Preparation and characterization of high molecular weight vinyl-containing poly[(3,3,3-trifluoropropyl)methylsiloxane]

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A B S T R A C T

Prior to crosslinking and vulcanization, fluorosilicone rubber is a linear polymer. This linear polymer contains 3,3,3,-trifluoropropyl methyl siloxane links, a few methyl vinyl siloxane links, and is formed by co-polymerization of 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl) cyclotrisiloxane (D_3F) with 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4) under alkaline conditions. To improve the performance of fluorosilicone rubber, three key points should be considered during the synthesis of vinyl-containing high-molecular-weight linear fluorosilicone polymers (fluorosilicone raw rubber): first, avoid the generation of low molecular weight equilibrium by-products; second, eliminate the influence of impurities; and third, increase the copolymerization participation rate of monomer V_4. From the three aspects above, this study optimized the reaction conditions for the synthesis of high-molecular-weight linear fluorosilicone polymers containing vinyl. Various factors influencing polymerization were thoroughly investigated. These factors include the initiation system, accelerator, equilibrium reaction, feeding ratio, feeding sequence, neutralization mode, impurity content, etc.

1. Introduction

Poly[(3,3,3-trifluoropropyl)methylsiloxane] (PTFPMS) is resistant to oil, fuel, solvents, and extreme heat and cold [1–5]. It can be used as a sealing material for aviation and automotive fuel tanks [6–8]. Because PTFPMS has good film-forming properties, it can also be made into various coatings [9–11], such as release agents and protective layers. In addition, fluorosilicone compounds have many other uses, including as defoamers [12] for organic emulsions, defoamers for cosmetics, and release agents [13] for pressure-sensitive adhesives. However, the most widely used product made from PTFPMS is fluorosilicone rubber, which is processed into various shapes and used in automotive, electronic, aerospace and other fields [14–16]. Since 1960 [17–19], researchers have conducted numerous studies on the synthesis of PTFPMS.

PTFPMS is usually synthesized from 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl) cyclotrisiloxane (D3F) by anionic ring-opening polymerization (ROP). The anionic ROP of cyclosiloxane monomers is initiated by basic materials [20,21], which can produce the silanolate anion as the active propagation center. Potassium hydroxide (KOH), tetramethylammonium hydroxide [(CH₃)₄NOH], and other strong bases [22,23] are commonly used in the field of silicone rubber. However, since D₃F is more susceptible to ring-opening reactions than octamethylcyclotetrasiloxane (D₄), less reactive bases have been chosen for many studies [24]. In practice, the alkali is usually used first to react with D₃F, and the resulting alkaline colloid (a low-molecular-weight oligomer

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containing silanolate) is then used as an initiator. This has two advantages: firstly, the activity of alkali hydroxides is almost as active as that of their corresponding silanolates, but the latter are more soluble in reaction monomers. Secondly, this reduces weighing errors due to the very low concentration of initiator used.

The mechanism of the anionic ROP of D_3F is similar to that of D_4, which can be divided into four stages [25–27]: chain initiation, chain propagation, chain transfer, and chain termination. Low-molecular-weight cyclosiloxanes are produced if chain transfer occurs in the same molecular chain. This process is also known as the back-biting reaction [28–30]. During the polymerization process, ROP of D_3F and cyclization rearrangement of macromolecules proceed simultaneously until the reaction reaches equilibrium. When the system reaches equilibrium, most of the products are cyclosiloxanes. The presence of these cyclosiloxanes seriously affects the molecular weight and distribution of the product, which in turn affects the physical, chemical, and mechanical properties of the fluorosilicone rubber. The choice of a low-activity initiator, supplemented by mild reaction conditions, helps to reduce the generation of back-biting reaction by-products. When low-activity initiators are used to initiate D_3F, promoters can be used to increase the reaction rate and reduce the reaction time. Some electron donor compounds can play an integral role in ROP and are called activators or promoters [31–35]. Notably, D_3F anionic ROP initiated by lithium silanolate or organolithium can produce PTFPMS with narrow molecular weight distribution and low back-bite by-product content [36–38].

The presence of impurities is the main reason for the low molecular weight of the polymer. The influence of impurities within the reaction system, especially moisture and residual bases, should not be ignored. The presence of water can stop the anionic polymerization process [39], so special attention should be paid to removing water throughout the reaction. In addition, the residual base in the reaction system needs to be neutralized in order to obtain PTFPMS with a stable molecular weight and performance [40]. If the system is not completely neutralized after the reaction, a portion of the molecular chains will transfer at high temperatures under the action of the residual alkaline initiator, this will lead to a decrease in the molecular weight of the product and a wider molecular weight distribution. There are many methods of neutralization, and the use of silyl phosphate [41–44] is the simplest and most common of them, because of its good dispersion in the polymer. Furthermore, silyl phosphate has the ability to form buffer systems with alkaline initiators without affecting polymer stability when used in excess.

The products obtained by copolymerization of D_3F and other cyclic siloxane monomers have a very wide range of applications [45–47]. The introduction of vinyl in PTFPMS increases the crosslinking point and gives the vulcanized rubber higher tensile strength, tear strength, and resilience. The copolymerization of vinyl cyclosiloxanes with D_3F allows the introduction of vinyl into the polymer chain. Different monomers are often difficult to copolymerize due to different ring opening temperatures, reaction rates, etc. It has been reported [48] that V_3 (trimethyltrivinylcyclotrisiloxane) is easily copolymerized with D_3F. But in fact, due to the strong induction effect of trifluoropropyl, the anion ring opening polymerization rate of D_3F is still much higher than that of V_3. In this study, tetramethyltetravinylcyclotetrasiloxane (V_4) [49,50], which has a very wide application in the field of silicones, was chosen as the vinyl monomer to copolymerize with D_3F, and the vinyl content of the polymer was increased by adjusting the addition sequence [51].

In summary, to improve the performance of fluorosilicone rubber, the synthesis of linear PTFPMS should pay attention to three key points: first, to avoid the generation of low molecular weight equilibrium by-products and improve the yield of linear polymers; second, to eliminate the influence of impurities and improve the molecular weight of the polymer; and third, to improve the reaction participation rate of copolymer monomer V_4. Based on the above three points, the reaction conditions were optimized in this study.

2. Experimental

2.1. Materials, preparation and analysis

1,3,5-Tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane (D_3F) was provided by Weihai Xinyuan Chemical Co., Ltd., Shandong, China. 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4) was supplied by Zhongyi Chemical Co., Ltd., Fujian, China. n-butyllithium (nBuLi), 1.6 mol/l n-hexane solution was provided by Aladdin, Shanghai, China; Octamethylcyclotetrasiloxane (D_4) was supplied by Xin'an Chemical Industrial Group Co., Ltd., Zhejiang, China. The following reagents are analytical grade, purchased from Kelong, Chengdu, China. Tetramethylammonium hydroxide [$(CH_3)_4NOH$]; Potassium hydroxide (KOH); Sodium hydroxide (NaOH); Lithium hydroxide (LiOH); N,N′-dimethylformamide (DMF); Hexamethyldisilazane (HMDS); ammonium dihydrogen phosphate (ADP). All the raw materials above were dewatered before use.

2.2. Preparation of alkaline colloids

2.2.1. Preparation of NaOH alkaline colloids

At room temperature, 1 mol% NaOH was added to D_3F and dispersed for 0.5 h. The temperature was then raised to 100–120 °C. After a period of time, a low-viscosity, transparent colloid was obtained. The product was abbreviated I–NaOH.

2.2.2. Preparation of nBuLi alkaline colloids

At room temperature, 1 mol% nBuLi was added to D_3F and dispersed for 0.5 h. Then the temperature was raised to 60–80 °C, and 0.1 mol% DMF was added as an accelerator. After a period of time, a low-viscosity, transparent colloid was obtained. I-nBuLi was the product's abbreviation.

2.2.3. Preparation of other alkaline colloids

The process of preparing an alkaline colloid using potassium hydroxide, lithium hydroxide, or tetramethylammonium hydroxide is

basically the same as the above method except for the difference in reaction temperatures. The reaction temperature of potassium hydroxide was 80–100 °C, that of lithium hydroxide was 120–140 °C, and that of tetramethylammonium hydroxide was 40–60 °C. The products were abbreviated as I–KOH, I–LiOH and I-(CH₃)₄NOH, respectively.

2.3. Preparation of silyl phosphate

Ammonium dihydrogen phosphate (ADP) and hexamethyldisilazane (HMDS) in a molar ratio of 2:1 were added to a reactor with a reflux condenser. At 120 °C, the materials were reacted, and ammonia was continuously expelled during the reaction. Finally, after distillation and hydrolysis, silyl phosphate was obtained.

2.4. Preparation of non-cross-linked rubbers

High-molecular-weight PTFPMS, also known as non-cross-linked fluorosilicone rubber, could be prepared by copolymerization of D_3F and V_4 initiated by alkaline colloids (I–NaOH or I-nBuLi). The experiments should be carried out under anhydrous conditions with nitrogen protection.

2.4.1. One-pot method
Add a small amount of alkaline colloids to the mixture of D_3F and V_4 at room temperature. Before heating up, the materials were well stirred. When the reaction is initiated with I-nBuLi, the accelerator DMF should be added. To neutralize the reaction, an appropriate amount of silyl phosphate was added after a period of reaction. After neutralization, the product was vacuumed to remove the low boiling matter.

2.4.2. Two-step method
Firstly, the vinyl-containing prepolymer was prepared. Self-polymerization of V_4 was initiated by I–NaOH at 150 °C. The low-viscosity prepolymer was obtained after a period of reaction time and cooled for storage. Secondly, the prepolymer was further polymerized with D_3F at 60 °C using I-nBuLi as an initiator, DMF as an accelerator. After a period of reaction, a neutralizer was added to terminate the reaction. The reaction expression of the two-step polymerization method is shown in Scheme 1.

2.5. Metal ion content

1 g of a commercially available fluorosilicone raw rubber sample was placed in a platinum crucible and burned in a muffle furnace at 600 °C. After the organic matter was completely burned, the obtained residue was dissolved in hydrofluoric acid (AHF) and then diluted. This sample was detected by an inductively coupled plasma emission spectrometer (ICP-OES, Angilent ICP 710), and the content of metal ions in the sample solution was calculated by external standard method. Based on this, the possible initiator of commercial fluorosilicone raw rubber was speculated, providing a reference for the selection of initiator system.

2.6. GPC examination

The number average molecular weight (MW) and polydispersity (PD) index of the polymer were studied by Angilent GPC 1260. The polymer was dissolved in tetrahydrofuran.

2.7. Acid-base titration

The base content of alkaline colloids was determined by potentiometric titration. Extract and titrate inorganic bases and organic bases in alkaline colloids separately. The proportion of organic base content in the total base content was calculated.

The acid content of silyl phosphate was also determined. The prepared silyl phosphate was sonicated, dissolved, and titrated by potentiometric titration. The titration solution was an aqueous KOH solution.
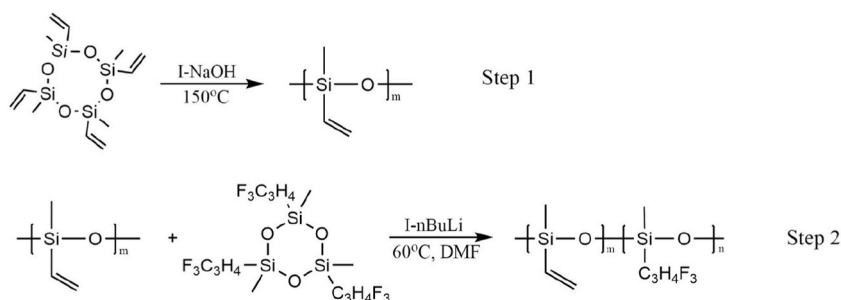
Scheme 1. Reaction expression of two-step polymerization.

Table 1
Performance comparison of five alkaline colloids.

Initiator	ROP temperature (°C)	Effective alkali content (%)	Appearance	Loss of effective alkali after one month of storage (%)	Initiating activity
I-(CH$_3$)$_4$NOH	40–60	90	transparent	8	excessively high
I–KOH	80–100	53	turbid	31	excessively high
I–NaOH	100–120	90	transparent	6	modest
I–LiOH	120–140	33	turbid	34	excessively low
I-nBuLi	60–80	82	transparent	5	modest

2.8. Moisture test

Karl Fischer back titration was used to measure the water content of the reaction system.

2.9. Vinyl content test

The vinyl content was characterized by iodometry. The mixed solvent of trifluorotrichloroethane and ethyl acetate (1:3) is selected. The excess iodine standard solution is added to fully react with vinyl, and then the remaining iodine solution is titrated with sodium thiosulfate. The vinyl content in the raw rubber to be measured is calculated.

2.10. ^{31}P NMR

^{31}P NMR spectra were acquired on the Varian Mercury spectrometer. 85 % phosphoric acid was used as the reference material, and deuterated chloroform was used as the solvent.

3. Results and discussion

3.1. Equilibrium reaction

3.1.1. Selection of initiator

Excessive reactivity may cause the reaction system to move toward equilibrium in a relatively short time, which may result in low yields of the desired linear polymer. To avoid the formation of low-molecular-weight products, the polymerization reaction should be terminated in time before the reaction reaches equilibrium. Using a mild catalyst and reacting at a lower temperature allows for a longer "window period" of the reaction and easier control.

Among the five initiators prepared in this study, I-(CH$_3$)$_4$NOH, I–KOH, and I–LiOH alkaline colloids had significant drawbacks. I–KOH and I–LiOH alkaline colloids were turbid in appearance and contained white particles. After one month of storage, the viscosity increases, the fluidity deteriorates, and the loss of alkali content reaches more than 30 %. These may be caused by an inadequate reaction. KOH is strongly basic and highly reactive, thus the molecular weight increases too fast during the reaction, and the dispersion of the system decreases sharply, resulting in an incomplete reaction of the KOH solid particles in the alkaline colloid. LiOH, on the other hand, cannot react completely even at 140 °C because of its low activity. I-(CH$_3$)$_4$NOH has the highest activity, which is not conducive to prolonging the reaction time.

In general, I-nBuLi and I–NaOH had a uniform and transparent appearance, good storage stability, moderate activity, a mild polymerization process, and a controllable reaction endpoint. They are suitable for the synthesis system of fluorosilicone PTFPMS. See Table 1 for details. Where effective alkali content refers to the proportion of organic alkali to total alkali, it can indirectly reflect the content of their corresponding silanolates other than I-(CH$_3$)$_4$NOH.

The type of initiator used in commercially available fluorosilicone raw rubber is tentatively assumed based on the test results of the metal ion content. The contents of Li$^+$, K$^+$, and Na$^+$ ions in the commercially produced raw rubber tested by ICP-OES are shown in Table 2. It can be seen that the Na + content is 17 μg. Considering the molecular weight of the raw rubber, we speculated that the initiator used for this commercial fluorosilicone raw rubber was likely to be sodium silanolate. That also verified our conjecture about using a low-activity initiator.

3.1.2. Monitoring of equilibrium state

During the polymerization reaction, samples were taken at different time points for GPC tests to analyze the molecular weight and distribution data, which can monitor the equilibrium process. The process of preparing PTFPMS by using the initiator I–NaOH and reacting at 120 °C is shown in Fig. 1, where a and b are the curves of the average molecular weight of the polymer and the content of the cyclosiloxane (equilibrium by-products) with time, respectively. It can be seen that the molecular weight of the polymer increased rapidly to 600,000 only 10 min after the start of the reaction, at which time there were almost no low-molecular-weight components in the system, indicating that this stage was dominated by the chain growth of the polymer. The reaction continued for 0.5 h, and there was no significant change in the above two indicators. When the reaction time reached 1 h, the average molecular weight of the polymer decreased slightly, and the content of the low-molecular-weight component increased to 4.55 %. Following that, the product's average molecular weight decreased while the content of the low-molecular-weight component increased until it stabilized after 3.5 h. At this time, low-molecular-weight components dominated the system, accounting for more than 70 % of its composition, which is consistent with literature reports [28].

Table 2
Test results of metal ion content of commercially available fluorosilicone raw rubber.

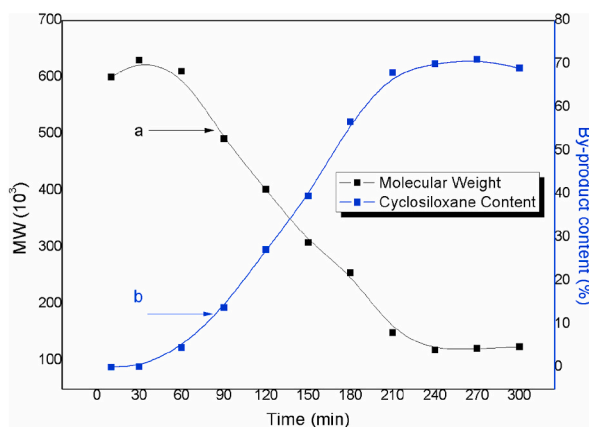| Sample	Metal ion content/ug (total amount of raw rubber sample is 1 g)		
	Li$^+$	K$^+$	Na$^+$
Commercial fluorosilicone raw rubber	0.0012	2.4021	17.1026

Fig. 1. The variation curves of molecular weight and by-product content of polymerization initiated by I–NaOH at 120 °C with time.

3.1.3. Obtaining high-yield PTFPMS

PTFPMS can be prepared by using I–KOH, I–NaOH, and I-nBuLi as initiators. However, the activity of I–KOH is too high, the reaction speed is too fast, the reaction process is difficult to control, and there is too much cyclosiloxane in the polymer. The polymerization of I-nBuLi and I–NaOH is mild at the appropriate temperature and time, and the yield of PTFPMS is higher than 95 %. In particular, when I-nBuLi is selected to initiate polymerization (with the use of an accelerator) and the reaction is conducted at 60 °C for 3 h, a high-molecular-weight PTFPMS containing almost no by-products can be obtained. The results of the GPC test by direct sampling without any post-treatment are shown in Table 3. It can be seen that the use of I-nBuLi as an initiator is conducive to stabilizing the reaction and reducing equilibrium by-products [33].

3.2. Improvement of molecular weight

3.2.1. Effects of moisture

The microamounts of water, oxygen, CO_2, and other impurities in the system have a great impact on the polymerization, especially the water, which can even prevent the reaction. When the reaction raw material D_3F is dewatered at 60 °C and −0.1 MPa, the water content in the raw material can be reduced to about 30 ppm. Nitrogen bubbling at normal pressure and 150 °C can keep the system's water content below 10 ppm. In addition to direct testing, the drying effect can also be judged by the molecular weight of the reaction product. Keeping other conditions unchanged, the higher the molecular weight of the product, indicating that the system is less affected by moisture. It can be seen from Table 4 that when the water content in the raw material is about 30 ppm, the molecular weight of the product is only about 300,000. When the water content in the raw material is lower than 10 ppm, the molecular weight of the product is more than 650,000.

3.2.2. Effects of residual initiator

As is often the case, the synthesized silyl phosphates are mixtures consisting of mono-substituted product $(CH_3)_3SiO](OH)_2P=O$, di-substituted product $(CH_3)_3SiO]_2(OH)P=O$, and tri-substituted product $(CH_3)_3SiO]_3P=O$. The tri-substitute is commonly used in Li-ion power battery electrolyte additives, but as a polysiloxane neutralizer, its trimethylsilyl content is high and easily affects the active end groups of polyfluorosiloxanes. Thus, the mono- and di-substituted products, which are more suitable as the active ingredients of neutralizing agents, are the ones this study hopes to access.

In the reaction of HMDS and ADP, By using of excessive amount of ADP and adding a hydrolysis step, the product composition is dominated by $[(CH_3)_3SiO](OH)_2P=O$ and $[(CH_3)_3SiO]_2(OH)P=O$. Fig. 2 shows the ^{31}P NMR test results of self-made silyl phosphate. From the results of spectral peak integration, it can be seen that the monosubstitute accounts for 36.81 %, the disubstitute accounts for 61.52 %, and the trisubstitute only accounts for 1.67 %. Despite the differences in methods and raw materials, the product composition was consistent with the ratios mentioned in the literature [52].
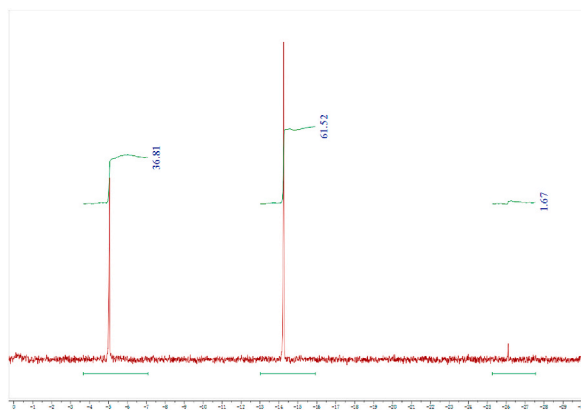
Table 3

Experimental conditions and molecular weight test results of the preparation of FTFPMS initiated by I–KOH, I–NaOH and I-nBuLi.

Initiator	Amount of initiator (ppm)	Reaction temperature (°C)	Reaction time (hours)	MW (Mn)	PD	Content of by-product (%)
I–KOH	16	80	0.5	735.300	1.82	19.20
I–KOH	16	100	0.5	641.800	1.91	21.52
I–NaOH	16	100	1	766.121	1.75	4.17
I–NaOH	16	120	1	684.328	1.86	4.31
I-nBuLi	16	60	3	768.100	1.62	0.74
I-nBuLi	16	80	3	691.100	1.81	0.83

Table 4
Molecular weight of PTFPMS prepared under different dehydration conditions.

Drying method	Drying time (h)	Content of moisture (ppm)	MW of polymer
60 °C, −0.1 MPa, vacuuming	2 h	33	235,400
60 °C, −0.1 MPa, vacuuming	4 h	28	334,500
150 °C, bubbling nitrogen	2 h	<10	687,600
150 °C, bubbling nitrogen	4 h	<10	881,600

Fig. 2. ^{31}P NMR of the prepared silyl phosphate.

The amount of neutralizer shall be adjusted according to the amount of alkaline initiator, so the acid content of silylphosphate shall be tested. The data processing results are shown in Table 5, and the acid content of the obtained silylphosphate is $3.31*10^{-3}$ mol g^{-1}。

3.2.3. Molecular weight distribution
It is also important that the molecular weight distribution be uniform when the molecular weight is increased. During the experiment, when the molecular weight of the polymer is very high, the mechanical stirring paddle used can no longer rotate, even at its maximum power. Therefore, it is necessary to investigate whether the stirring and dispersion effects in the later stage of the reaction will affect the homogeneity of the polymerization products. After the materials are fully dispersed and mixed at room temperature, without stirring, the reaction temperature is raised to make the materials react in a standing state. The MW and PD of the polymer are essentially the same in the same reaction at different sampling points during the same period, see Table 6 for details. This shows that the homogeneity of the product is not affected by the stirring effect at the later stage but mainly depends on the dispersion and compatibility of the materials at the earlier reaction stage. When the stirring power is insufficient, a standing reaction is also feasible.

3.3. Increasing of vinyl content

3.3.1. Effects of steric hindrance, reaction time, and initiator dosage
When D_3F and V_4 are directly copolymerized, the vinyl content of the product is very low. Under the same conditions, the vinyl content of the product did not increase when D_4 was used to replace D_3F. See Table 7 for details. This shows that the difference in ring tension between tricyclic and tetracyclic molecules and the influence of the trifluoropropyl groups are not the main reasons for the difficulty of copolymerization.

Apart from that, we tried to extend the reaction time and increase the amount of initiator, neither of which could improve the vinyl content of the polymer.

3.3.2. Effects of reaction temperature and initiating activity
The higher the reactivity of the system, the more favorable the participation of V_4 in the reaction, thus increasing the vinyl content of the product.

The activity of the initiator is one of the influencing factors. When the copolymerization of D_3F and V_4 is initiated by low-activity I-

Table 5
Analysis of silyl phosphate acid-base titration (KOH calibration concentration is 0.0899 mol/l).

Number of tests	Sampling quantity	EP-V(ml)	[H](10^{-3}mol)/g	
1	0.2694	9.8883	3.30	3.31
2	0.2852	10.5500	3.32	

Table 6
Homogeneity test of molecular weight distribution by standing reaction.

Reaction time (min)	MW of Sampling point 1	PD of Sampling point 1	MW of Sampling point 2	PD of Sampling point 2
10	207,100	1.29	205,900	1.29
30	392,700	1.47	393,300	1.44
60	682,300	1.64	641,900	1.68
120	693,500	2.19	691,300	2.07

Table 7
Vinyl content of products from different copolymers.

Main monomer	Vinyl monomer	Theoretical vinyl content (mol%)	Measured vinyl content (mol%)
D_3F	V_4	0.3	0.02
D_4	V_4	0.3	0.02

nBuLi (supplemented with accelerator DMF), although the reaction temperature is higher than 140 °C, the vinyl introduction rate is only about 10 %. This is because I-nBuLi can only initiate D_3F self-polymerization under this condition and cannot make V_4 participate in the reaction. Compared with I-nBuLi, the activity of I–NaOH is stronger. The introduction rate for vinyl can be kept above 30 %. See Table 8 for details. The experiment shows that the higher the activity of the initiator, the better V_4 can participate in the reaction. However, combined with previous studies, excessive initiating activity is not conducive to the stability of the reaction process. Because when the reaction conditions are sufficient to enable the polymerization of V_4, D_3F will react very quickly, even undergoing burst polymerization. The stability and reproducibility of the reaction process are poor, and the end point of the reaction is difficult to control.

Another influencing factor is the reaction temperature. As shown in Fig. 3, using I-nBuLi as the initiator, keeping other conditions unchanged, and increasing the copolymerization temperature can slightly increase the vinyl content of the polymerization product. This further shows that increasing the activity of the reaction system is conducive to V_4 participating in the reaction. However, the effect is limited. The theoretical vinyl content is 0.3 mol%, but the actual value is only 0.05 mol%.

3.3.3. Effects of feeding quantity and feeding sequence

Increasing the amount of vinyl monomer has an obvious positive effect on increasing the vinyl content in the product. As shown in Table 9, under the same reaction conditions, with the increased V_4 feeding amount, the measured vinyl content in the polymerization products also increased significantly.

Adjusting the feeding order of reaction monomers and adopting a two-step reaction can increase the vinyl content of polymerization products [51]. The first step is to prepare a vinyl siloxane prepolymer at a higher temperature with I–NaOH as an initiator and V_4 as the reaction monomer. The second step is to mix the V_4 prepolymer with D_3F at a lower temperature, add I-nBuLi and the accelerator DMF, initiate a reaction to prepare raw rubber. In this way, the advantages of the two initiators can be brought into play. While increasing the vinyl content of the product, the generation of low-molecular-weight cyclosiloxane by-products is reduced. Table 10 shows the results of GPC and vinyl content tests for fluorosilicone raw rubber prepared by repeated experiments using the two-step reaction method described above. It can be seen that this method has good reproducibility.

4. Conclusion

There are three difficulties in preparing high molecular weight vinyl-containing PTFPMS as fluorosilicone raw rubber: control of the equilibrium reaction, improvement of molecular weight, and increase of vinyl content. Through comprehensive and systematic experiments, this study summarizes the following synthesis methods and key points:

The mild I–NaOH and I-nBuLi alkaline colloids were prepared as initiators. First, a low-molecular-weight prepolymer was prepared by V_4 self polymerization initiated by I–NaOH at high temperature, then mixed with D_3F and copolymerized by I-nBuLi at low temperature. The amount of initiator was about 20 ppm, the water content of the system was strictly controlled below 10 ppm throughout the process, and the reaction was terminated in time before a large number of equilibrium products were generated. After the polymer was fully neutralized with one or two substituted silyl phosphates, the high-molecular-weight vinyl-containing fluorosilicone polymer could be prepared, which had a vinyl introduction rate greater than 30 %, a molecular weight greater than 700,000, and almost no low-molecular-weight by-product.

Data availability statement

Data included in article/supp. material/referenced in article.

Additional information
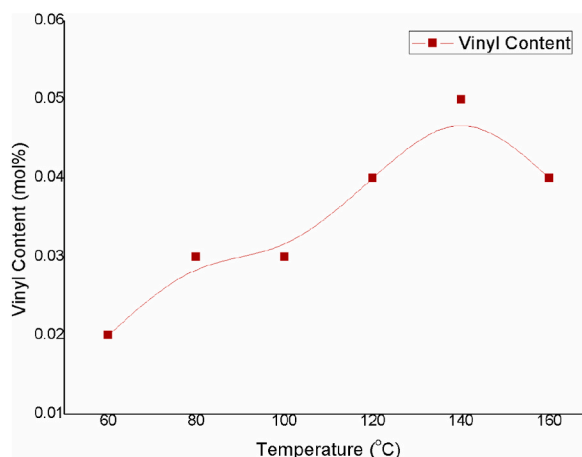
No additional information is available for this paper.

Table 8
Vinyl content of copolymer products made with different initiators.

Initiator	Reaction Temperature (°C)	Reaction Time (h)	Theoretical vinyl content (mol%)	Measured vinyl content (mol%)	Vinyl conversion (%)
I-nBuLi	140	2	3	0.31	10.3
I-nBuLi	160	2	3	0.35	11.6
I–NaOH	140	1	3	0.90	33.3
I–NaOH	160	1	3	1.03	34.3

Fig. 3. Variation curve of vinyl content of product with polymerization temperature.

Table 9
Vinyl content test results of polymer with different V_4 feeding amounts.

Number of experiments	Theoretical vinyl content (mol%)	Measured vinyl content (mol%)	Vinyl reaction ratio (%)
1	0.5	0.07	14.0
2	0.5	0.06	12.0
3	1.7	0.21	12.0
4	1.7	0.24	14.0
5	5	1.66	33.2
6	5	1.71	34.2

Table 10
Test results of vinyl-containing PTFPMS prepared by two-step method.

Number of experiments	MW of product	PD of product	Measured vinyl content (mol%)	Content of by-product (%)
1	689,000	1.44	0.36	1.01
2	644,000	1.61	0.32	1.90
3	654,000	1.65	0.38	1.83
4	703,500	1.82	0.35	1.67

CRediT authorship contribution statement

Yuanyuan An: Conceptualization, Data curation, Investigation, Software, Supervision, Validation, Visualization, Formal analysis, Methodology, Project administration, Writing - original draft, Writing - review & editing. **Cuifang Lu:** Data curation, Formal analysis. **Mengmeng You:** Data curation, Formal analysis. **Xinshuo Liu:** Resources, Methodology. **Wenqiang Yao:** Methodology, Writing - review & editing. **Yitao Li**: Resources, Project administration

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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