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Synthesis of α,ω-bis(3-aminopropyldiethoxylsilane) Poly(tri fluoropropylmethyl)siloxanes

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Abstract: High molecular weight α,ω-bis(3-aminopropyldiethoxylsilane) poly(tri fluoropropylmethyl)siloxanes (APTFPMS) were prepared via a "one-step" process, based on the ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl) cyclotrisiloxane (F_3) in the presence of water and 3-aminopropyltriethoxysilane (APTES). GPC, FT-IR and ^{1}H NMR confirmed the structure of the polymers. It was found that the amount of APTES had significant influence on the reaction rate and the molecular weights of polymers decreased with the increasing amount of water. It was probably because both water and the amino group of APTES favoured generation of hydroxyl ions, which efficiently initiate the polymerization of F_3 to achieve APTFPMS. In order to verify this mechanism, another "two-step" process was also performed: Firstly the α,ω-dihydroxylated poly(trifluoropropylmethyl) siloxanes were synthesized from F_3 catalyzed by both diaminoethane and water, then reacted with APTES to achieve APTFPMS. All the syntheses had high yields and the molecular weight of the polymers ranged from 2000 to 25000.

Introduction

Poly(trifluoropropylmethyl)siloxane (PTFPMS) and Polydimethylsiloxane (PDMS) have attracted great interest in the past decades, owing to their good chain flexibility and high performances such as low permeability to water, low electrical conductivity [1, 2], good thermal and oxidative stability, low glass transition temperature, resistance to ultraviolet radiation, good gas permeability and biocompatibility [3-5]. McGrath, etc. reported very good mechanical properties of a series of segmented silicone polyurea block copolymer elastomers from the chain extension of the highly reactive α, ω-bis(aminopropyl) terminated PDMS with diisocyanates [6, 7]. Recently, the high molecular weight PDMS and PTFPMS diamines have drawn more and more interests [8-10]. The polyureas derived from higher molecular weight PDMS diamines possess wider service temperature windows than those derived from their low molecular weight counterparts [8].

PDMS diamines were usually synthesized by the ring-opening polymerization of 2,2,4,4,6,6,8,8-octamethylcyclotetrasiloxane (D_4) in the presence of the disiloxane and catalysts [11]. The disiloxane was prepared by the hydrosilation of dimethylchlorosilane with protected allylamine, followed by deprotection, hydrolysis and coupling [12]. Although potassium hydroxide may have some commercial advantages, organic catalysts such as tetramethylammonium hydroxide have been successfully utilized by some researchers [13]. The quaternary hydroxide can generate the analogous siloxanolate, which then effectively attacks the Si-O ring to open the rings at 80 °C. The disiloxane serves as a chain end-blocker because the Si–C bonds are covalent, but the Si–O bonds are partially ionic, and hence it can participate in the reaction and effectively produce the difunctional oligomer. The equilibrium reaction produces about 85% of linear oligomers, and the remaining monomers can be easily vacuum removed and the catalyst can be decomposed at about 150 °C to produce a neutralized, stable oligomer [14, 15].

Hoffman and Leir have reported the synthesis of high molecular weight α,ω-bis(aminopropyl) polydimethylsiloxanes (APT-PDMS) using a " two-stage" procedure [9]. The tetramethylammonium 3-aminopropyl dimethylsilanolate synthesized in the first step would catalyze the reaction between bis(3-aminopropyl) tetramethyl disiloxane (BAPTMDS) and D_4 to provide the silicone diamines, at 85 ^{o}C under argon atmosphere. In a word, the complicated catalysts, disiloxane, inert gas and higher temperatures were usually necessary for the conventional processes. Very recently, Ekin and Webster have continued the exploration for synthesizing the high molecular weight APT-PDMS by comparing four different reaction routes including the method reported by Hoffman and Leir [16]. In their report, both the method used low molecular weight APT-PDMS and D_4 as the starting materials with tetramethylammonium hydroxide as the catalyst, and the other method used BAPTMDS and D_4 with benzyltrimethylammonium hydroxide as a catalyst, could achieve the APT-PDMS with a wide range of molecular weights. The latter could obtain the polymer whose molecular weight was closer to the target value.

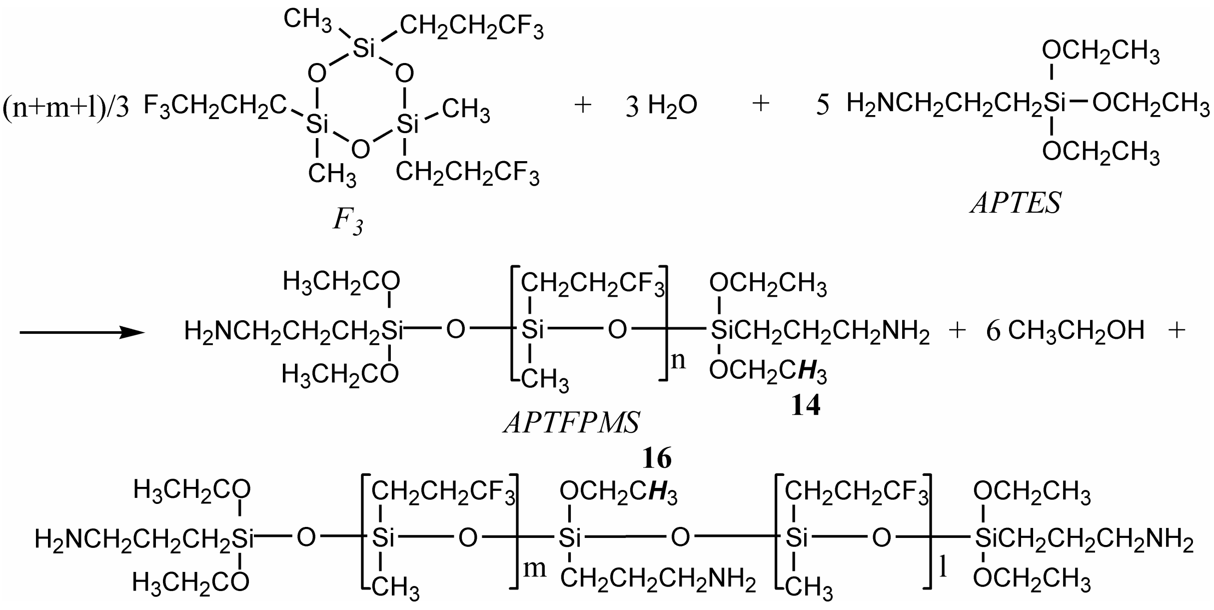
The synthesis of poly(trifluoropropylmethyl)siloxane (PTFPMS) has seldom been reported since 1960s [17-24]. Recently, Maitre, et al. studied the synthesis of PTFPMS by anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl) cyclotrisiloxane (F_3) in miniemulsion, using didodecyldimethylammonium bromide (DDDBr) as emulsifier and sodium hydroxide as initiator. This polymerization process can produce well-defined α,ω-dihydroxylated polymer with molar masses ranging from 2000 to 30000 [25]. However, to our knowledge, the synthesis of the high molecular weight aminoalkyl terminated poly(trifluoropropylmethyl)siloxanes (APTFPMS) has seldom been reported before. Interestingly, Deka and Baruah, et. al. has reported that the diphenylsilanediol in acetonitrile catalyzed by triethylenetetramine could result in selective formation of octaphenyltetrasiloxane and the side product, water. In term of this result, we could conceive a reverse reaction for opening the siloxane rings [26].

In this paper, to take into account the simplifying of the polymerization process and achieving environmental friendly products, we provide a facile way to achieve high molecular weight APTFPMS. In a one-step process, through the ring-opening polymerization of F_3 catalyzed by both water and 3-aminopropyltriethoxysilane (APTES), we obtained APTFPMS with high molecular weight. ^{1}H NMR, FT-IR and GPC were used to characterize the end products. In order to investigate the mechanism of this one-step polymerization, a two-step process to prepare high molecular weight APTFPMS was also performed for comparison.

Results and discussion

One-step Synthesis of APTFPMS

Aminoalkyl terminated poly(trifluoropropylmethyl)siloxanes were prepared by the ring-opening polymerization of F_3 in the presence of both water and APTES, as outlined in Scheme 1. The molar ratio of F_3, water and APTES was 43.7:1:2.7. Both water and amino groups of APTES were used to catalyze the ring-opening polymerization of F_3 to form the α,ω-dihydroxylated poly(trifluoropropylmethyl)siloxane (HPTFPMS, a reaction intermedium). In the ^1H NMR spectrum of the sample collected at 18 h during reaction, the silanol hydroxyl peak was found clearly at 5.70 ppm (Figure 1).



Scheme 1. Ring-opening Reaction Route.

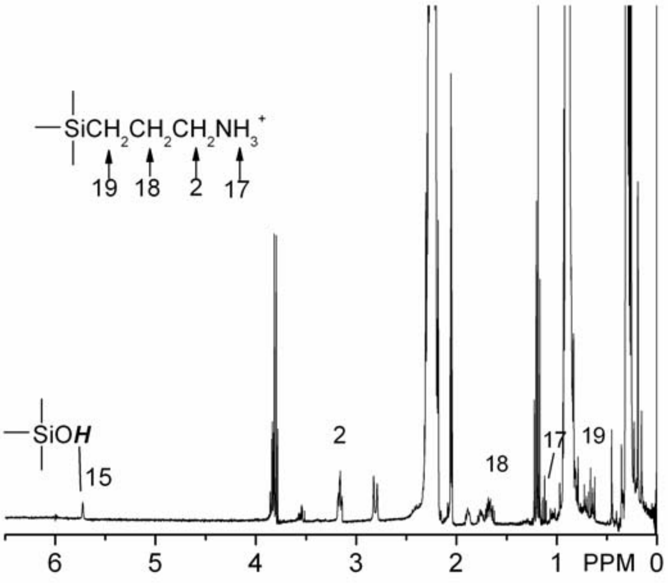


Fig. 1. The spectrum of the sample collected at 18 h during reaction.

The APTES was excessively added since it was used not only as a catalyst but also as an amine functional end group to cap the HPTFPMS chains. A condensation reaction between the hydroxyl groups and –$SiOC_2H_5$ groups of APTES was reported recently [27, 28]. Therefore, in the ^1H NMR spectrum of the final product, the silanol hydroxyl peak had disappeared since the hydroxyl groups were terminated by APTES (Figure 2). Figure 3 provided the FT-IR spectrum of the final product. –NH_2 showed broad peaks at 3395 cm^{-1}, Si–$CH_2CH_2CF_3$ displayed very strong absorption peaks at 1209 cm^{-1}, Si–CH_3 had the same strong absorption peaks at 1267, Si–O–Si exhibited broad and strong bands at 1131-1013 cm^{-1} corresponding to asymmetric stretching vibration.

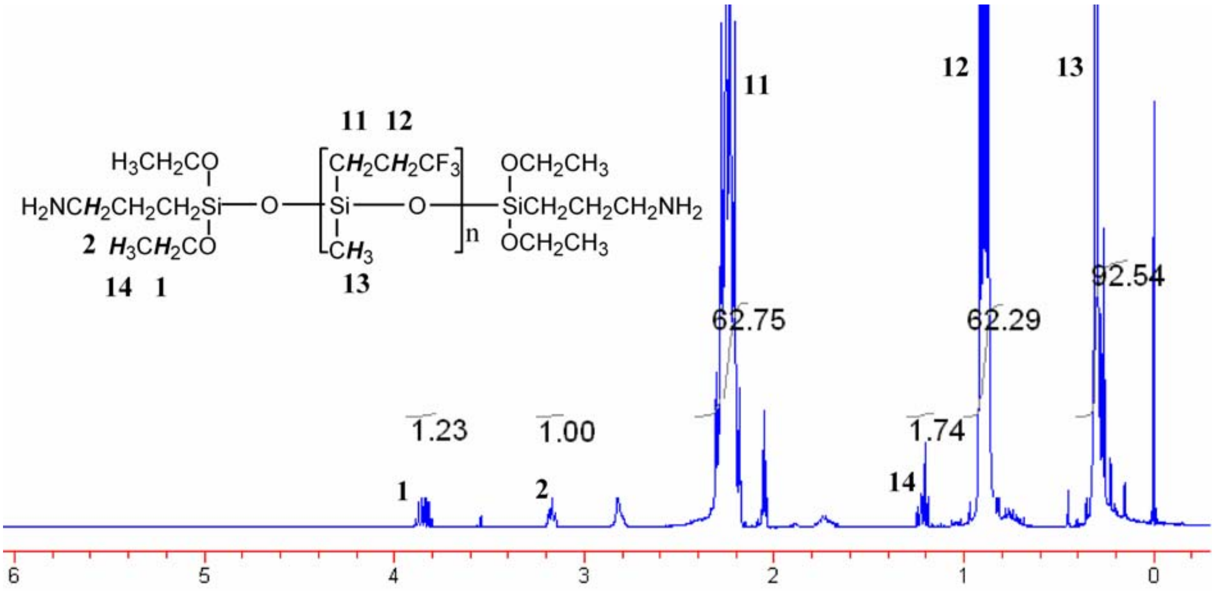


Fig. 2. The ^1H NMR spectrum of the final product.

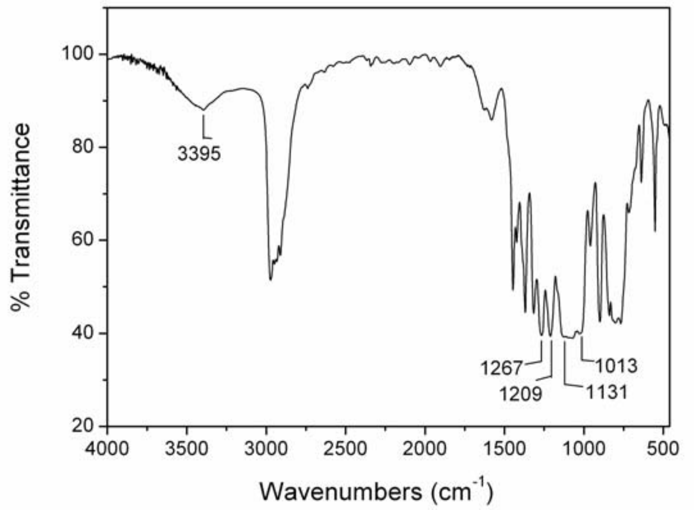


Fig. 3. The FT-IR spectrum of the final product.

The amount of water could be used to control the molecular weight of the polymers since one water molecule can initiate one polymer chain. The number average molecular weight (M_n) of the final product determined by GPC was 20600 g mol^{-1} (Sample 1), which was close to the value, 19900, calculated M_n from the integration of groups in Figure 2. Most probably some APTES molecules were connected with two PTFPMS chains because the integration of the Si–OC***H***$_2$– group was less than 2 comparing with the integration of the methylene in –C***H***$_2$NH$_2$. Therefore, the reaction also could result in the dibasic product from APTES as shown in Scheme 1.

Further experiments showed that the polymeric rate was accelerated by the increasing molar ratio of APTES. The M_n of the polymer decreased with the increasing amount of water which would be the important factor to control the molecular weight of the polymers. All the syntheses had yields of more than 90%. The polymerization parameters, molecular weights and polydispersities are presented in Table 1. The M_ns obtained by titration should be somewhat less than the real values.

Tab. 1. Polymerization Parameters, molecular weights and polydispersities of Polymers.

Sample	Reactant ratio (D_3^F: H_2O: APTES)	Reaction time (hours)	Yield %	$M_n \times 10^3$	$M_w \times 10^3$	Polydispersity
1	43.7:1:2.7	42	93.5	20.6	24.2	1.17
2	47.2:1:5.8	30	93.3	22.3	27.4	1.23
3	31.5:1:3.8	30	94.2	12.8	15.0	1.17
4	13.2:1:3.1	18	95.4	5.9	7.02	1.19
5*	10.0:1:3.0	18	95.5	4.4		
6*	6.2:1:2.7	15	96.7	2.8		
7*	3.4:1:2.5	15	96.4	1.8		

*: The molecular weight of the product was determined by titration of a sample in THF/IPA with 0.05N HCl to a bromophenol blue end point [9].

Reaction Mechanism

-Generation of Hydroxyl Ions

Figure 4 describes the generation of hydroxyl ions in the reaction system. The amino group and the –SiOC$_2$H$_5$ groups of APTES were protonated by water to produce 3-aminopropyldiethoxysilanol (a byproduct). Figure 4 presented the chemical shifts of the groups of all materials in the reaction system. It was notable that the peak **2** (t, 2 H) centering at 3.18 ppm was contributed by the methylene of –C***H***$_2$NH$_3^+$ in APTES, but the chemical shift of the methylene of –C***H***$_2$NH$_2$ was present at 2.65 ppm in the standard ^{1}H NMR spectrum of APTES in CDCl$_3$ reported by Ni and Aaserud [29]. The reason was that the ammonium positive ion led to the movement of the chemical shift of the methylene of –C***H***$_2$NH$_3$ downfield in ^{1}H NMR. Therefore, it could be concluded that the amino groups were protonated.

Another evidence to illustrate the generation of hydroxyl ions was the intensity change of the amino peak of APTES (Figure 5). In contrast to another unchanged methylene peak of APTES, we found the amino peak became strong with the water consumed during reaction. It indicated that the exchange of protons between water and the amino groups had decreased gradually since the beginning mixture of reactants, resulting in the change of the amino peak from the weak to the strong. Therefore, the hydroxyl ions should be generated due to the protonation of amino groups and the exchange of protons between water and amino groups.

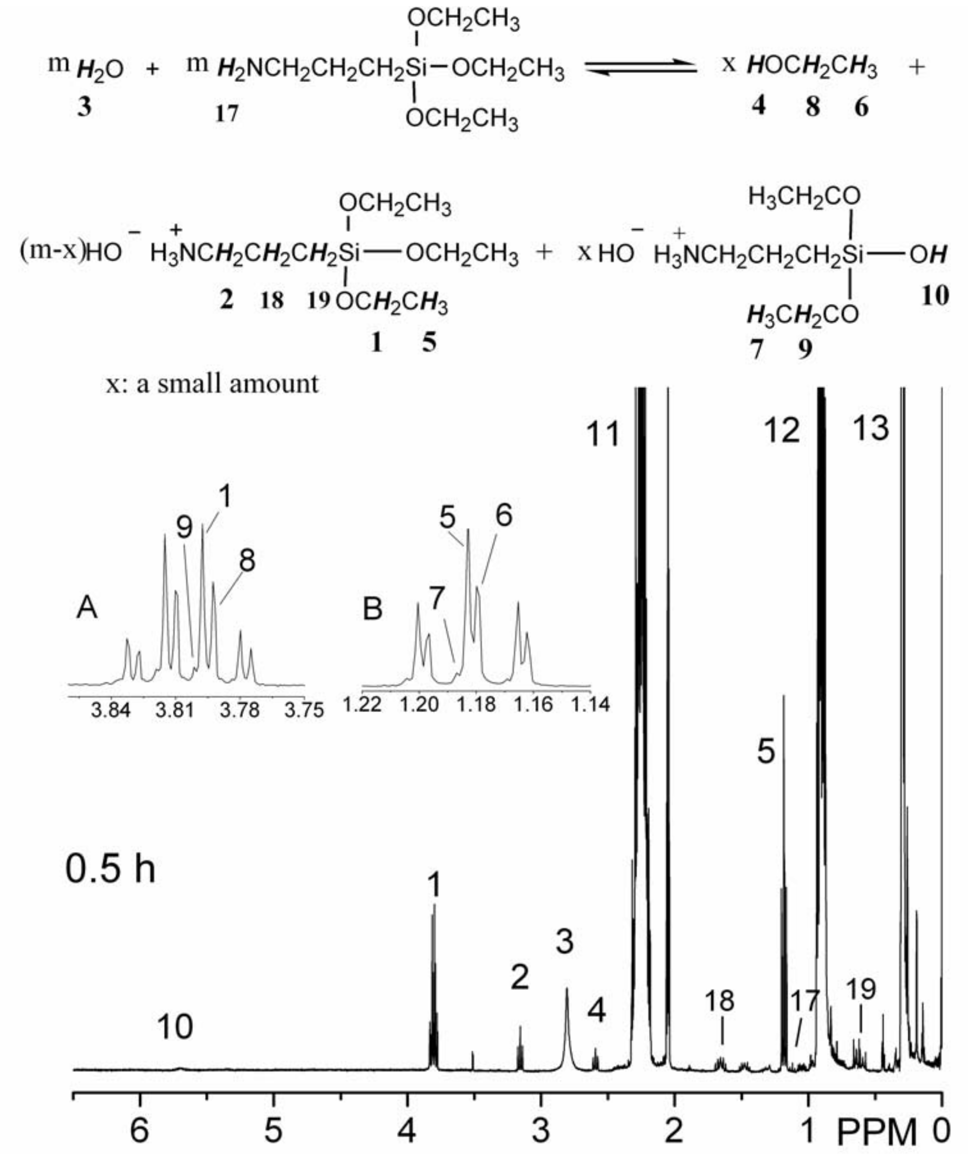


Fig. 4. Scheme describing generation of Hydroxyl Ion and the ^{1}H NMR spectrum of the sample collected at 0.5 h during reaction. A: Enlargement of the peak at 3.8 ppm; B: Enlargement of the peak at 1.18 ppm.

-Ring-opening Polymerization

Hydroxyl ions attacked Si-O rings to induce the F_3 opening to generate the HPTFPMS. As shown in Figure 1, the peak **15** at 5.70 ppm should be assigned to the hydroxyl of HPTFPMS. Another presumable initiator was the 3-aminopropyldiethoxy silanol (the byproduct) shown in Scheme 2. However it would be functional and predominant for both water and amino groups generating hydroxyl ions to open the rings comparing with 3-aminopropyldiethoxysilanol generating anions. The further evidence will be given later.

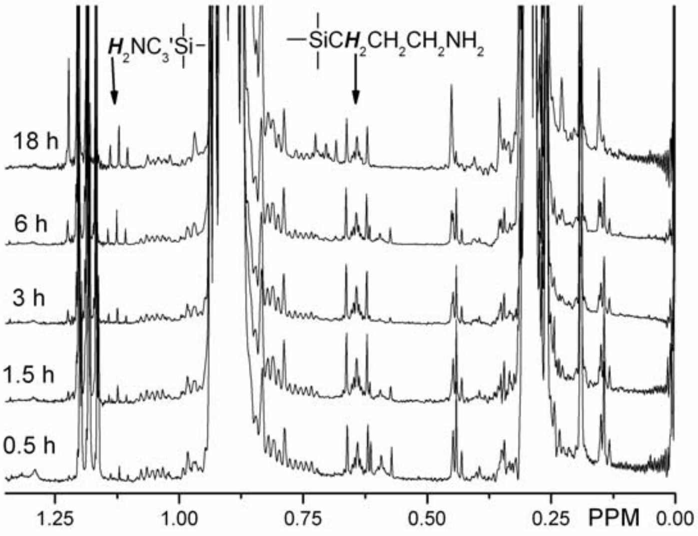
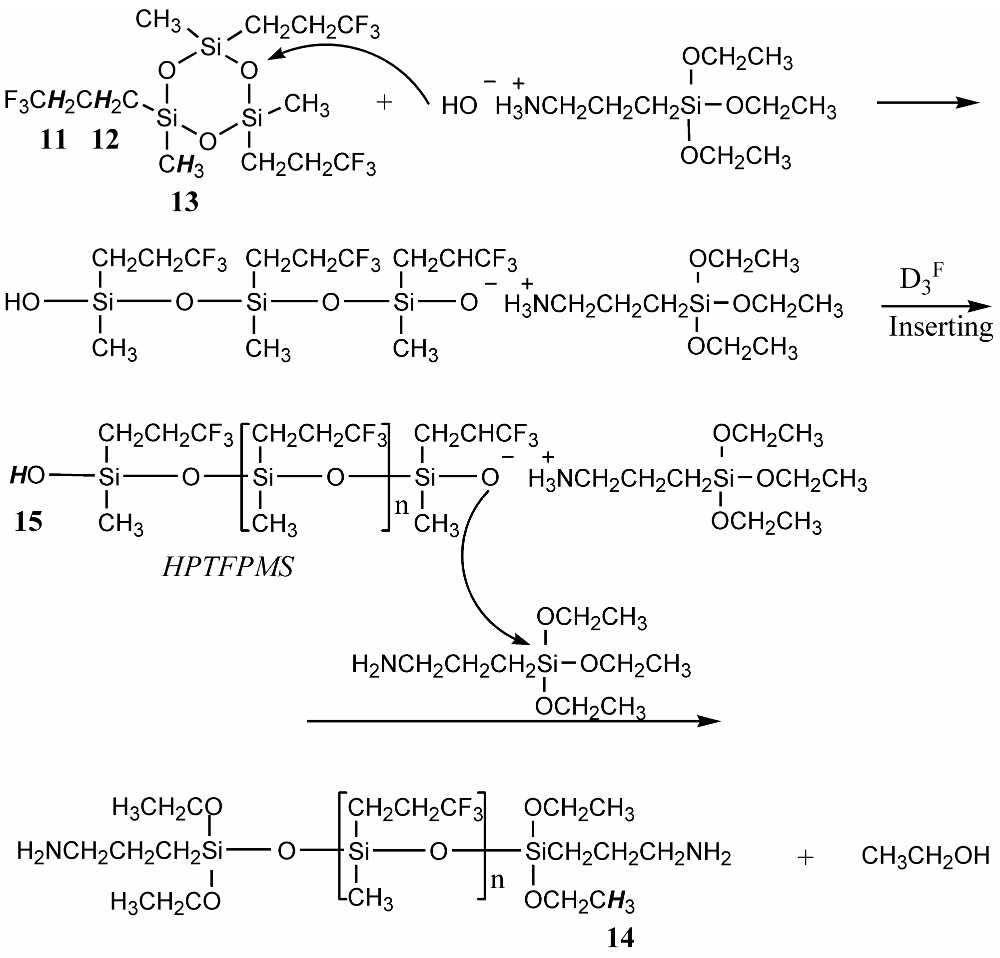


Fig. 5. The intensity change of the amino peak during reaction.

-Formation of APTFPMS through Reaction of HPTFPMS with APTES

Scheme 2 depicted the formation of APTFPMS. The hydroxyl ions initiated the ring-opening polymerization of F_3, and then the APTES capped the generated polymer chains. Figure 6 presented the change of the characteristic peaks of ethanol and water in contrast to the unchanged methylene peak (peak **2**) of the $–C\boldsymbol{H}_2NH_3^+$ in APTES. The amount of the water was gradually reduced in the beginning 6 hours (Figure 6, 0.5 h to 6 h). The reaction for generating hydrogen ions (as shown in Scheme 2) dominated the reaction system during first 3 hours, therefore, the amount of ethanol reached its maximum value in first 0.5 h, but decreased to the minimum at about 3 h during reaction since it escaped gradually, as well as it was found that the reaction between APTES and HPTFPMS (shown in Scheme 3) possibly began after about 3 h, thus, ethanol increased again at 6 h during reaction, finally, almost disappeared at 18 h (Figure 6, ethanol peak). In surprise, the peak **2** was divided into two close shorter peaks at 18 h (Figure 6, 18 h), and the new peak appeared discernibly at 6 h (Figure 6, 6 h), which would be a diagnostic marker for APTFPMS. It could be resulted from the movement of the chemical shift of the methylene in $Si–OC\boldsymbol{H}_2CH_3$ to downfield because $Si–(OC\boldsymbol{H}_2CH_3)_2$ was influenced by the connected partially ionic –Si–O– bond. Meanwhile, in Figure 6, 18 h, the peak of water was changed into two small peaks possibly, and it was probably due to the effect of the free amino groups (those in APTES) and the relative fixed amino groups (those in APTFPMS). If the 3-aminopropyldiethoxysilanol (the byproduct) initiated the polymerization, the ethanol peak would have presented clearly at 3 h, or the ethanol peak present at 6 h would have been smaller than that present at 3 h.



Scheme 2. Ring-opening reaction mechanism.

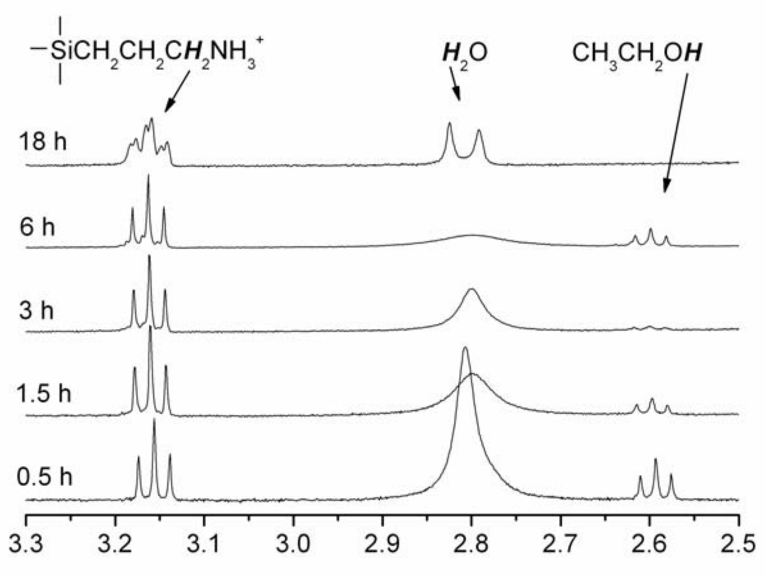


Fig. 6. The change of ethanol and water during different reaction times.

Enlarging the methyl peaks of samples (Figure 7), it was observed that the peak centering at 1.204 ppm appeared and increased (the peak **14**, Figure 7, 6 h and18 h), which was assigned to the methyl of ethoxyls of 3-aminopropyldiethoxysilane terminated to one macromolecule of HPTFPMS (namely, that of APTFPMS). This result indicated that the APTFPMS was formed in increasing amount. Meanwhile, the peak centering at 1.183 ppm assigned to the methyl of ethoxyls of the free APTES became weak (Figure 7, 18 h), suggesting the APTES was consumed due to the reaction between it and HPTFPMS. Evidently, the polymerization proceeded gradually and more APTFPMS macromolecules were produced.

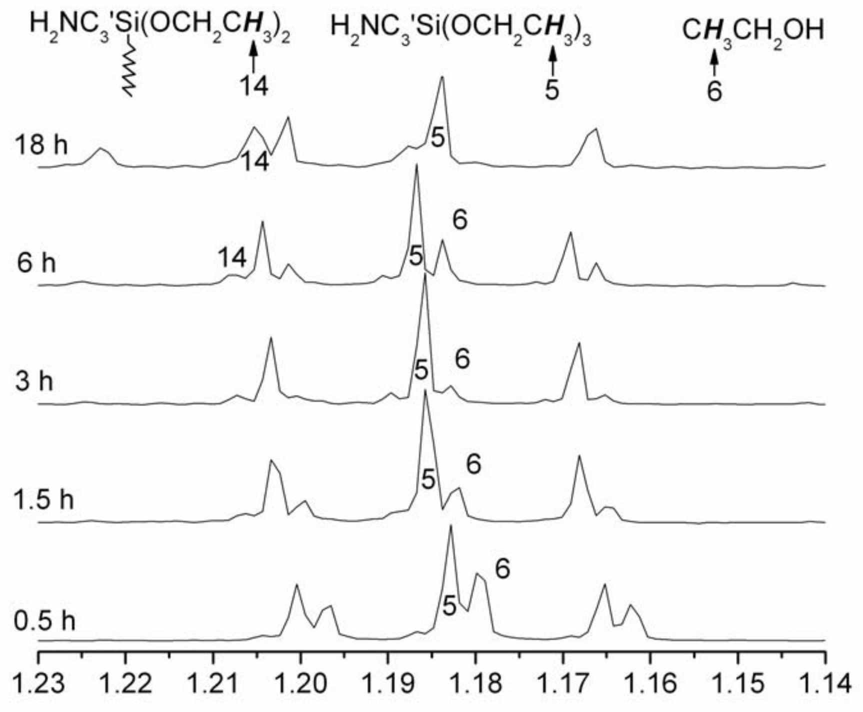


Fig. 7. The magnified spectrum of the methyl peak of samples at different time.

The reason for chain growth not being immediately terminated by APTES would be that ring-opening polymerization has almost no reaction enthalpy and the trimer rings have a great tension to make the ring-opening easy [30, 31], as well as the F_3 has a high concentration.

The Extent of Reaction and Purity of Products

^{1}H NMR was employed to determine the extent of the reaction and the purity of the product. It was to analyze the different samples which were obtained through continuously treating the polymer collected at 18 h during reaction. In Figure 8, ***a*** was the sample obtained at 18 h; ***b*** was obtained as follows: The sample ***a*** was kept in a vacuum oven at 60 ^{o}C to continue reaction for 24 h, then the sample was kept at 120 ^{o}C under vacuum for 4 hours; ***c*** was obtained as follows: The sample ***a*** was continuously kept at 60 ^{o}C under vacuum for 48 hours, then was kept at 150 ^{o}C under vacuum for 2 hours.

A variety of phenomena can be observed: Firstly, the ethanol methyl peak **6** centering at 1.178 ppm had disappeared completely (Figure 8, a); secondly, the peak **5** assigned to the free APTES decreased (Figure 8, b); thirdly, the peak **14** contributed by 3-aminopropyldiethoxysilane of APTFPMS increased; fourthly, a new peak **16** appeared, which was assigned to the ethoxyl methyl of the 3-

aminopropylethoxysilane connecting with two poly(trifluoropropylmethyl)siloxane chains. That the chemical shifts of the ethoxyl methyl peak **14** and **16** were higher than the ethoxyl methyl peak **5** was probably because the more partially ionic –Si–O– bonds connecting with Si–OCH$_2$C***H***$_3$ caused the movement of the chemical shifts of the methyl to downfield in ^{1}H NMR, so as to form the peak **14** and **16**. This new polymer was generated at the high temperature and for longer time. (Figure 8, b); finally, for the sample ***c***, there was less new polymer (peak **16**) because of shorter time at a high temperature and the free APTES (peak **5**) disappeared completely, mainly due to the vacuum at 150 °C (Figure 8, c). The trisubstitution product from the APTES hasn't been found in ^{1}H NMR spectra. To our knowledge, if the temperature was further elevated, the polymer would have formed crosslink structure.

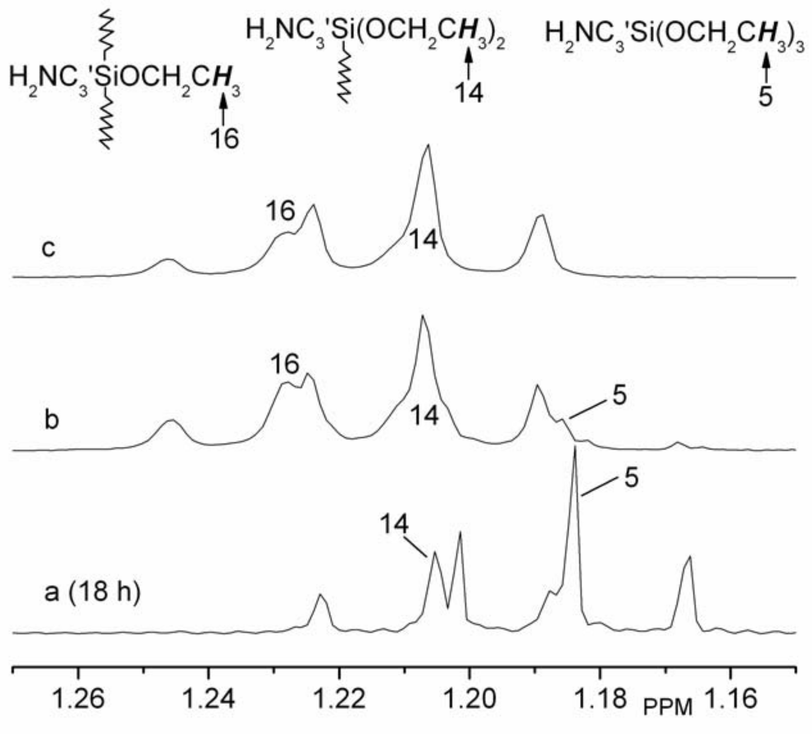


Fig. 8. Enlargement of the peak centering at 1.18 ppm of different samples.

Verification of the Mechanism by a two-step process

If the polymerization mechanism as shown in Figure 4 and Scheme 2 is robust, the amino group and water can initiate the ring-opening polymerization of F$_3$ to form HPTFPMS, and then the HPTFPMS can react with APTES to achieve APTFPMS, as well as the hydroxyl ions are the initiator. Thus, in order to verify the mechanism, we carried out a two-step reaction. At the first step, F$_3$ was catalyzed by both water and ethylenediamine for polymerization and HPTFPMS was obtained. In fact, the reaction cannot proceed without water or ethylenediamine. The molar ratio of F$_3$, water and ethylenediamine was 52.4:1:4.8. The obtained HPTFPMS was measured by ^{1}H NMR (Figure 9). Its M$_n$ was determined by GPC to be 22300 g mol^{-1}. The results indicated that the amino groups were protonated due to water, then, the water released hydroxyl ions to open the cyclic trimers and produce HPTFPMS, and its hydroxyl groups appeared at 5.70 ppm in the ^{1}H NMR spectrum (Figure 9). In the FT-IR spectrum of HPTFPMS, Si–OH exhibited clear absorption peaks at 3700 cm^{-1} (Figure 10), and the other peaks were similar with those in Figure 3.

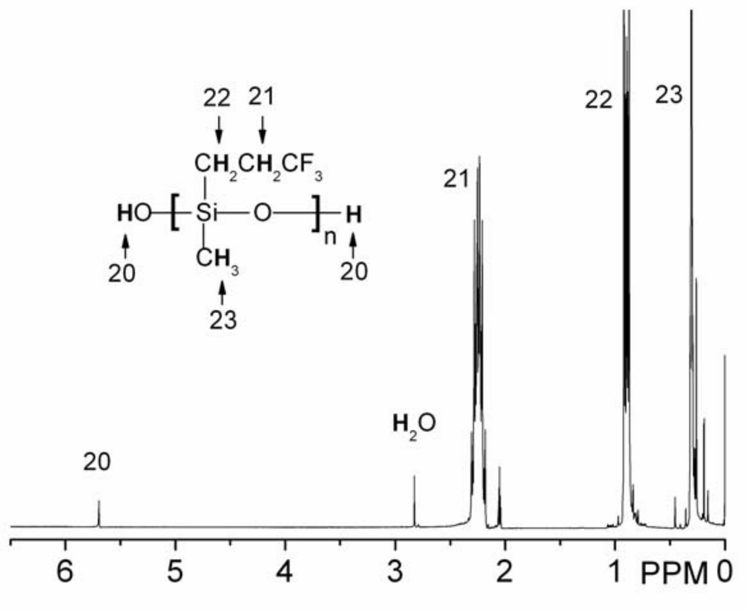


Fig. 9. Spectrum of the HTPTFMS.

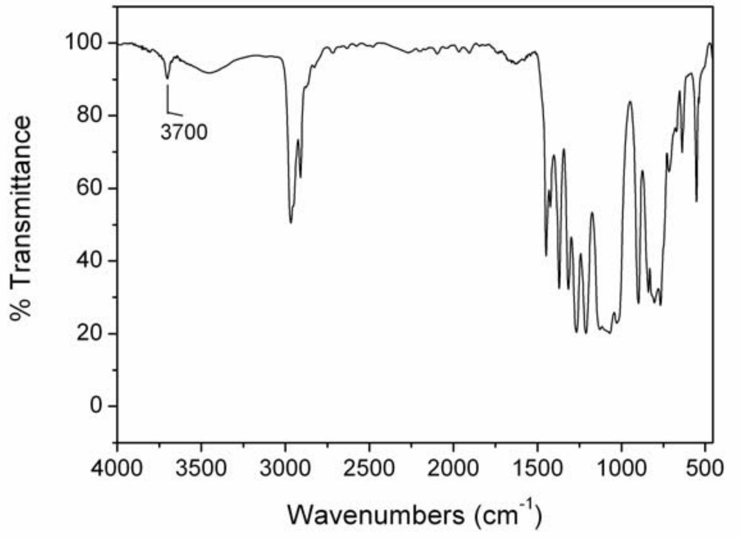


Fig. 10. The FT-IR spectrum of the HTPTFMS.

At the second step, the hydroxyl groups of HPTFPMS reacted with the $–SiOC_2H_5$ group of APTES to form APTFPMS at the same conditions with the first step. The resulting product had similar ^1H NMR spectrum as shown in Figure 2, and the silanol hydroxyl peak disappeared completely. This polymer had a M_n of 23100 g mol^{-1}. Therefore, to our knowledge, all the results could verify the mechanism as shown in Figure 4 and Scheme 2. Furthermore, it could be expected that the much higher molecular weight APTFPMS could be prepared through the two-step process if the ratio of water is reduced.

Conclusions

The high molecular weight APTFPMS was synthesized by the ring-opening polymerization of F_3 in the presence of water and APTES via a one-step process. A reaction mechanism was investigated using ^{1}H NMR, the results indicated that both amino and water catalyzed the polymerization of F_3 and the APTES terminated the polymer. The two-step reaction was performed to verify the mechanism, which used the same materials and obtained the same product as the one-step process. The simple one-step process would be a promising method for preparing the aminoalkyl terminated polysiloxanes, and the much higher molecular weight polymer could be prepared through the two-step process. Both the two polymerization processes are practical and economical for synthesizing PDMS and PTFPMS diamines because aminopropylmethyldimethoxysilane or aminopropyldimethylmethoxysilane may replace APTES and D_4 may replace F_3. Furthermore, the PDMS diamines containing alkoxy groups can cater to wider application fields, and they will form crosslink structure at high temperature and moisture.

Experimental part

Materials

F_3 was received from Shanghai 3F New Material Co., Ltd., China and dehydrated before use. 3-aminopropyltriethoxysilane was received from Dow Corning Corporation, USA, and dehydrated before use.

Synthesis

One-step procedure: 47.7 g F_3 (0.102 mol), 1.4 g APTES (0.0063 mol) and 0.042 g de-ionized water (0.0023 mol) were added into a 150 mL flask, and stirred at the rate of 500 r/min at 50 ^{o}C for 18 hours. The flask was not sealed completely. During reaction, a series of samples were taken out from the flask at different reaction times and characterized by ^{1}H NMR, respectively. After the reaction was over, the product, colourless and viscous oil, was kept at 60 ^{o}C in a vacuum oven for 24 hours and then distilled under vacuum at 125 ^{o}C for 2 hours. The final product was weighed to be about 44.6 g.

Two-step procedure: 51.3 g F_3 (0.110 mol), 0.6 g ethylenediamine (0.01 mol) and 0.038 g de-ionized water (0.0021 mol) were added into a 150 mL flask, stirred at the rate of 500 r/min at 50 ^{o}C for 5 hours. The intermedium (HPTFPMS), colorless viscous oil, about 49.4 g, was transferred to a vacuum oven at 60 ^{o}C for 24 hours, and characterized by ^{1}H NMR. Then, 1.4 g APTES (0.0063 mol) was added into the flask, and stirred at the rate of 500 r/min at 50 ^{o}C for 4 hours. Finally, the product was kept at 60 ^{o}C in a vacuum oven for 24 hours and then distilled under vacuum at 125 ^{o}C for 2 hours, and the weight of the product was 47.1 g.

Analysis

Gel permeation chromatography (GPC) was performed at 70 ^{o}C using a Perkin Elmer Series-200 system with PL gel (10 μm) 300 mm ×7.5 mm mixed-B columns and N, N-dimethylformamide (DMF) modified with 0.1 M LiBr as the solvent. A PE pump (series 200) and a refractive index detector (series 200) were used. The GPC was calibrated at 70 ^{o}C using molecular weight distribution standards of polystyrene (PS). The sample concentration in DMF is 1.5 g L^{-1},100 μ l of which is injected into sample loop with flow rate of 1.0 ml min^{-1} in the columns.

The ^{1}H NMR was performed on a Varian MERCURY plus 400 spectrometer using acetone-d_6 as the solvent at ambient temperature. Tetramethylsilane was used as outer standard with chemical shift located at 0.00 ppm.

The fourier transform infrared spectroscopy (FT-IR) was taken with a Perkin Elmer Paragon 1000 FT-IR spectrometer. The data of 100 scans were averaged.

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