

## Improved synthesis and properties of hydroxyl-terminated liquid fluorosilicone

Guo-Dong Zhang,<sup>1,2</sup> Ying-Qian Hu,<sup>2</sup> Ji-Rong Wu,<sup>2</sup> Jia-Yun Li,<sup>2</sup> Guo-Qiao Lai,<sup>1,2</sup> Ming-Qiang Zhong<sup>1</sup>

<sup>1</sup>College of Chemical Engineering and Materials, Zhejiang University of Technology, Hangzhou, 310014, China

<sup>2</sup>Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, 310012, China

Correspondence to: G.-Q. Lai (E-mail: zgd830@sina.com) and M.-Q. Zhong (E-mail: zhongmq@zjut.edu.cn)

**ABSTRACT:** The synthesis of hydroxyl-terminated poly(trifluoropropylmethyl)siloxane (PTFPMS-OH) by anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (D<sub>3</sub>F) was studied in bulk using potassium hydroxide as an initiator in the presence of several reaction stabilizers. The promoting effect of the reaction stabilizers for the polymerization of D<sub>3</sub>F was investigated by GPC and NMR analyses. Results showed that the selected reaction stabilizers exhibited a significant promoting effect. This new process of polymerization produced well-defined  $\alpha,\omega$ -dihydroxylated polysiloxane in very high yields. The addition of reaction stabilizers could almost completely suppress back-biting reactions during the polymerization. It was found that there lies an exponential decay relationship between the molecular weight of PTFPMS-OH and amount of end-capping agent. Thus, by adjusting the reaction conditions strictly, the molecular weight of the fluorosilicone could be controlled accurately, and meanwhile a broad “terminate window” could be implemented. Thermogravimetric (TG) analysis indicated that PTFPMS-OH could be used in a wide range of operational temperatures. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43220.

**KEYWORDS:** properties and characterization; ring-opening polymerization; thermal properties

Received 5 August 2015; accepted 11 November 2015

DOI: 10.1002/app.43220

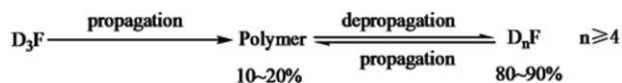
### INTRODUCTION

Organopolysiloxanes having 3,3,3-trifluoropropyl groups bonded to the silicon atoms are widely used as the principal constituent of various kinds of silicone products by virtue of their unique properties such as low surface energy and excellent oil resistance, and thus it is a promising material for different commercial and military applications.<sup>1–11</sup> The introduction of F atom would increase the polarity of polysiloxane molecules, and thus the oil and fuel resistance properties of the silicone rubber could be well improved.<sup>5,12</sup> Fluorosilicone gums can be made into fluorosilicone rubbers of both heat cured, and room-temperature vulcanizable varieties.<sup>13–15</sup> Among many possible fluoro-substituted diorganopolysiloxane compositions, the hydroxyl-terminated poly(trifluoropropylmethyl)siloxane (PTFPMS-OH) fluids are especially valuable. PTFPMS-OH is usually used to prepare room-temperature vulcanized PTFPMS rubber,<sup>5,16–18</sup> and in general, it is synthesized by the ring-opening polymerization of D<sub>3</sub>F.<sup>19–22</sup>

Despite its wide applications, only limited literatures<sup>6–8,21,23</sup> have been published on the preparation of PTFPMS-OH, largely because of the unfavorable equilibrium between the linear poly-

mers and cyclic by-products during the polymerization (Scheme 1).

As shown in Scheme 1, the linear polymers are formed by the consumption of D<sub>3</sub>F (the chain propagation), while the unexpected cyclic by-products, D<sub>n</sub>F, are also formed simultaneously through the chain redistributions or the back-biting by chain ends of linear polymers (the chain depropagation) and a content as high as 80~90 wt % has been proved at equilibrium.<sup>9</sup> This highly unsatisfactory result drives the organosilicon chemists to explore new methods to suppress the cyclics content for both scientific interest and industrial consideration. Veith *et al.*<sup>21</sup> carried out the kinetic analysis of the polymerizations of D<sub>3</sub>F to determine the optimal polymerization conditions for the maximal yield of PTFPMS (85–90 wt %). However, most of these studies focus on emulsion polymerization<sup>23–25</sup> or the conventional two step water splitting preparation, and so far, there are only a few researchers who paid attention to the bulk polymerization of D<sub>3</sub>F.<sup>26,27</sup> The main advantage of the anionic polymerization in bulk is that it is a very simple process that does not require any purification or an inert atmosphere, but there is still a key problem to be solved: How to precisely control the viscosity of PTFPMS-OH and effectively inhibit the side



**Scheme 1.** Equilibrium between polymer and cyclic products in bulk or solution polymerization of  $\text{D}_3\text{F}$ .

reaction. This question has been troubling organosilicon chemists and thus drove us to explore a satisfactory solution.

For this purpose, we developed a novel process for producing PTFPMS-OH in high yield while minimizing the production of undesirable cyclic byproducts, which will seriously affect the properties of the final cured fluorosilicone elastomers. In this paper, three different additives were employed as reaction stabilizers in the anionic bulk polymerization of  $\text{D}_3\text{F}$ . The mechanism of their remarkable promoting effect on the polymerization and the great improvement in controllability of the molecular weight (MW) were also discussed in detail.

## EXPERIMENTAL

### Materials

1,3,5-Tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane ( $\text{D}_3\text{F}$ , 99.5%), obtained from Weihai New Era Chemical Co., Ltd (Weihai, Shandong Province, China) was used as received.

Potassium hydroxide (KOH, 99.99%) was provided by Sigma Co., Ltd. Calcium chloride ( $\text{CaCl}_2$ ), the stabilizers A-fatty alcohol polyoxyethylene ether AEO-9 (Rhodia, Beijing), the stabilizers B-tetrabutylammonium hydrogen sulfate (Aladdin, Shanghai) and the stabilizers C-Tween 20 (ethoxylate derivative polysorbate 20, Haian, Jiangsu Province), and other chemicals were of analytical grade and used as received.

### Measurements

Gel-permeation chromatography (GPC) analysis was performed on a Waters 515 system consisting of a 515 high-pressure liquid chromatography (HPLC) pump and a 2410 differential refractive index (RI) detector.

$^1\text{H-NMR}$  and  $^{29}\text{Si-NMR}$  analyses were conducted with a Bruker Avance 400 MHz NMR spectrometer (Bruker, Germany) operating respectively at 400.13 and 79 MHz, at room temperature with  $\text{CDCl}_3$  as the solvent.

Thermo gravimetric analysis (TGA) was performed on a Shimadzu instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere, and temperatures ranged from  $20^\circ\text{C}$  to  $600^\circ\text{C}$ .

The accurate mass spectra (MS) measurements were performed on a micro-TOF QII(Q-TOF) mass spectrometer from Bruker Daltonics (Billerica, MA, USA), in a positive ESI mode. The diluted solution was directly infused into the electrospray ionization source of the mass spectrometer with a syringe pump at a flow rate of  $180 \mu\text{L}/\text{h}$ . The parameters of Q-TOF mass spectrometers were set as follows: drying gas flow in the ion source was set up to  $2.2 \text{ L}/\text{min}$  and nebulizer gas pressure to 0.4 Bar (both were  $\text{N}_2$ ), the temperature of ion source was  $200^\circ\text{C}$ , and voltage was 4.5 kV. The instrument was operated at a resolution higher than 15,000 full width at half maximum using the microTOF-Q control program ver. 2.3. The data were analyzed using the Data Analysis ver. 4 software package delivered by Bruker Daltonics.

### Polymerization

A mixture of  $\text{D}_3\text{F}$ , deionized water (varied in the range from 200 to 700 ppm) and solid KOH (60, 90, or 120 ppm) was introduced into a reactor equipped with a thermometer, mechanical stirrer, condenser and addition port, which was kept in an oil bath maintained at  $35^\circ\text{C}$ . Then polymerization was triggered by the addition of reaction stabilizers (fixed at 60 ppm) into the reactor. The early stage of the subsequent 90-minute period of polymerization proved to be an exothermic course as the temperature of the reaction mixture rose from  $35^\circ\text{C}$  to  $45^\circ\text{C}$  spontaneously, and meanwhile, the viscosity increased gradually. Whereafter, the temperature dropped back to  $35^\circ\text{C}$  gradually along with the appearance of a viscosity platform. The polymerization was quenched quickly with a silicone phosphoric acid at a desired time, and then the sample was taken out from the reactor and dried by calcium chloride before testing.

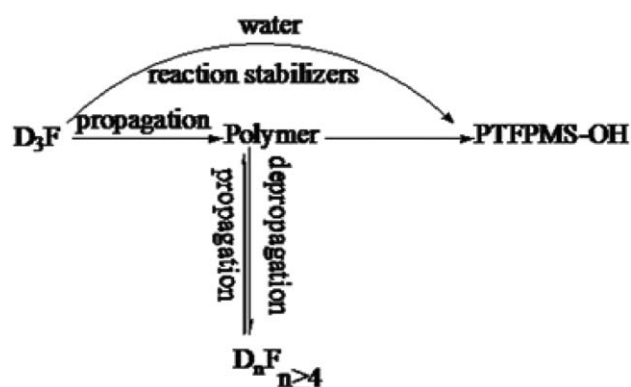
### Purification of the Product

PTFPMS-OH was obtained by precipitating the sample into a large excess of MeOH. After decantation, PTFPMS-OH was washed three times with MeOH and dried to a constant weight in a vacuum oven at  $40^\circ\text{C}$ . The isolated yield of PTFPMS-OH was calculated by the weight ratio of pure PTFPMS-OH isolated from the crude product to  $\text{D}_3\text{F}$ . The methanol solution was collected and then concentrated to analyze the small molecules in the resultant reaction mixture by Q-TOF.

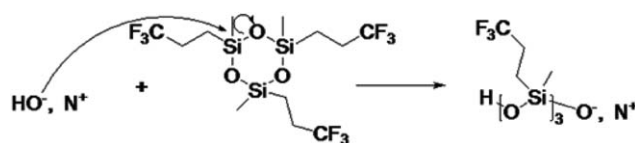
## RESULTS AND DISCUSSION

### Effect of Stabilizers on the Reaction Results

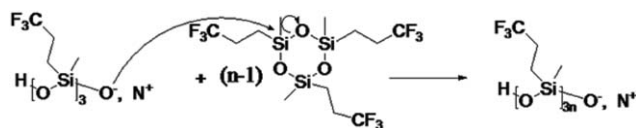
Scheme 2 shows the synthesis route of PTFPMS-OH employing reaction stabilizers. In the presence of reaction stabilizers, the preparation of PTFPMS-OH via bulk polymerization exhibited a remarkable result compared with the traditional emulsion polymerization and two step water splitting method.



**Scheme 2.** The synthesis of PTFPMS-OH.



**Scheme 3.** Equation of alkali initiated ring-opening.



**Scheme 4.** Equation of the propagation step.

GPC was utilized to analyze PTFPMS-OH in tetrahydrofuran (THF) using deactivated reaction mixture directly. Figure 1 shows the GPC curves of the crude reaction mixtures obtained by the polymerization of  $D_3F$  at 300 rpm and  $35^\circ\text{C}$  after 30 min with and without reaction stabilizers.

In the case of reactions at  $35^\circ\text{C}$  without reaction stabilizers, the GPC curves of the resultant mixture are almost consistent with those of the starting materials. In contrast, GPC revealed obvious peak shifts when reaction stabilizers were added, and monomodal distributions with polydispersity indexes (PDI) under 1.36 were presented, indicating that high purity fluorosilicone products were formed. This result suggests that the reaction stabilizers played a crucial role in these reactions, which could initiate and promote the polymerization of  $D_3F$  under the aforementioned condition.

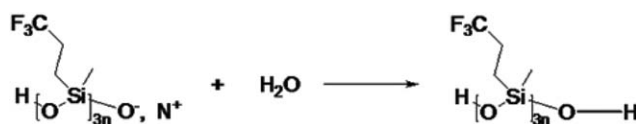
#### NMR Analysis

$^{29}\text{Si}$ -NMR spectroscopy turned out to be a powerful tool for exploring the structure of polysiloxanes.<sup>5</sup> Representative  $^{29}\text{Si}$ -NMR spectra of the raw material  $D_3F$  and PTFPMS homopolymer are displayed in Figure 2.

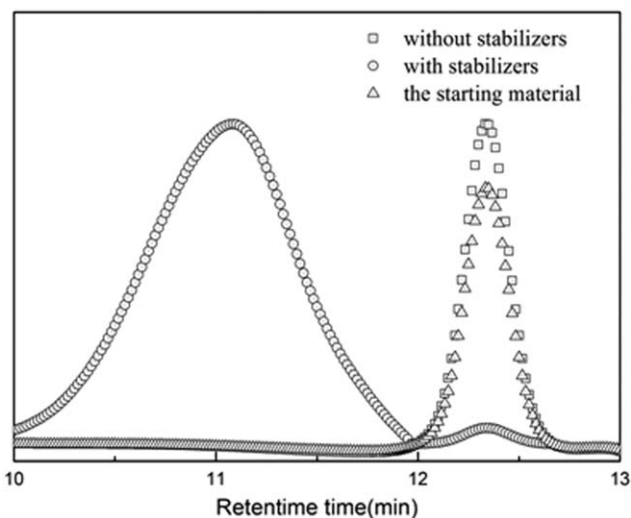
The chemical shift of the fluorosilicone backbone at  $-22.2$  ppm is in agreement with the reference values of the regions of 22.3 to 25 ppm.<sup>28</sup> The monomer  $D_3F$  resonates at  $-9.23$  ppm, which is in agreement with the reference value of 9.3 ppm. However, it is very difficult to distinguish the signals of the product from the raw material by the  $^1\text{H}$ -NMR spectra, owing to their almost complete overlapping.

#### Effect of Reaction Factors on the Reaction Process

**Effect of the Reaction Time.** Figure 3 shows the dependence of the  $M_n$  of PTFPMS-OH on the reaction time in the range from 30 to 180 min. In the presence of reaction stabilizers, the polymerization could be initiated and proceed smoothly under lower temperature. The whole reaction process could be divided into three stages. In the first stage,  $D_3F$  was consumed rapidly and the MW of the PTFPMS-OH also increased rapidly, with PDI rising from 1.19 to 1.36. After most  $D_3F$  accomplished the ring-opening reaction, the MW increment was no longer noticeable with the PDI almost constant and furthermore, cyclic byproducts could hardly be detected, which means the second stage. That is to say, the chain redistributions and backbiting reactions were completely suppressed and consequently, the whole reaction system tended to be stable. Therefore, this offered a broad "termination window" for achieving both pre-



**Scheme 5.** Equation of the termination with water.



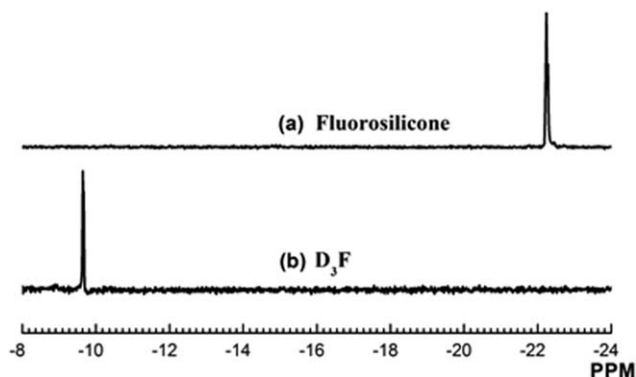
**Figure 1.** GPC traces for the polymerization of  $D_3F$  in the presence and absence of stabilizers A at 300 rpm and  $35^\circ\text{C}$  after 30 min.

determined MW and high polymer yield. In other words, highly controllable polymerization process could be conveniently realized only by employing reaction stabilizers and low reaction temperature.

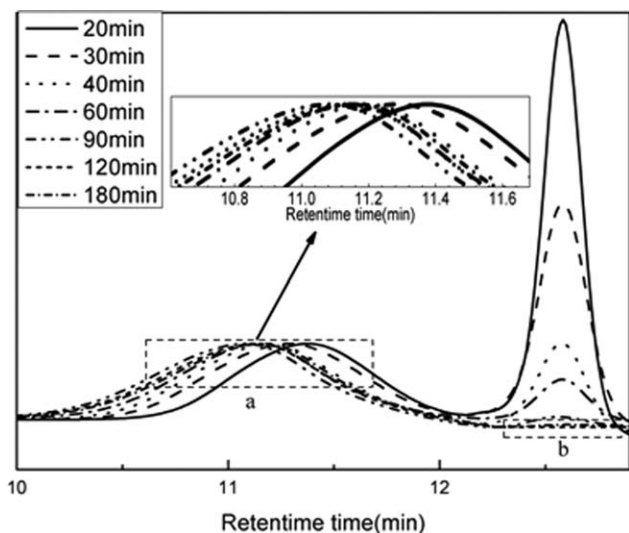
As the reaction time increased to more than 120 min, the third stage began and a decrease of the MW and increase of the cyclic-byproduct content became apparent, resulting in the reduction of PTFPMS-OH yield, demonstrating that the back-biting reactions become active.

As shown in Figure 3, the optimal reaction time was confirmed as 90–120 min, where almost no presence of cyclic byproducts. The decrease in both the  $M_n$  and yield of PTFPMS-OH indicated that the back-biting reactions began after 120 min of polymerization.

According to the results of GPC as well as  $^{29}\text{Si}$ -NMR, when the whole reaction system tended to be stable (the second stage), the content of the small molecules species were quite low. Further quantitative calculation was conducted by the isolated yield of the PTFPMS-OH and the values of more than 97% were confirmed, demonstrating that the  $D_3F$  was almost transformed into linear fluorosilicones.



**Figure 2.**  $^{29}\text{Si}$ -NMR spectra of PTFPMS-OH (a) and  $D_3F$  (b).



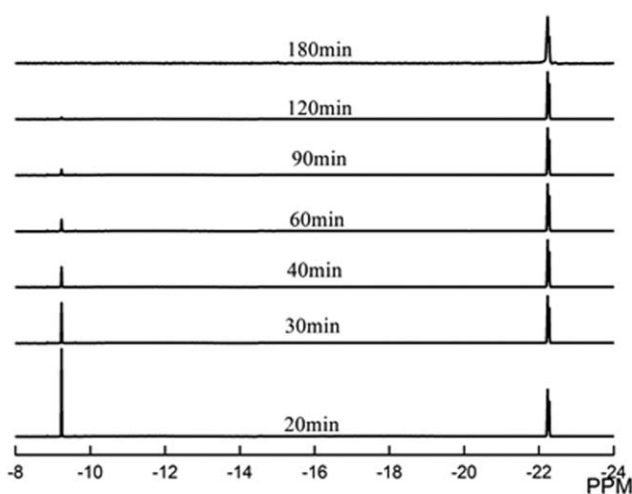
**Figure 3.** GPC traces for the polymerization of  $D_3F$  in the presence of reaction stabilizers at  $35^\circ\text{C}$  and 300 rpm.

The  $^{29}\text{Si}$ -NMR spectra (Fig. 4) were in accordance with the result revealed by GPC, which confirmed the stepwise consumption of  $D_3F$  in the course of the polymerization.

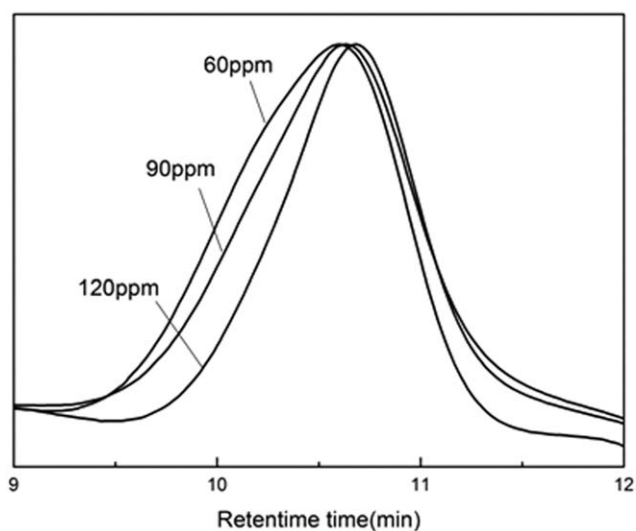
**Effects of Water or Initiator Concentration on the Molecular Weight of PTFPMS-OH.** The molecular weight and its distribution of liquid fluorine silicone molecules is one of the key structure parameters, which is an important basis for quality control of cured fluorosilicone elastomers.

Figure 5 shows the  $M_n$  and PDI of PTFPMS-OH in relation to the initiator concentration. Three initiator concentrations of 60, 90, and 120 ppm were investigated. As seen in Figure 5, the  $M_n$  increased and molecular weight distribution of PTFPMS-OH widened slightly with decreasing initiator concentration under otherwise equal conditions.

In the case of the reactions with fixed monomer concentration, reducing the initiating activity point led to an increase in



**Figure 4.**  $^{29}\text{Si}$ -NMR spectra of PTFPMS-OH at different reaction times in the presence of reaction stabilizers at  $35^\circ\text{C}$  and 300 rpm.



**Figure 5.** GPC curves of PTFPMS-OH with various initiator concentrations.

molecular weight and at the same time its distribution broadened. The experimental data are listed in Table I.

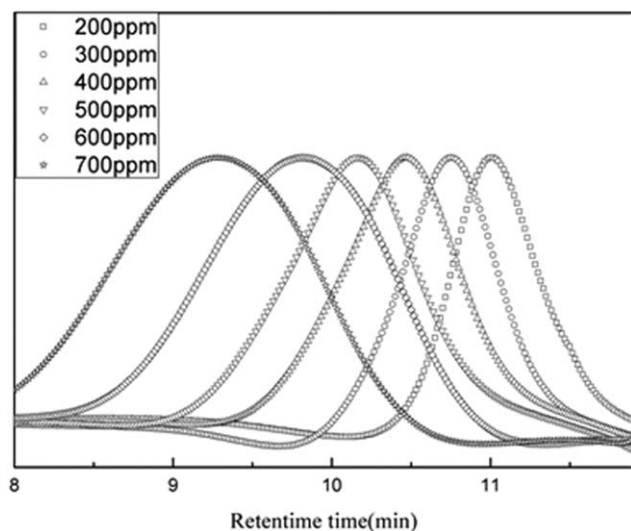
For studying the influence of the water concentration on the molecular weight, the concentration of the reaction stabilizers and initiator (KOH) were fixed at 60 and 90 ppm, respectively, while water concentration was varied in the range from 200 to 700 ppm. Figure 6 and Table II shows the  $M_n$  and PDI of PTFPMS-OH in relation to water concentration. Six different concentrations of 200, 300, 400, 500, 600, and 700 ppm were investigated. As seen in Figure 7, the relationship between the MW of PTFPMS-OH and water concentration fitted an exponential decay curve perfectly. Consequently, efficient molecular-weight control could be attained conveniently in this ROP in the presence of reaction stabilizers by adjusting the water concentration.

#### Analysis of the Small Molecules

The small molecules were obtained from the resultant reaction mixture and Q-TOF MS was used to characterize their mass information and their corresponding intensities. The molecular structures of the residual products were deduced on the base of the mass information ( $m/z$ ) obtained by the attachments of sodium cations. The ions distributions in Figure 8 were detected between  $m/z$  400 and  $m/z$  1000 and included a spacing of  $m/z$  156 corresponding to the mass of PTFPMS repeat unit. The stronger peaks were mostly attributed to the oligomers, such as

**Table I.** Effect of Initiator Concentration on the Molecular Weight, Apparent Viscosity, and Molecular Weight Distribution of PTFPMS-OH

Initiator concentration (ppm)	$M_n$	Apparent viscosity (mPa s)	$M_w/M_n$
60	23524	1.15	1.31
90	22266	1.13	1.26
120	21046	1.10	1.18



**Figure 6.** GPC curves of PTFPMS-OH with various water concentrations.

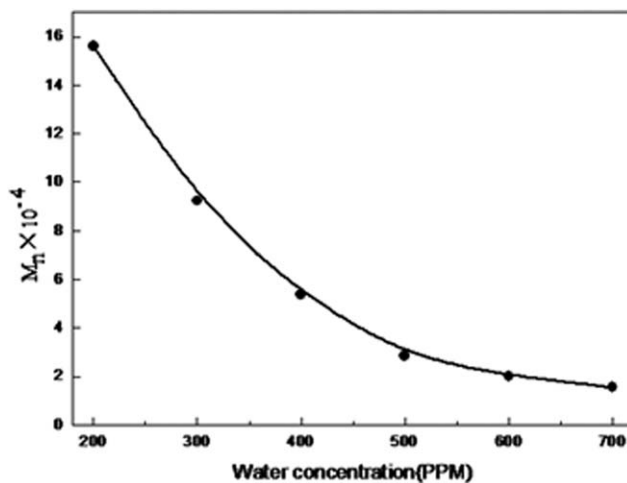
HO (F)<sub>3</sub>OH (*m/z* 509.1), HO (F)<sub>4</sub>OH (*m/z* 665.1), HO (F)<sub>5</sub>OH (*m/z* 821.1), and so on. The weaker peaks were identified as other oligomers, the monomer and Fn ( $n \geq 4$ ) formed either by intermolecular redistribution or back-biting reactions. Cyclic by-products during the preparation of polysiloxanes have been also observed by some researchers.

#### Thermal Stability

Polysiloxanes are well known mostly for their high thermal stability because of the strong strength of Si-O bond ( $108 \text{ kcal mol}^{-1}$ ).<sup>29,30</sup> In order to eliminate the influence of molecular weight, i.e. OH group content, on the thermal stability, stabilizers-containing and stabilizers-free PTFPMS-OHs with similar molecular weights were chosen to analyze the effect of stabilizers on the thermal stability. As shown in Figure 9, all samples showed similar thermal stability. The reaction stabilizers had no evident effect on the thermal stability of PTFPMS-OH. The onset weight loss determined from 20 to 300°C was less than 2.0 wt %, which should be attributed to the evaporation of the oligomeric contaminants and trace amounts of residual cyclic by-products. The threshold of the degradation temperature was higher than 400°C, demonstrating that PTFPMS-OH

**Table II.** Effect of Water Concentration on the Molecular Weight, Apparent Viscosity, and Molecular Weight Distribution of PTFPMS-OH

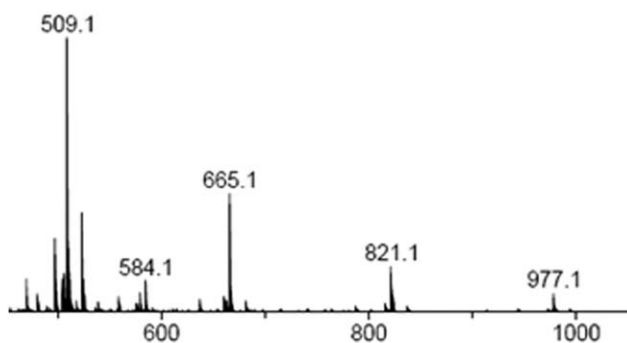
Water concentration (ppm)	$M_n$	Apparent viscosity ( $\times 10^3 \text{ mPa s}$ )	$M_w/M_n$
200	1,56,065	1010	1.40
300	92,095	400	1.36
400	53,788	120	1.33
500	28,424	28	1.19
600	20,054	11	1.15
700	15,484	6	1.15



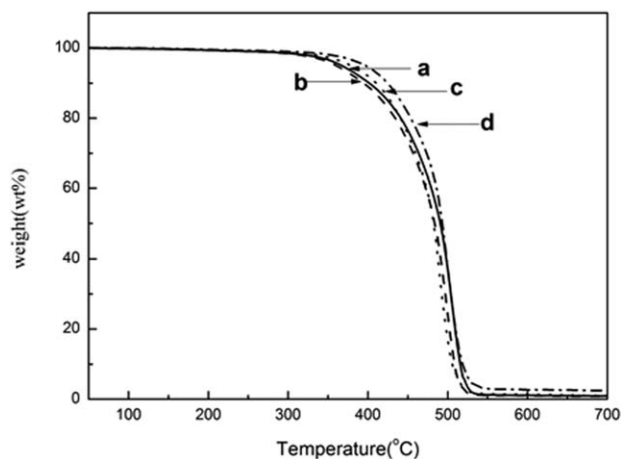
**Figure 7.** Relationship between water concentration and the molecular weight.

had good thermal stability. The temperature at 5% and 10% weight loss was 360°C and 393°C, respectively.

There was a significant weight loss from 400 to 600°C and less than 5.0 wt % residue was found above 580°C.



**Figure 8.** Q-TOF MS spectrum of the small molecules extracted from the resultant reaction mixture.



**Figure 9.** TGA curves of PTFPMS-OH: (a) without stabilizer; (b) with stabilizer A; (c) with stabilizer B; (d) with stabilizer C.

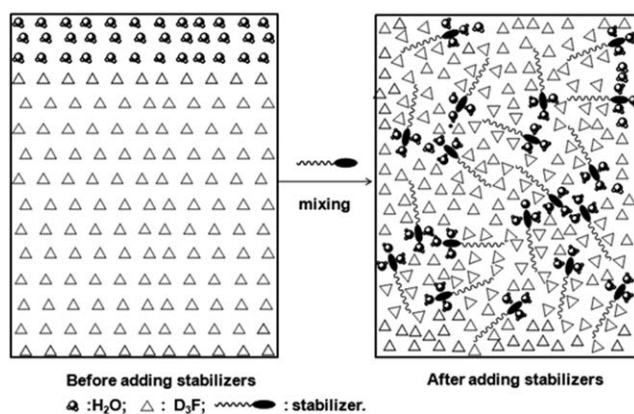


Figure 10. Scheme for the formation of PTFPMS-OH.

### The Polymerization Mechanism Analysis

The anion ring-opening polymerization mechanism could be used to explain the homopolymerization process of polysiloxane. In the initial phase of the polymerization, the reaction between the cyclosiloxanes and the end-capping agent was initiated by KOH (Scheme 3–5).

As mentioned by Grubb *et al.*, the anionic polymerization of cyclosiloxane was initiated by the free anions. Moreover, the stronger the solvation of the promoters to ion pairs of initiators was, the higher the initiators activity should be. In the presence of reaction stabilizers, more free ions were produced through the specific solvation of reaction stabilizers to the cations (K<sup>+</sup>) of initiators. As a result, the anionic polymerization of D<sub>3</sub>F was accelerated and the viscosity of the reaction mixture increased dramatically, which was reflected by GPC curves in Figure 1. Furthermore, the reaction stabilizers in this reaction should also facilitate the migration of water into D<sub>3</sub>F phase where reaction occurred in Figure 10.

It is well known that ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of phase-transfer catalyst.

In other words, the reaction stabilizers acted as not only solvation promoters but also phase transfer catalysts.

By using the reaction-stabilizers-containing process, we can achieve faster reactions, obtain higher conversions and yields, make fewer byproducts, avoid the employment of expensive or dangerous solvents for homogeneous reaction, eliminate the need for expensive raw materials and/or minimize waste problems.

### CONCLUSIONS

A successful preparation of PTFPMS-OH was carried out using potassium hydroxide as an initiator together with reaction stabilizers.

Well-defined PTFPMS-OH could be prepared efficiently and conveniently with tunable molecular weight and narrow distribution by adjusting the water concentration. Compared to classical anionic polymerization in bulk or in solution, high

conversion and good controllability were accomplished simultaneously under mild conditions in this research.

### ACKNOWLEDGMENTS

The authors thank the Natural Science Foundation of China (21274131), Zhejiang Provincial Natural Science Foundation (Y14E030031), and Qianjiang Talent Project of Zhejiang Province (2009R10021) and the Foundation of Zhejiang Educational Committee (Y201327588) for financial support.

### REFERENCES

1. Aliev, R. *Radiat. Phys. Chem.* **1999**, *56*, 347.
2. Furukawa, Y.; Shin-Ya, S.; Saito, M.; Narui, S.; Miyake, H. *Polym. Adv. Technol.* **2002**, *13*, 60.
3. Conrad, M. P. C.; Shoichet, M. S. *Polymer* **2007**, *48*, 5233.
4. Liu, Y. T.; Liu, H. Z.; Zhang, R.; Zhou, C. J.; Feng, S. Y. *Polym. Eng. Sci.* **2013**, *53*, 52.
5. Kählig, H.; Zöllner, P.; Mayer-Helm, B. X. *Polym. Degrad. Stab.* **2009**, *94*, 1254.
6. Paulasaari, J. K.; Weber, W. P. *Polym. Mater. Sci. Eng.* **2000**, *82*, 71.
7. Grunlan, M. A.; Mabry, J. M.; Weber, W. P. *Polymer* **2003**, *44*, 981.
8. Yang, J.; Yang, H.; Xu, J.; Li, H. Q. *China Pet. Process. Pe.* **2011**, *13*, 53.
9. Donskoi, A. A.; Baritko, N. V. *Polym. Sci. Ser. C.* **2007**, *49*, 182.
10. Pagliani, M.; Gross, C.; Tonge, L. *Rubber World* **2008**, 237, 22.
11. Fujino, M.; Hisaki, T.; Fujiki, M.; Matsumoto, N. *Macromolecules* **1992**, *25*, 1079.
12. Li, B.; Chen, S. J.; Zhang, J. J. *Elastom. Plast.* **2014**, *46*, 695.
13. Osamu, H.; Kazuhiro, O.; Atsuhito, K. E.P. Patent 2883,903; **2015**.
14. Xu, T.; Liu, H.; Song, J.; Shang, S.; Song, Z. Q.; Zou, K. F.; Yang, C. *J. Polym. Sci. Pol. Chem.* **2015**, *53*, 1769.
15. Xu, T.; Liu, H.; Song, J.; Shang, S.; Song, Z. Q.; Zou, K. F.; Yang, C. *J. Appl. Polym. Sci.* **2015**, *132*, 41888.
16. Li, B.; Chen, S. J.; Zhang, J. J. *J. Appl. Polym. Sci.* **2014**, *131*, 39708.
17. Dziark, J. J.; Spa, B. U.S. Patent 5,354,833; **1994**.
18. Wyatt, N. B.; Grillet, A. M. *J. Appl. Polym. Sci.* **2014**, *131*, 40034.
19. Yang, P.; Gao, Y. J.; Guan, Y.; Zheng, A. N. *Chem. J. Chinese. U.* **2011**, *32*, 1431.
20. Furukawa, Y.; Kotera, M. *J. Polym. Sci. Polym. Chem.* **2002**, *40*, 3120.
21. Veith, C. A.; Cohen, R. E. *J. Polym. Sci. Polym. Chem.* **1989**, *27*, 1241.
22. Gao, Y. J.; Yang, P.; Guan, Y.; Wei, D. F.; Zheng, A. N. *Polym. Mater. Sci. Eng.* **2011**, *27*, 20.

23. Bouanani, F.; Bendedouch, D.; Maitre, C.; Teixeira, J.; Hemery, P. *Polym. Bull.* **2005**, *55*, 429.
24. Barrère, M.; Maitre, C.; Dourges, M. A.; Hémerly, P. *Macromolecules* **2001**, *34*, 7276.
25. Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689.
26. Yi, L. M.; Zhan, X. L.; Chen, F. Q. *Chem. Eng. Chin. Univ.* **2008**, *22*, 299.
27. Yi, L. M.; Zhan, X. L.; Chen, F. Q.; Du, F.; Huang, L. B. *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 4431.
28. Li, B.; Chen, S. J.; Zhang, J. *Polym. Chem.* **2012**, *3*, 2366.
29. Terman, L. M.; Klapshina, L. G.; Kurskii, Y. A.; Zislina, S. S. *Polym. Sci. U.S.S.R.* **1987**, *29*, 1330.
30. Gao, Y. J.; Jiang, W.; Guan, Y.; Yang, P.; Zheng, A. *Polym. Eng. Sci.* **2010**, *50*, 2440.