$ attached to silicon, peak 2 (from δ 0.87 to δ 0.91 ppm) corresponds to α $-CH_2-$ of trifluoropropyl and peak 3 (from δ 2.14 to δ 2.30 ppm) corresponds to β $-CH_2-$ of trifluoropropyl. Both of the methylene groups appear to be multiple peaks duo to the coupling action between hydrogen and fluorine. Peak 4 (from δ 7.21 to δ 7.75 ppm) (Figure 5B) is assigned to the phenyl group. Peak 5 (from δ 5.60 to δ 6.76 ppm) is assigned to end group, vinyl. Peak 6 (δ 5.67 ppm) is assigned to end group, hydroxyl. Peak 7 (δ 4.78 ppm) is assigned to end group, hydrogen, and peak 8 (δ 2.91 ppm) is assigned to end group, chloromethyl.

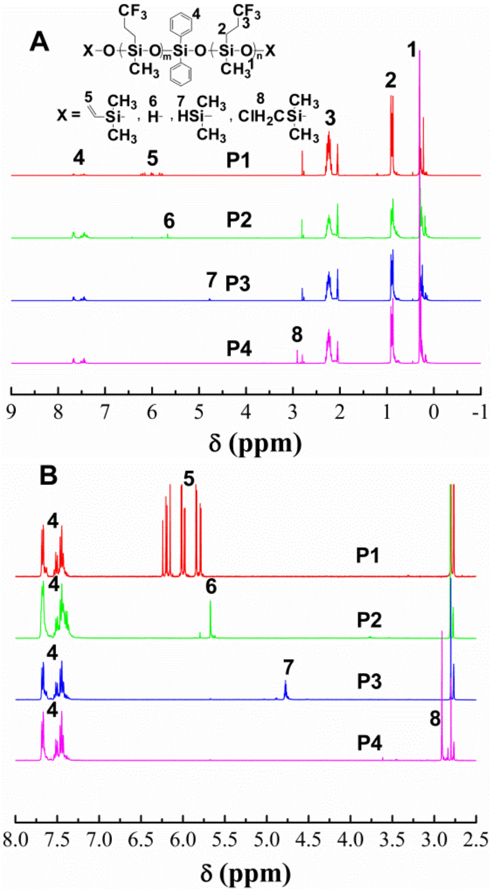


Figure 5 (A) ^{1}H NMR spectra of PMTFPS with vinyl (P1), hydroxyl (P2), hydrogen (P3) and chloromethyl (P4) end groups. (B) The zoomed view of Figure 5A from δ 8.0 to δ 2.5 ppm.

^{29}Si NMR analysis. Polymers P1, P2, P3 and P4 are characterized by ^{29}Si NMR also. As shown in Figure 6, peak a (δ –22.3 ppm) corresponds to silicon of repeat unit; peak b (δ –46.1 ppm) corresponds to silicon in the main chain that is from initiators. Both of peaks appear for all the polymers, which mean the initiators were successful in initiating the polymerization. Peak c (δ 1.8 ppm) is assigned to silicon of $-OSi(CH_3)_2CHCH_2$; peak d (δ –14.5 ppm) is assigned to silicon of $-OSiCH_3CH_2CH_2CF_3OH$; peak e (δ –4.7 ppm) is assigned to silicon of $-OSi(CH_3)_2H$; peak f (δ 3.7 ppm) is assigned to silicon of $-OSi(CH_3)_2CH_2Cl$. Both of the ^{1}H NMR and ^{29}Si NMR data clearly demonstrates that the PMTFPS with different end groups were synthesized successfully and the living ends of polymers were terminated completely.

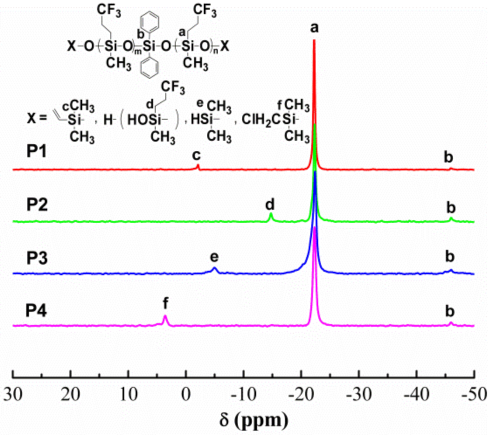


Figure 6 ^{29}Si NMR spectra of PMTFPS with vinyl (P1), hydroxyl (P2), hydrogen (P3) and chloromethyl (P4) end groups.

FT-IR analysis. These polymers are further characterized by FT-IR. As displayed in Figure 7. Peaks at 1068.6 and 1017.6 cm^{-1} corresponds to the extension vibration of Si–O–Si in the backbone; Peaks at 1210.9, 1127.7, and 898.7 cm^{-1} are attributed to extension vibration of $SiCH_2CH_2CF_3$ present in the side chains; Peaks at 1369.5 and 1446.4 cm^{-1} are attributed to flexural vibration of $SiCH_3$; Peaks at 2966.6 and 2909.9 cm^{-1} corresponded to the extension vibration of $-CH_2-$ and $-CH_3$, respectively. The peaks observed at 3057.2 and 1594.1 cm^{-1} are ascribed to the end Si–CHCH$_2$ groups and phenyl groups. Peaks at 3699.4 cm^{-1} is ascribed to the end Si–OH groups, Peaks at 2130.8 cm^{-1} is ascribed to the end Si–H groups. The absorption bands of C–Cl are from 800 to 600 cm^{-1}, which are covered by those of other groups. The amount of initiators and termination reagents added was so little that the characteristic absorption bands of end groups exhibited in the ^{1}H NMR, ^{29}Si NMR and FT-IR spectra are very weak.

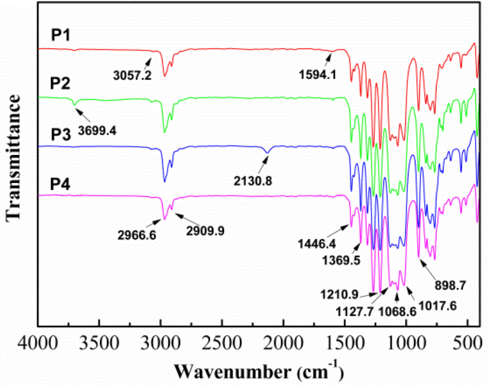


Figure 7 FT-IR spectra of PMTFPS with vinyl (P1), hydroxyl (P2), hydrogen (P3) and chloromethyl (P4) end groups.

Thermal stability analysis. α, ω-vinyl and hydroxyl PMTFPS are very important addition type and condensation type fluorosilicone rubber, respectively; and they are widely used as heat resistance materials. Therefore, the thermal stability of the polymers with vinyl and hydroxyl as end groups under N_2 and air were evaluated by TGA studies (Figures 8(A) and 8(B)). Figure 8(A) displays that the temperature at which there is 5% weight loss (Td_5) is 417 ℃ for divinyl-terminated PMTFPS (**P1**) and Td_5 is around 327 ℃ for dihydroxyl-terminated PMTFPS (**P2**) when the TGA analysis was performed under N_2. Thomas and Kendrick studied the thermal degradation of PDMS and proposed the formation of the cyclic dimethylsiloxane due to the rearrangement of the siloxane bond during the depolymerization[31, 32]. Probably, similar process happened during the thermal analysis of PMTFPS. For **P2**, the hydroxyl groups at the end attack the Si–O bond readily leading to the formation of D_m^F; thus, resulting in the weight loss (Schemes 5(1)); however, for **P1**, a higher temperature is needed for random intermolecular and intramolecular degradations, among which only intramolecular degradations produce D_m^F (Schemes 5(2) and 5(3)). The weights of the residues from **P1** and **P2** are nearly zero, which indicates that all the samples are degraded to the volatile D_m^F with small repeat units.

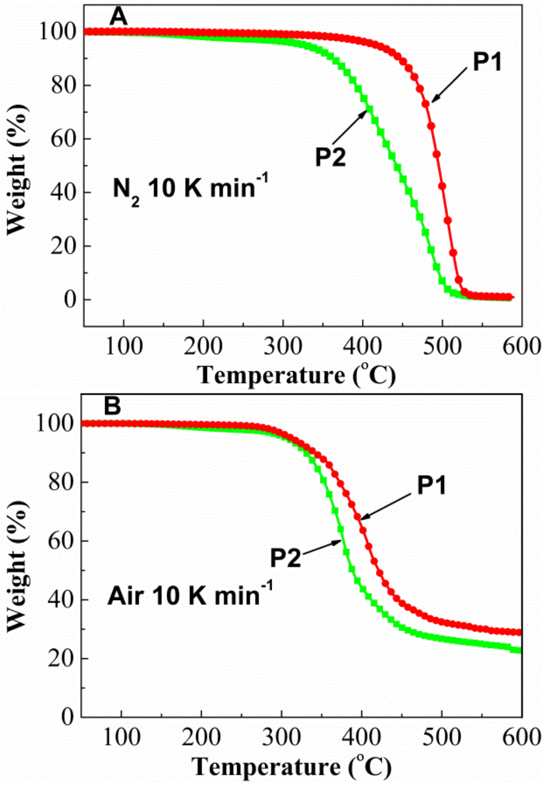
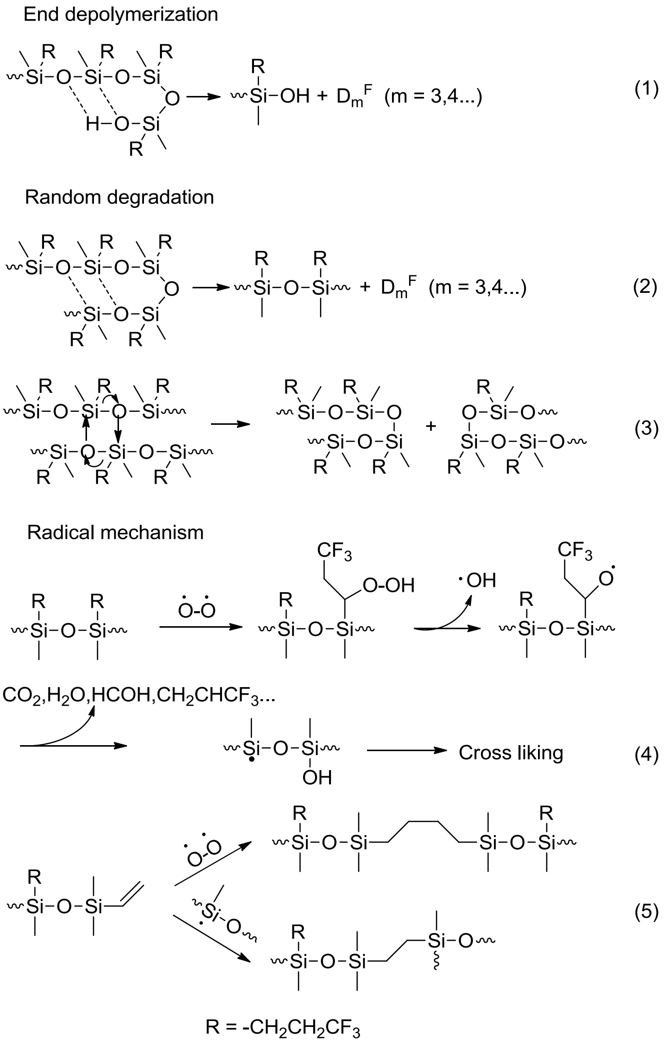


Figure 8 TGA of **P1** (divinyl-terminated PMTFPS, $Mn = 1.2 \times 10^4$ g mol^{-1}) and **P2** (dihydroxyl-terminated PMTFPS, $Mn = 1.4 \times 10^4$ g mol^{-1}). (A) **P1** and **P2** were under nitrogen atmosphere with heating rate 10 K min^{-1}; (B) **P1** and **P2** were under air atmosphere with heating rate 10 K min^{-1}.

When the thermal analysis was performed under air, the Td_5 are 312 ℃ for **P1** and 306 ℃ for **P2**, which are close to each other. This is because not only the end depolymerization and random degradation (Schemes 5(1) and 5(2)) occur, but also in the presence of O_2, the free radicals are formed and the side chains of the polymer start degrading, CO_2, H_2O, HCHO and a few of CF_3CHCH_2 are released (Schemes 5(4)). The free radicals from the oxidative degradation of the side chain cross-links with each other. The formation of volatile D_m^F led to the lowering of the weight percentages of the residues of **P1** and **P2** compared to their theoretical value (38%), if it was assumed that only the reactions represented in Schemes 5(4) happened and SiO_2 was the sole product. Furthermore, the weight percentage of the residue of **P1** was higher than that of **P2**. This is probably because vinyl groups at the end of **P1** undergo the free radical reaction more easily and form the cross-linking structures on the surface of the polymer (Scheme 5(5)); thus, preventing the random depolymerization to some extent.

Scheme 5 Possible Depolymerization and Oxidation at High Temperature for PMTFPS with vinyl or hydroxyl end group.



Conclusions

The kinetics studies of polymerization of D_3^F using three promoters with different ability to facilitate the reactions at various ratios of [P] to [I] showed that the backbiting reactions and intermolecular redistribution could be suppressed by using weak promoters or by decreasing the concentration of promoters. Therefore, a broad "termination window" with high yield of linear polymer and narrow molar mass distribution could be achieved by manipulating the types of the polymer and values of [P]/[I]. PMTFPS with end groups such as α, ω-vinyl, hydroxyl, hydrogen and chloromethyl were successfully synthesized with quantitative transformation. Moreover, the results indicated that MALDI–TOF was extremely effective in investigating the intermolecular redistribution during the polymerization. PMTFPS with vinyl end groups showed higher thermo stability than those with hydroxyl end groups under nitrogen. This study helped to better understand the mechanism and process of D_3^F anionic polymerization and provided a simple and efficient method to prepare PMTFPS with different end groups exhibiting unique properties.

Experimental

Materials. D_3^F was purchased from Weihai Newera Chemical Co., Ltd., dried using calcium hydride (CaH_2), and distilled under reduced pressure. The purity of D_3^F (99.5%) was assessed by ^{29}Si NMR and ^{1}H NMR. n-Butyllithium (2.5 molL^{-1} solution in n-hexane), dimethylchlorosilane ($(CH_3)_2SiHCl$; purity: 97%) and chloromethyldimethylchlorosilane ($ClCH_2(CH_3)_2SiCl$; purity: 97%) were purchased from Beijing InnoChem Science &Technology Co., Ltd. DMF, bis(2-methoxyethyl)ether (Diglyme), and 1,2-dimethoxyethane (DME) were bought from J&K Chemical Co., Ltd. (purity: 99%). Chlorodimethylvinylsilane ($(CH_3)_2ViSiCl$; purity: 97%) was purchased from Aldrich. $Ph_2Si(OLi)_2$ was synthesized in our laboratory whose purity was 97% estimated by solid state ^{29}Si NMR, ^{7}Li NMR, and titration.

Measurements. Gel permeation chromatography (GPC) was performed on a system composed of a Waters 515 HPLC Pump, a set of Waters μ-styragel columns (pore size: 10^3, 10^4, 10^5 Å), and a Waters 2410 refractometric detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set at 1 mL min^{-1} (30 °C). Samples were prepared in THF at 5–10 mg mL^{-1} and rapidly injected after preparation to avoid depolymerization. Molar mass and molar mass distribution of PMTFPS was determined from a calibration curve based on narrowly dispersed polystyrene standards. The data were collected and analyzed with Millennium 3.05.

A Bruker Autoflex III time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector was used for the MALDI–TOF analysis. 4-Chloro-alpha-cyanocinnamic acid was used as matrix and it was dissolved in THF at 10 mg mL^{-1}. Polymer solution (10 μL, 2–5 mg mL^{-1}) in THF was mixed with the matrix solution (50 μL), and sodium iodide solution (10 μL, 5 mg mL^{-1} in THF) was added to facilitate the ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides) were used to calibrate the mass scale. The data were collected and analyzed with FlexControl and FlexAnalysis, respectively.

The PMTFPS terminated by $(CH_3)_2ViSiCl$ was dissolved in deuterated acetone and their ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at ambient temperature. Chromium acetylacetonate was added to the polymer solution in deuterated acetone, as a relaxing reagent and the ^{29}Si NMR spectra were recorded on a Bruker DMX 300 spectrometer.

Solid state NMR experiments were carried out at room temperature on a Bruker AVANCE III 400 spectrometer operating at a static magnetic field of 7.05 T using a 4 mm magic angle spinning (MAS) probe. ^{29}Si and ^{7}Li NMR spectra were recorded under MAS conditions (sample rotation frequency: ^{29}Si NMR was 5 kHz, and ^{7}Li NMR was 12 kHz.) with cross polarization (CP) excitation, using π/2 pulse widths of 4.0 μs. The ^{29}Si and ^{7}Li NMR chemical shifts were determined relative to external standards of TMS and LiCl (δ = 0 ppm), respectively. CP MAS ^{29}Si NMR: δ –34.57 [s, $(C_6H_5)_2\mathbf{Si}(OLi)_2$]. CP MAS ^{7}Li NMR: δ 2.62 [s, $(C_6H_5)_2Si(O\mathbf{Li})_2$].

Fourier transform infrared (FT-IR) of PMTFPS with different end groups spectra were collected on a Bruker TENSOR-27 IR spectrometer.

Thermogravimetric analyses (TGA) were performed on a SII EXTRA 6300 TG/DTA apparatus, using 6–10 mg of polymer, at a heating rate of 10 K min^{-1} with nitrogen or air as the purge gas at 20.0 mL min^{-1}.

Synthesis of Dilithium Diphenylsilanediolate ($Ph_2Si(OLi)_2$). The initiator, $Ph_2Si(OLi)_2$ was prepared in a three neck flask from a solution of dry diphenylsilanediol (10.80 g, 50 mmol) dissolved in 60 mL THF under dry nitrogen atmosphere. n-Butyllithium (21.00 mL, 52.5 mmol) was slowly introduced to the solution in 1 h at −78 °C so that it turned to a primrose yellow color. THF was removed with rotary evaporation; the resulting solid product was washed 3 times with n-hexane; and a 10.40 g faint yellow powder was obtained[33].

Polymerization. For all the reactions, D_3^F (9.36 g, 20 mmol) and $Ph_2Si(OLi)_2$ (0.1142 g, 0.5 mmol) were well mixed by sonication in a polymerization tube under nitrogen. Then, the mixture was heated to 40 °C in an isothermal oil bath and continuously stirred at 300 rpm. The process of polymerization started when the promoters were added to the reaction tubes. The amount of the promoters added to the reaction were determined according to the value of [P]/[I]. Aliquots were taken from the reaction mixture, quenched by adding slightly excess amount of chlorodimethylvinylsilane, acetic acid, dimethylchlorosilane or chloromethyldimethylchlorosilane (scheme 2), and analyzed by ^{29}Si NMR in order to monitor the progress of polymerization. PMTFPS with different end groups were synthesized using $Ph_2Si(OLi)_2$ as initiator and DME as the promoter, [P]/[I] = 2.0. Samples were purified before TGA test as follows: 5 g of the synthetic polymer was dissolved in 10 mL of ethyl acetate and then precipitated through adding 10 mL of methyl alcohol. Repeated this manipulation several times until the lithium chloride was removed completely.

Acknowledgements

We are grateful to National Nature Sciences Foundation of China (No.50803070) for financial support. Special acknowledgements are given to Prof. Xie Zemin for his enduring help during the work and Mrs. Guiyun Xu for her assistance on TGA tests.

Notes and references

[a]Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
[b]Graduate University of Chinese Academy of Sciences, Beijing 100049, China.
Corresponding Author: Prof. Zhang Zhijie
E-mail: zhangzj@iccas.ac.cn

† Electronic Supplementary Information (ESI) available: [CP MAS ^{29}Si-NMR spectra, CP MAS ^{7}Li-NMR]. See DOI: 10.1039/b000000x/

1 Y. Liu, H. Liu, R. Zhang, C. Zhou and S. Feng, *Polymer Engineering and Science*, 2013, **53**, 52-58.
2 S. Luciano and H. William, *Industrial & Engineering Chemistry*, 1958, **50**, 1583-1584.
3 J. M. Nielsen, *Journal of Polymer Science: Polymer Symposia*, 1973, **40**, 189-197.
4 D. K. Thomas, *Polymer*, 1972, **13**, 479-483.
5 G. Budden, *Journal of Coated Fabrics*, 1998, **27**, 294-308.
6 S. Z. Wu and J. E. Mark, *Polymer Reviews*, 2007, **47**, 463-485.
7 K. E. Polmanteer, *Rubber Chemistry and Technology*, 1988, **61**, 470-502.
8 T. Hu, L. Dai, X. Gao, J. Xie, W. Xie, Z. Xie and Z. Zhang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2014, **52**, 1408-1421.
9 T. M. Madkour and J. Mark, *Macromolecules*, 1995, **28**, 6865-6870.
10 Y. Liu, C. Zhou, and S. Feng, *Materials Letters*, 2012, **78**, 110-112.
11 H. Inoue, A. Matsumoto, K. Matsukawa, A. Ueda and S. Nagai, *Journal of Applied Polymer Science*, 1990, **40**, 1917-1938.
12 B. Li, S. Chen and J. Zhang, *Polymer Chemistry*, 2012, **3**, 2366-2376.
13 H. Kobayashi and W. Nishiumi, *Makromolekular Chemistry and Physics*, 1993, **194**, 1403-1410.
14 C.-M. Kuo, J. C. Saam and R. B. Taylor, *Polymer international*, 1994, **33**, 187-195.
15 L. M. Yi, X. L. Zhan, F. Q. Chen, F. Du, and L. B. Huang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2005, **43**, 4431-4438.
16 C. A. Veith, R. E. Cohen, *Journal of Polymer Science Part A: Polymer Chemistry*, 1989, **27**, 1241-1258.
17 M. Barrère, C. Maitre, M. A. Dourges and P. Hèmery, *Macromolecules*, 2001, **34**, 7276- 7280.
18 W. Peng and Z. Xie, *Macromolecular Chemistry and Physics*, 2000, **201**, 1292-1294.
19 Z. Shi, and X. Wang, *Polymers for Advanced Technologies*, 2009, **20**, 1017-1023.
20 J. E. Mark, *Accounts of Chemical Research*, 2004, **37**, 946-953.
21 A. K. Sutar, T. Maharana, S. Dutta, C.-T. Chena and C.-C. Lin, *Chemical Society Reviews*, 2010, **39**, 1724-1746.
22 Y. A. Yuzhelevskii, V. V. Pchelintsev, and Y. G. Kagan, *Journal of Polymer Science USSR*, 1973, **15**, 1795-1799.
23 Y. A.Yuzhelevskii, Y. G. Kagan, N. P. Timofeyeva, T. D. Doletskaya and A. L. Klebanskii, *Journal of Polymer Science USSR*, 1971, **13**, 208-216.
24 Y. A. Yuzhelevskii, Y. G. Kagan and N. N. Fedoseyeva, *Journal of Polymer Science USSR*, 1970, **12**, 1800-1809.
25 Y. A. Yuzhelevskii, Y. G. Kagan, E. V. Kogan, A. L. Klebanskii and N. N. Nikiforova, *Journal of Polymer Science USSR*, 1969, **11**, 1745-1750.
26 Y. Zhang, Z. Zhang, Q. Wang and Z. Xie, *Journal of Applied Polymer Science*, 2006, **102**, 3510-3516.
27 H. W. Ahn, S. J. Clarson, *Silicon*, 2011, **3**, 157-161.
28 X. Gao, Q. Wang, H. Sun, Y. Tan, Z. Zhang and Z. Xie, *Phosphorus, Sulfur, and Silicon and the Related Elements.* DOI:10.1080/10426507.2013.860534.
29 T. Suzuki, *Polymer*, 1989, **30**, 333-337.
30 M. Cypryk, B. Delczyk, A. Juhari and K. Koynov, *Journal of Polymer Science Part A: Polymer Chemistry*, 2009, **47**, 1204-1216.
31 T. H. Thomas and T. C. Kendrick, *Journal of Polymer Science Part A-2: Polymer Physics*, 1970, **8**, 1823-1830.
32 T. H. Thomas and T. C. Kendrick, *Journal of Polymer Science Part A-2: Polymer Physics*, 1969, **7**, 537-549.
33 P. B. Kevin, C.-M. Kuo, L. M. Robert, and C. S. John, *Macromolecules*, 1995, **28**, 790-792.