Synthesis of MQ Silicone Resins Through Hydrolytic Condensation of Ethyl Polysilicate and Hexamethyldisiloxane

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ABSTRACT: MQ silicone resins were synthesized through hydrolytic condensation of ethyl polysilicate and hexamethyldisiloxane. The structure of the MQ resins was characterized by NMR and GPC. The concentration of an acid catalyst was essential for the capping of functional groups with the monofunctional units. The acid-catalyzed resins had a narrow molecular weight distribution. After postcondensation catalyzed by a base, the molecular weight distribution became bimodal. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1753–1757, 1998

Key words: MQ silicone resin; hydrolytic condensation; molecular weight distribution; ethyl polysilicate; hexamethyldisiloxane

INTRODUCTION

MQ silicone resin represents a broad range of hydrolytic condensation products of monofunctional silane (M) and tetrafunctional silane (Q). Materials of molecular weight in the range 1000– 10,000 are very useful in pressure-sensitive adhesives, silicone rubbers, coatings, and additives.^{1–7} Acting as the tackifier, they are the indispensable ingredient of silicone pressure-sensitive adhesives.⁷ When used in silicone rubber, they can greatly enhance the mechanical properties and improve adhesion.^{3–4,6} They also play an important role in preparing clear, tough, flexible silicone adhesives and coatings.^{1,2,5} Besides, they are also an important ingredient of high-performance defoamers and releasing agents.

In the early process for the preparation of MQ silicone resins, sodium silicate and trimethyl

chlorosilane were used as starting materials.^{8,9} Sodium silicate was acidified to silica sol, which was capped by the M units to produce MQ resins. Although the starting materials were the least expensive, structure control of the resin product was not easy; gels were also easily produced.

More recently, less reactive tetraethoxysilane or ethyl polysilicate and hexamethyldisiloxane were used as starting materials.^{10–14} Improvements have been made in avoiding gel formation, better control of structure parameters such as M/Q ratio, molecular weight and its distribution, as well as reducing environment pollution.

Basic principles for the hydrolysis and condensation of alkoxysilanes have been known for a long time.^{15,16} However, the preparation of MQ silicone resins can be found only in the patent literature. A systematic study on the synthesis of MQ silicone resins is therefore needed. This article was devoted to a better understanding of the influence of experimental parameters on the structure of MQ resins prepared through hydrolytic condensation of ethyl polysilicate and hexamethyldisiloxane. It would be helpful in obtaining

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MQ resins with different structure parameters which have decisive effects on their application.

EXPERIMENTAL

Materials

Ethyl silicate 40, produced by the Shanghai Resins Factory (Shanghai, China) was a mixture of ethyl polysilicate with a 40% silica content. Hexamethyldisiloxane (HMD) was produced by the Second Chemical Factory of Beijing (Beijing, China; bp 100°C). Toluene, hydrochloric acid, and sodium hydroxide were chemical reagents from Beijing Chemical Factory (Beijing, China).

Preparation of MQ Silicone Resins

In a flask equipped with a stirrer and reflux condenser, HMD and ethyl silicate 40 were charged. An aqueous hydrochloric acid solution was dropped under vigorous stirring. The temperature was enhanced to 78°C. After refluxing for a given time, aliquots were taken for analysis. They were precipitated with deionized water and washed to pH 7, and then the volatile was removed in a vacuum at 70-80°C.

To conduct the postcondensation in basic media, the pH was adjusted to 10–11 by sodium hydroxide. Toluene, 1.8 mL per gram resin was added, and the reaction was carried out at 80°C for 1 h. Then, the base was neutralized with hydrochloric acid. Water and ethanol were removed by distillation as the temperature was increased to 110°C in about 1 h. The precipitated sodium chloride was removed by filtration, and a toluene solution of the MQ resin of concentration about 50% by weight was obtained. After toluene was removed in a vacuum at about 80°C, a white solid MQ resin was obtained. Characterization was conducted using the fresh samples, which were stored not over 2 weeks.

Characterization of MQ Resins

The number-average molecular weight (M_n) was obtained by standard techniques using a Knauer vapor pressure osmometer, Model 11.00. The reference solvent was chloroform. The molecular weight distribution was determined by gel permeation chromatography (GPC), using a Waters Model 6000A equipped with DuPont Zorbax PSM bimodal-S columns. The eluent was toluene at a flow rate 0.6 cm³ min⁻¹.

NMR spectra were recorded on a Varian Unity-200 at 200 MHz for ¹H and at 39.75 MHz for ²⁹Si. In the ²⁹Si-NMR experiments, 0.01*M* of Cr(acac)₃ was added as a relaxation reagent, double pulses were used with $T_{\rm ac} = 1.5$ s and $T_d = 10$ s, and the decouple mode was nny. The background ²⁹Si signal of the sample tube was deducted from the spectrum using a computer program. The chemical shift was relative to TMS in ¹H-NMR and to HMD in ²⁹Si-NMR.

RESULTS AND DISCUSSION

Hydrolytic Condensation Catalyzed by Acid

Hydrolytic condensation of a mixture of ethyl silicate 40 and HMD was inhomogeneous at the beginning. After several minutes, the system became clear because ethanol formed in reaction (1) is a common solvent for silanes and water. Siloxane chains were formed by reactions (2) and (3). Both acid and base can be used to accelerate the reactions. Acid was more preferable because the reactions were difficult to control by using a base as the catalyst:

$$\equiv Si - OR + H_2O \rightarrow \equiv Si - OH + ROH \quad (1)$$

$$\equiv Si - OR + \equiv Si - OH \rightarrow \equiv Si - O - Si \equiv + ROH$$
(2)

$$\equiv Si - OH + \equiv Si - OH \rightarrow \equiv Si - O - Si \equiv + H_2O$$
(3)

It is obvious that polycondensation of tetrafunctional silicate will easily lead to gel formation. This trend was depressed by capping the functional groups with monofunctional units. In the synthesis, HMD was the source of the monofunctional unit, and hydrochloric acid was used to effect the capping of functional groups through reactions (4)–(6) (Ref. 17):

$$(CH_3)_3SiOSi(CH_3)_3 + HCl \rightarrow$$

 $(CH_3)_3SiOH + (CH_3)_3SiCl$ (4)

$$(CH_3)_3SiOH + \equiv Si - OH \rightarrow$$

 $(CH_3)_3SiOSi = + H_2O$ (5)

$$(CH_3)_3SiCl + \equiv Si - OH \rightarrow$$

 $(CH_3)_3SiOSi = + HCl$ (6)

| Code | HCl Concentration (wt %) | ${M_n}^{ m a}$ | Softening Point ^a (°C) | Remarks |
|-------|-----------------------------|----------------|--------------------------------------|-----------------------------------|
| MQ101 | 0.24 | | | Gel formation during hydrolysis |
| MQ102 | 0.58 | _ | | Gel formed on removal of volatile |
| MQ103 | 0.91 | 4260 | 180–190 | |
| MQ104 | 1.36 | 4210 | 180–190 | |
| MQ105 | 5.60 | 4956 | 220-230 | |

Table I Effect of HCl Concentration on the Condensation Product of Ethyl Silicate 40 and HMD

Molar ratio $[M]/[Q]\colon$ 0.6/1; $[\mathrm{H_2O}]/[\mathrm{ethoxy\ group}]\colon$ 0.8/1.

^a Refluxing time at 78°C: 2.5 h.

The concentration of the acid catalyst is essential to the synthesis. If reaction (4) is not fast enough, the hydrolytic condensation will lead to gel formation. Examples are given in Table I. In the experiment coded MQ101 using 0.24 wt % hydrochloric acid, the reactant mixture gelled during hydrolysis. In another experiment coded MQ102 using 0.58 wt % hydrochloric acid to effect the hydrolysis, the resin obtained was unstable and gels formed on removal of the volatile.

The concentration of hydrochloric acid in the range of 0.91-1.36 wt % was satisfactory for ensuring the conversion of HMD. By using gas chromatography to monitor the expenditure of HMD, it was demonstrated that the HMD peak became negligible after refluxing at 78°C for 0.5 h when 0.91 wt % hydrochloric acid was used for the hydrolysis. Further increase of the acid concentration did not bring in additional advantages for the synthesis.

The hydrolytic condensation catalyzed by the acid was rapid. However, a period of refluxing at the boiling point of ethanol is necessary to avoid the gel formation during processing and upon storage. It is shown in Table II that the resin of M/Q = 0.6/1, coded MQ 201, prepared by reflux-

Table IIMolecular Weight and Softening Pointof MQ Resins

| Code | Refluxing Time at 78°C (h) | M_n | Softening Point |
|----------------|-------------------------------|---|------------------------|
| MQ201 | 0.5 | а | а |
| MQ202 | 1.5 | 4165 | 120-130 |
| MQ103 MQ204 | 2.5 | $\begin{array}{c} 4260 \\ 4323 \end{array}$ | 180 - 190 180 - 190 |

Molar ratio $[M]/[Q]\colon$ 0.6/1; [H_2O]/[ethoxy group]: 0.8/1; HCl concentration: 0.91 wt %.

^a Gel formation on removal of volatile.

ing at 78°C for 0.5 h, was unstable: Gel formed on removal of the volatile. The other resins given in Table II were stable after processing. It is seen that as the refluxing time increased from 1.5 to 5 h the change in the molecular weight was marginal while the softening point of the resin was enhanced remarkably. It is supposed that intramolecular condensation dominated this stage. Further extension of the refluxing time did not bring significant changes either in the molecular weight or in the softening point. It seems that the system approached an equilibrium state. This is understandable considering reactions (1)–(6) are reversible.

Important structure parameters, which are closely related to the application of MQ resins, are the ratio of the M unit to the Q unit, the molecular weight and its distribution, and the number of residual groups. The ratio of the M unit to the Q unit was calculated according to the ²⁹Si-NMR data. A typical NMR spectrum for the MQ resin is shown in Figure 1, which is very similar to that found in the literature.¹⁸ The resonances at 5, -107, and -117 ppm were due to the M units, the hydroxylated and ethoxylated Q units, and the Q units, respectively. The unit ratio of the resins



Figure 1 ²⁹Si-NMR spectrum for the resin MQ 307. The composition and the parameters of the hydrolytic condensation are given in Table III.

| | Acid-catalyzed Resins ^a | | | MQ Resins After Postcondensation | | |
|---|------------------------------------|-------|----------------------|----------------------------------|-------|----------------------|
| Unit Ratio [<i>M</i>]/[<i>Q</i>] | Code | M_n | Softening Point (°C) | Code | M_n | Softening Point (°C) |
| 1/1 | MQ301 | 2633 | 70-80 | MQ304 | 2916 | 100–110 |
| 0.9/1 | _ | _ | | MQ305 | 3243 | 150 - 160 |
| 0.8/1 | MQ303 | 3688 | 130-140 | MQ306 | 3978 | 220-230 |
| 0.7/1 | <u> </u> | | | MQ307 | 5327 | No softening point |
| 0.6/1 | MQ103 | 4260 | 180–190 | MQ308 | 6088 | No softening point |

Table III Effect of [M]/[Q] Ratio on Molecular Weight and Softening Point of MQ Resins

 $^{\rm a}$ HCl concentration: 0.91 wt %; [H_2O]/[ethoxy group]: 0.8/1; refluxing time 2.5 h.

found by ²⁹Si-NMR was in good agreement with that calculated from the molar ratio of the starting materials. For example, the unit ratio of MQ 307 calculated from the molar ratio of the starting materials is 0.70 and the unit ratio found by ²⁹Si-NMR is 0.70; the calculated unit ratio of MQ 309 is 0.90 and the unit ratio found by ²⁹Si-NMR is 0.88. Therefore, it is easy to produce MQ silicone resins of different unit ratios by changing the composition of the feed.

From the data given in Table I–III, it is seen that the molecular weight of the MQ resins was dependent of the concentration of the acid catalyst, the ratio of the M unit to the Q unit, as well as the time of refluxing. Increasing the Q unit in the reactant mixture, enhancing the catalyst concentration, and extending the reaction time will lead to an increase in the molecular weight of the obtained resin.

The number of residual ethoxy groups and hydroxyl groups was determined by ¹H-NMR. Figure 2 shows an NMR spectrum with the assignment of the chemical shift for the resin MQ307. The peak centered at 0.2 ppm is the resonance of the methyl protons in the M unit, and the quar-



Figure 2 ¹H-NMR spectrum for the resin MQ 307. The composition and the parameters of the hydrolytic condensation are given in Table III.

tets centered at 3.85 and 1.22 ppm are the resonances of the methylene protons and methyl protons of the ethoxy groups, respectively. The hydroxyl protons appear as a broad peak at 1.5–3 ppm depending on their concentration. Based on the data of the M/Q unit ratio, the number of residual groups, and the molecular weight, the average structural formulas were calculated (see Table IV).

Postcondensation Catalyzed by Base

For many applications, MQ silicone resins of a more condensed structure are preferred. In this case, base-catalyzed hydrolytic condensation is preferable. However, it is not practicable to prepare MQ resins directly from ethyl polysilicates and HMD using a base catalyst. The hydrolytic condensation often leads to gel formation because, on the one hand, HMD is sluggish toward a base and, on the other hand, each subsequent step of hydrolysis of the polysilicate will have a larger rate constant. Therefore, acid-catalyzed resins were synthesized first, and a postcondensation in the presence of a base followed.

After postcondensation, the number of residual ethoxy and hydroxyl groups decreased. Whereas a significant increase in the molecular weight can

| Table IV | Average Structural | Formulas of MQ |
|----------|--------------------|----------------|
| Resins | | |

| Code | Unit Ratio [M]/[Q] | Average Structural Formula |
|-------------------------|-----------------------|---|
| MQ303 MQ306 MQ307 | 0.8 0.8 0.7 | $\begin{array}{c} Si_{27.4}O_{39.2}M_{21.9}(OEt)_{5.8}(OH)_{3.3}\\ Si_{30.5}O_{46.1}M_{24.4}(OEt)_{4.1}(OH)_{1.7}\\ Si_{44.3}O_{70.4}M_{31.0}(OEt)_{3.1}(OH)_{3.5}\\ \end{array}$ |
| MQ308 | 0.6 | ${\rm Si}_{60.7}{\rm O}_{97.9}{\rm M}_{36.4}{\rm (OEt)}_{6.7}{\rm (OH)}_{4.6}$ |



Figure 3 GPC chromatogram for (a) resin MQ 103 and (b) resin MQ 308. The composition and the parameters of the hydrolytic condensation are given in Table III.

be seen, the profound change in the structure is reflected in the softening point (Table III).

It is interesting to indicate the change in the molecular weight distribution after the postcondensation. As shown in Figure 3, the acid-catalyzed resin MQ103 had a monomodal and narrow molecular weight distribution. Contrarily, the resin after postcondensation (MQ308) showed a bimodal and very broad distribution in the GPC chromatogram.

CONCLUSIONS

MQ silicone resins were synthesized through hydrolytic condensation of ethyl polysilicate and HMD catalyzed by acid. The concentration of the acid was essential to the synthesis. The molecular weight of MQ resins increased rapidly in the early stage of the reaction and then the system approached an equilibrium state. The acid-catalyzed resins had a narrow molecular weight distribution.

Postcondensation in the presence of a base was carried out for further modification of the resin structure. The resins after the postcondensation had a more condensed structure and a bimodal molecular weight distribution.

The great difference between the acid-catalyzed resins and the resins after postcondensation can be traced back to the mechanism of the formation of the Si—O—Si chains. The acid-catalyzed condensation involves the nucleophilic attack of the silanol oxygen atom to the silicon atom of the silanol in the oxonium form [reaction (7)]:

$$\equiv Si \longrightarrow O^{-} H + \equiv Si \longrightarrow OH \rightarrow$$

$$\equiv Si \longrightarrow O^{-} H = Si \longrightarrow OH \rightarrow$$

$$\equiv Si \longrightarrow O^{-} H = Si \longrightarrow OH \rightarrow$$

$$= Si \longrightarrow OH \rightarrow Si = H^{-} H + H_{2}O \quad (7)$$

$$\equiv Si - O^{-} + \equiv Si - OH \rightarrow \equiv Si - O - Si \equiv + OH$$
(8)

Substitution of the hydroxyl group or the ethoxy group with siloxanyl groups will reduce the partial negative charge on the silanol oxygen. As a result, the higher crosslinked molecules will be less likely to participate in the further condensation.

Contrarily, the condensation catalyzed by a base involves a nucleophilic attack of the silanol anion on the silicon atom of another silanol group [reaction (8)].¹⁹ The substitution of siloxanyl groups for hydoxy groups or ethoxy groups will make the silanol more reactive.²⁰ Therefore, the higher crosslinked molecules will be more likely to participate in the further condensation.

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