

SYNTHESIS OF HIGH THERMOSTABLE SILICONE GELS CONSTRUCTED WITH LADDERLIKE POLYSILSESQUOXANES*

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Abstract Heat-resistant silicone gels were synthesized by replacing the single main chain polymethylhydrosiloxane with reactive ladderlike polyhydrosilsesquioxane copolymers. Because of the interaction between polydimethylsiloxane chains and the ladderlike polysilsesquioxanes chains, the cyclization of the polydimethylsiloxane chains is hindered. The high thermal stability of the ladderlike polymers can improve the thermal stability of the silicone gels without sacrificing their good comprehensive properties.

Keywords Heat-resistant, Silicone gels, Ladderlike polysilsesquioxane, Interaction

INTRODUCTION

Due to the high bond energy of the Si—O bond, silicone elastomers have pronounced heat-resistant properties. They are also chemically inert and water-repellent. So they are resistant towards oxidation, ozonization and weathering. Besides, the silicone elastomers have excellent electrical properties. Because of these outstanding properties they are often the only candidates for some applications and have widely been used in many commercial fields^[1-3].

Generally, silicone elastomers can be divided into three categories: free radical curing silicone elastomers, condensation type silicone elastomers and addition type silicone elastomers. The latter are usually prepared by cross-linking vinyl-terminated polydimethylsiloxane with polyhydromethylsiloxane. They have been used in many applications without pollution because they do not release any low molecular weight molecules during their formation. Their physical mechanical properties, elongation and tear strength are fair. They could be used at -50 ~200°C. To further improve their heat-resistance and to lower their coefficient of thermal expansion (CTE), polymethylhydrosiloxane was replaced with an excellently heat-resistant ladderlike polysilsesquioxane.

Ladderlike polysilsesquioxanes were first synthesized by Brown *et al.* in 1960^[4] by equilibration of hydrolysate of trichlorophenylsilane in the presence of an alkaline catalyst at high temperature. Other ladderlike polysilsesquioxanes were also synthesized by the same method such as polymethylsilsesquioxane, etc.^[5, 6] as reported in patents. But under such severe reaction conditions, the ladderlike polysilsesquioxane containing functional groups or reactive bonds such as Si—H, C=C could not be synthesized. Zhang *et al.* successfully synthesized a series of ladderlike polysilsesquioxanes including ladderlike polyhydrosilsesquioxane (H-T), ladderlike polyvinylsilsesquioxane (V-T), ladderlike polyallylsilsesquioxane (A-T), etc.^[7-10] with high molecular weight and molecular regularity by stepwise coupling polymerization method, from which many functional

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ladderlike polysilsesquioxanes were derived^[11–17].

Here we report a new way to greatly improve the heat-resistance of the silicone gels by replacing the polyhydromethylsiloxane with ladderlike polyhydrosilsesquioxane copolymers.

EXPERIMENTAL

Materials and Measurement

IR spectra were recorded on a Specord 75-IR spectrophotometer (Carl Zeiss, Jena), ¹H-NMR spectra were obtained from a JNH-FX100 (JBOX) spectrometer. DSC was performed on a Perkin-Elmer DSC-7 instrument at a heating rate of 10 K/min. TGA was performed on a Perkin-Elmer 7 thermal analysis system under N₂ at a heating rate of 10 K/min. The dynamic viscoelastic property was measured on a Perkin-Elmer 7 thermal analysis system.

Hydroxy terminated polydimethylsiloxanes ($M_n \sim 5 \times 10^4$), vinyl terminated polydimethylsiloxanes ($M_n \sim 5 \times 10^4$) and polyhydromethylsiloxane were purchased from Chengguang Chemical Company. THF was dried by anhydrous Na₂SO₄ and distilled over sodium. Toluene was washed with concentrated H₂SO₄ to remove thiophene and distilled over sodium. Triethylamine was refluxed with ninhydrin and distilled, then dried by KOH. Methyltrichlorosilane, vinyltrichlorosilane, trichlorosilane and allyl chloride were distilled before use. Hexamethyldisiloxane (MM) (> 98% GC) and tetramethyldisiloxane (H-MM) (> 98% GC) were obtained from Fluka Chemika Co. Cp₂PtCl₂ catalyst was prepared by as described in the literature^[18]. All the solvents and reagents are commercially available and of analytical grade, and were purified by standard methods.

Synthesis of Ladderlike Polyhydromethylsilsesquioxane (H-Me-T)

10.6 mL (0.09 mol) of methyltrichlorosilane and 100 mL of toluene were added to a 500 mL three-necked flask. A solution of 4.86 g (0.045 mol) of *p*-phenylenediamine (PDA) and 12.5 mL (0.09 mol) of triethylamine in 130 mL of THF was added dropwise to the flask under stirring for 3 h at -15~-20°C. After addition, 1.0 mL (0.01 mol) of trichlorosilane was added to the flask, then a solution of 0.54 g (0.005 mol) of *p*-phenylenediamine (PDA) and 1.39 mL (0.01 mol) of triethylamine in 20 mL of THF was added dropwise under stirring for 3 h at -15~-20°C. Stirring was continued for 30 min at -10°C after the addition. Then 2.7 mL (0.15 mol) of water in 70 mL of THF was added dropwise to the flask at -15~-20°C within 5~6 h. The reaction system was further stirred at room temperature for a few hours then filtered to remove the salt. The filtrate was washed with water until neutral and dried with anhydrous Na₂SO₄ overnight. To the filtrate, three drops of concentrated sulfuric acid was added and stirred for 24~48 h, then 0.1~0.2 mL of hexamethyldisiloxane (MM) was added to the reaction system and stirred continuously for 6 h. After completion of the condensation reaction the solution was washed with water until neutral. 5.2 g of the product was obtained with a yield of 80%. The product can form a transparent film after the solvent was evaporated.

All the other different ratio of H-Me-T and H-Ph-T were synthesized by the same method.

Synthesis of Ladderlike Polyallyldecylsilsesquioxane (A-Dec-T)

5.5 g (0.02 mol) of decanyltrichlorosilane, 13.9 mL (0.1 mol) of triethylamine and 200 mL of toluene were added to a 1000 mL three-necked flask. A solution of 1.08 g (0.01 mol) of *p*-phenylenediamine (PDA) in 30 mL of THF was added dropwise to the flask under stirring within 3 h at -10~-15°C. 14 g (0.08 mol) of allyltrimethylchlorosilane was added to the flask, then a solution of 4.32 g (0.04 mol) of PDA in 110 mL of THF was added dropwise under stirring for 3 h at -10~-15°C. The reaction system was stirred continuously for 1 h at -10°C after the addition. Then 3.6 mL (0.2 mol) of water in 50 mL of THF was added dropwise at -10~-15°C within 5~6 h. The reaction system was further stirred at room temperature for a few hours and then filtered to remove the salt. To the filtrate, 1 mL of triethylamine and 1~2 g of CaH₂ were added and stirred for 24~48 h at room temperature. After completion of the condensation reaction, the solution was washed with water until neutral. 9.1 g of the product was obtained with a yield of 80%.

Synthesis of Hydrogen Terminated Polydimethylsiloxane

To a 250 mL flask, 200 mL of CH₂Cl₂, 20 g of HO-terminated polydimethylsiloxane, 0.35 mL of H-MM and 2

drop of conc. H_2SO_4 were added. Then about 1 g of anhydrous Na_2SO_4 was added to the flask. The reaction system was stirred for 1 day at room temperature, then filtered to remove the salt. The filtrate was washed with water until neutral and dried by anhydrous Na_2SO_4 overnight.

Preparation of Silicone Gel from Vinyl Terminated Polydimethylsiloxane (HT-Gel)

H-Me-T was dried under vacuum. 0.5 g of dried H-Me-T and 1 mL of THF solution of Cp_2PtCl_2 (containing 1 mg of Cp_2PtCl_2) were added to 5 g of vinyl-terminated polydimethylsiloxane. The mixture was stirred thoroughly, then the solvent was removed under vacuum and charged with Ar. The mixture was heated at about 110°C until the silicone gel had formed sufficiently.

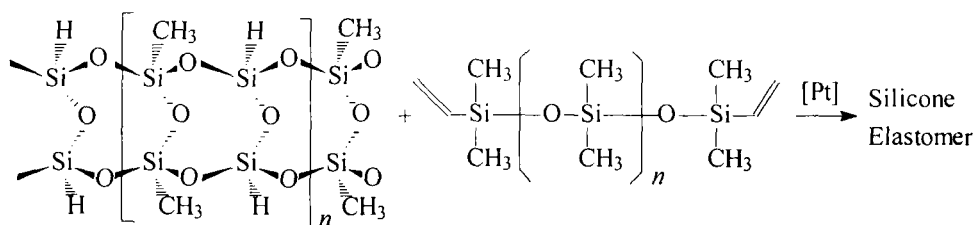
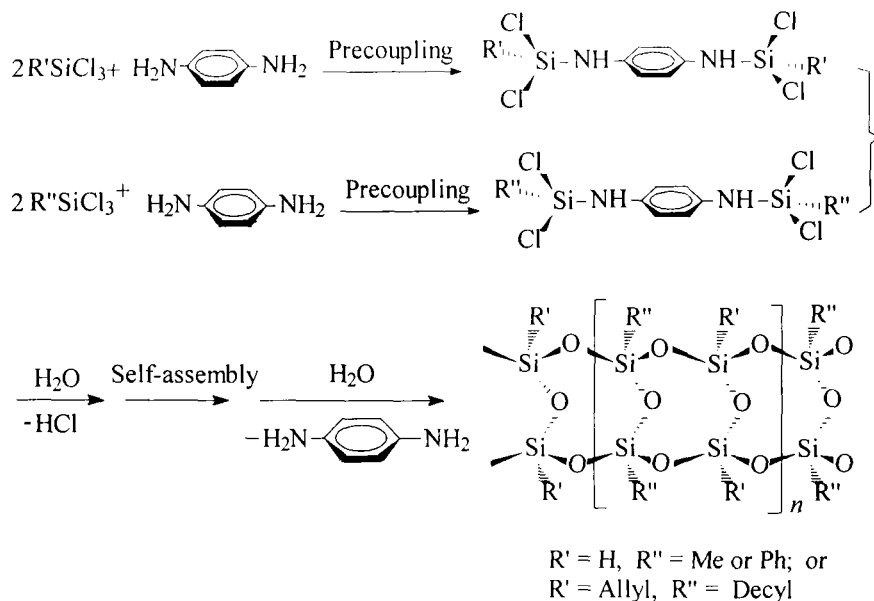
Preparation of Silicone Gel from Hydrogen Terminated Polydimethylsiloxane (ADT-Gel)

0.5 g of A-Dec-T and 2 mg of Cp_2PtCl_2 were added to 5 g of H-terminated polydimethylsiloxane in 50 mL of CH_2Cl_2 . The solvent was removed under vacuum. The mixture was heated at about 100°C until the silicone gel had formed sufficiently.

RESULT AND DISCUSSION

Addition type silicone gels were usually prepared by hydrosilylation of vinyl-terminated polydimethylsiloxane with polyhydromethylsiloxane of single main chain. Because of the high thermostability of ladderlike polysilsesquioxane, polyhydromethylsiloxane was replaced by H—Si bonds containing ladderlike polysilsesquioxane and silicone gels prepared by hydrosilylation reaction of vinyl-terminated polydimethylsiloxane with H—Si containing ladderlike polysilsesquioxane. Silicone gels prepared by reaction of H—Si terminated polydimethylsiloxane with vinyl or allyl containing ladderlike polysilsesquioxane were also synthesized for comparison.

Preparation of Ladderlike Polysilsesquioxane



Scheme 1

H-Me-Ts were synthesized by the stepwise coupling polymerization method, but the synthesis of H-Me-Ts is different from that of other ladderlike homopolysilsesquioxanes, because the reactivity of HSiCl_3 is much higher than that of MeSiCl_3 and PhSiCl_3 . As shown in Scheme 1, during the synthesis of H-Me-T, HSiCl_3 and MeSiCl_3 were aminolyzed separately. At first, PDA was added to the solution of MeSiCl_3 to react with MeSiCl_3 to form an intermediate, $\text{MeSiCl}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{Cl}_2\text{SiMe}$. After that, HSiCl_3 was added to the reaction system and then PDA was added to aminolyze HSiCl_3 to form a second intermediate, $\text{HSiCl}_2-\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{Cl}_2\text{SiH}$. After aminolysis, the two reaction intermediates were hydrolyzed and condensed to obtain the ladderlike copolymer. If HSiCl_3 and MeSiCl_3 were aminolyzed simultaneously, HSiCl_3 may form di-PDA substituted products and the regularity of the final ladderlike copolymer would deteriorate.

Since ladderlike polyphenylsilsesquioxane (Ph-T) is more heat-resistant than ladderlike polymethylsilsesquioxane (Me-T) and polymerization of Ph-T is easy to control, we also synthesized a series of ladderlike polyhydrophenylsilsesquioxanes (H-Ph-T) by the same method.

Table 1 shows the compatibility of various ladderlike polymers with a vinyl- or H-terminated polydimethylsiloxane.

Table 1. Compatibility of various ladderlike polymers with a vinyl- or H-terminated polydimethylsiloxane

Ladderlike copolymers	Feed ratio (mol/mol)	Film-forming ability	Compatibility with vinyl- (or H-) terminated polydimethylsiloxane
Me-H-T	7/3	Good	Yes
	8/2	Good	Yes
	9/1	Good	Yes
Ph-H-T	7/3	Good	No
	8/2	Good	No
	8.5/1.5	Good	No
A-Dec-T	8/2	Good	Yes

H-Me-T can mix well with polydimethylsiloxane to form a homogeneous system, but Ph-H-T can not. This may be caused by the dissimilarities between H-Ph-T and polydimethylsiloxane, so H-Ph-T was not used to synthesize silicone gels.

For comparison, A-Dec-T was also synthesized by the same method. Decyl was introduced into the ladderlike copolymer to improve the compatibility of ladderlike polymer with polydimethylsiloxane. A-Dec-T can mix well with polydimethylsiloxane.

Preparation and Thermal Properties of Silicone Gels

Silicone gels were prepared by cross-linking vinyl- or H-terminated polydimethylsiloxane with corresponding reactive ladderlike polymers in the presence of a platinum catalyst at elevated temperature. The structure of the silicone gels is illustrated in Fig. 1.

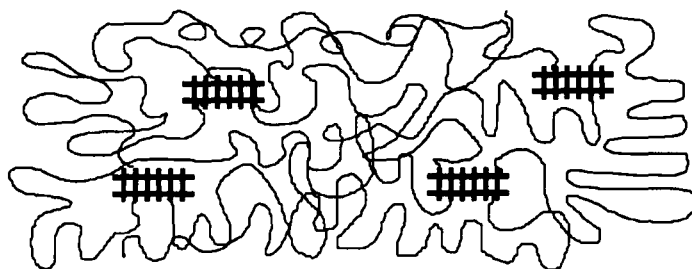


Fig. 1 Structure of ladderlike polysilsesquioxane cross-linked silicone gel

Because of the excellent thermostability of ladderlike polysilsesquioxane, silicone gels containing ladderlike polymers are expected to have good thermal properties.

The thermostabilities of silicone gels were measured by TGA. Table 2 lists the TGA results of the silicone

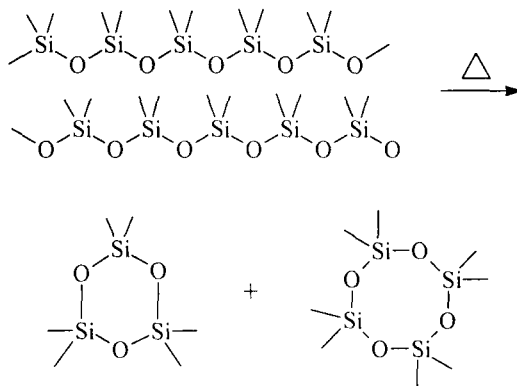
gels.

Table 2. Decomposition temperature (T_d) of the silicone gels

Ladderlike polymers used in silicone gels	T_d of silicone gels ($^{\circ}\text{C}$)
General silicone gel	363.2
H-Me-T (H/Me = 3/7)	391.3
H-Me-T (H/Me = 2/8)	444.8
H-Me-T (H/Me = 1/9)	450.4
A-Dec-T (A/Dec = 4/1)	426.6

It can be seen from Table 2 that the thermostability of the silicone gels is greatly improved by using ladderlike polymers instead of polyhydromethylsiloxane. The T_d of silicone gel was evidently raised from 363.2°C for general silicone gel to 450.4°C for silicone gel prepared by using ladderlike polyhydromethylsilsesquioxane. The silicone gels prepared from H-terminated polydimethylsiloxane and allyl-containing ladderlike polymers also have high T_d . The T_d of silicone gel prepared from H-terminated polydimethylsiloxane and A-Dec-T is as high as 426.6°C .

As shown in Scheme 2, due to the cyclization of polydimethylsiloxane chains, the polydimethylsiloxane chain can easily be depolymerized to form hexamethylcyclotrisiloxane (D_3) or octylmethylcyclotetrasiloxane (D_4) at high temperature. Figure 2 shows the molecular simulation model of ladderlike polysilsesquioxane. Their oxygen atoms are arranged on one side and Si atoms on the other side, so the ladderlike polysilsesquioxanes are more polar than single polydimethylsiloxane chains. As shown in Fig. 3, for those silicone gels containing ladderlike polymers, there are interactions between the polydimethylsiloxane chains and the ladderlike polymers. Due to the high thermal stability of the ladderlike polymers, the cyclization of polydimethylsiloxane chains is reduced and the thermal stability of the silicone gels is improved.



Scheme 2

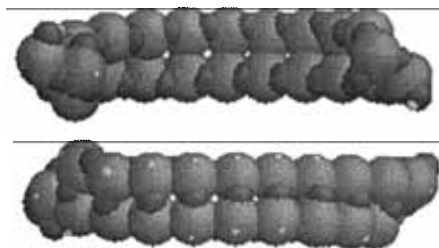


Fig. 2 Molecular simulation model of ladderlike polysilsesquioxane

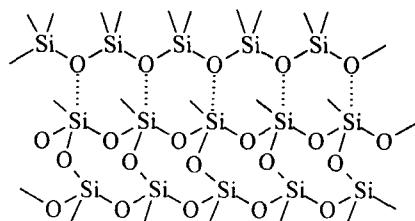


Fig. 3 Interaction between polydimethylsiloxane and ladderlike polysilsesquioxane

There are some merits of improving the heat-resistance of silicone elastomers by using ladderlike polymers, because they can be dissolved in polydimethylsiloxane to form homogeneous silicone gels. Ladderlike polymers do not contain —OH groups; they will not promote the decomposition of polydimethylsiloxane. The introduction of ladderlike polymers can significantly improve the thermal stability of silicone gels without sacrificing their other good properties, because these properties originate from the polydimethylsiloxane chains. The glass transition temperatures (T_g) of the silicone gels were measured by DSC and dynamic viscoelastometry and are listed in Table 3.

Table 3. Glass transition temperatures (T_g) of the silicone gels	
Ladderlike polymers used in silicone gels	T_g of silicone gels ($^{\circ}\text{C}$)
General silicone gel	-100.3
H-Me-T (H/Me = 1/9)	-92.8
H-Me-T (H/Me = 2/8)	-93.3

As can be seen from Table 3, the T_g of the silicone gels that contain ladderlike polysilsesquioxane are similar to that of the general silicone gel prepared by cross-linking vinyl-terminated polydimethylsiloxane with polyhydromethylsiloxane. On using ladderlike polysilsesquioxane instead of polyhydromethylsiloxane, the T_g of the silicone gels is slightly affected, because the T_g of the silicone gels mainly originates from polydimethylsiloxane. The silicone gels can perform well at low temperature.

Other properties, such as modulus and thermal expansion coefficient, also behave similarly.

CONCLUSION

To decrease the decomposition of silicone gels mainly caused by cyclization of polydimethylsiloxane and to improve the thermal stability of silicone gels, ladderlike polysilsesquioxanes were introduced instead of the single main chain polyhydromethyl; at the same time the overall properties of silicone gels can be maintained.

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