

THE EFFECT OF THE ACID CATALYST ON THE PREPARATION OF MQ SILICONE RESINS

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Abstract MQ silicone resins were prepared through hydrolytic condensation of ethyl polysilicate or tetraethoxysilane and hexamethyl disiloxane. The unit ratio of the MQ resins was determined by ^{29}Si -NMR. The relationship of the unit ratio of the product resins with that in the feed was studied. When the reaction was catalyzed by aqueous hydrochloric acid, and the unit ratio of M to Q in the feed was more than 1, the unit ratio of the product was usually lower than that of the feed. The MQ silicon with an unit ratio of $\text{M/Q} > 2$ could not be obtained. However, if the reaction was catalyzed by concentrated sulfuric acid and the reverse hydrolysis process was employed, MQ silicone resin with very high M/Q ratio was successfully prepared.

Keywords MQ silicone resin, Hydrolytic condensation, Ethyl polysilicate, Tetraethoxysilane, Hexamethyl disiloxane, Catalyst

INTRODUCTION

MQ silicone resins are a kind of interesting polymers. They represent a broad range of hydrolytic condensation product of monofunctional silane (M) and tetrafunctional silane (Q). They are being used extensively in pressure sensitive adhesives^[1-4], silicone rubbers^[5, 6], water repellents^[7, 8] and surfactants^[2].

In the early process for the preparation of MQ silicone resins, sodium silicate and trimethyl chlorosilane were used as the starting materials^[8, 9]. More recently, less reactive tetraethoxysilane or ethyl polysilicate and hexamethyl disiloxane were used instead^[10-14]. Yet it is very difficult to locate literature reference for the synthesis of MQ resins except some patents.

The key point in the synthesis is the structure control of the resin product, i.e. to obtain MQ resins with definite structure parameters by controlling the reaction conditions. The ratio of the M unit to the Q unit (M/Q) is of the utmost importance. In our previous paper^[15], it was reported that the M/Q ratio could be controlled by varying its ratio in the feed, and the unit ratio of the product was roughly in agreement with that in the feed. However, in that paper all the M/Q values of the feed were less than one. In fact, the MQ resins usually used in pressure sensitive adhesives and silicone rubbers are of M/Q values smaller than 1. However MQ resins with high M/Q values would be more preferable when they are used in the area such as water repellent and surfactant. In the present paper, the effect of an acid catalyst on the preparation of the MQ silicone resins will be discussed.

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EXPERIMENTAL

Materials

Ethyl Silicate 40, produced by the Shanghai Resins Factory, was a mixture of ethyl polysilicates with 40% silica content. Hexamethyl disiloxane (HMD) was obtained from the Second Chemical Factory of Beijing, b.p. 100 °C. Tetraethoxysilane (TEOS), hydrochloric acid, concentrated sulfuric acid and toluene were chemical reagents from Beijing Chemical Factory.

Preparation of MQ Silicone Resins

The reaction catalyzed by hydrochloric acid

In a 150 mL flask equipped with stirrer and reflux condenser, 15 g Ethyl Silicate 40 or 20.8 g tetraethoxysilane and a predetermined amount of HMD were charged. An aqueous hydrochloric acid solution was added under vigorous stirring. The temperature was raised to 78 °C. After refluxing for 2.5 h, the acid in the mixture was neutralized with sodium hydrogen carbonate. The solvent in the mixture was replaced with toluene and the mixture was filtered to give a toluene solution of MQ resin. After toluene was removed under vacuum at about 80 °C, a white solid MQ resin or a viscous liquid was obtained. Characterization was conducted using the fresh samples, which were stored for under two weeks.

The reaction catalyzed by sulfuric acid

To a mixture of HMD, concentrated sulfuric acid and tetraethoxysilane, water was added within an hour with vigorous stirring. Then the same process as for the reaction catalyzed by hydrochloric acid was followed.

Characterization

The M/Q ratio of the MQ silicone resins was calculated according to the ^{29}Si -NMR data. A typical NMR spectrum of the MQ resin is shown in Fig. 1, which is very similar to that found in the literature^[16]. The resonances at $\delta = 5$, $\delta = 107$ and $\delta = 117$ were due to the M units, the incompletely trimethylsilylated Q units and the completely trimethylsilylated Q units, respectively.

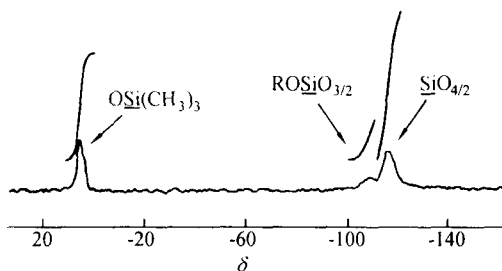


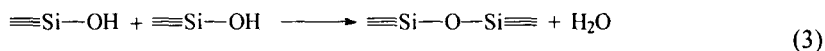
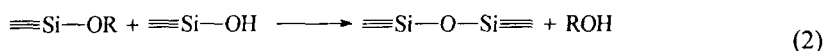
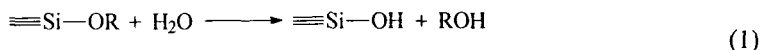
Fig. 1 ^{29}Si -NMR spectrum of MQ resin.

^{29}Si -NMR spectra were recorded on a Varian Unity-200 at 39.75 MHz. In the ^{29}Si -NMR experiments, $\text{Cr}(\text{acac})_3$ was added as relaxation reagent, double pulses were used with $T_{\text{ac}} = 1.5$ s and $T_{\text{d}} = 10$ s, the decouple mode was nny. The background ^{29}Si signal of the sample tube was deducted from the spectrum, using a computer program. The chemical shift was relative to HMD.

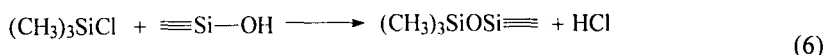
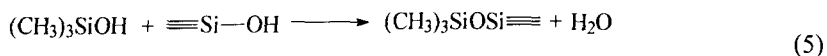
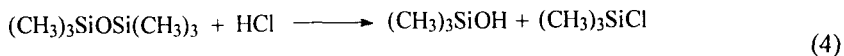
RESULTS AND DISCUSSION

The Synthesis Using Hydrochloric Acid as Catalyst

Hydrolytic condensation of a mixture of Ethyl Silicate 40 or TEOS and HMD proceeded inhomogeneously at the beginning. After several minutes the system became clear because ethanol formed in the reaction (1) is a common solvent for silanes and water. Siloxane chains were formed by the reactions (2) and (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 reaction (4)–(6)^[17].



For a non-equilibrium process the M/Q ratio of the product was determined by the relative rate of the condensation (2) and (3) to the capping reaction (5) and (6). If the capping reaction rate is much higher than that of the condensation, and the unit ratio of the M unit to the Q unit in the feed is lower than ca. 2.44 for ethyl silicate-40 or 4 for tetraethoxysilane, the unit ratio of the product would approach that of the feed. On the other hand, if the condensation is much faster than the capping reaction, the unit ratio would be very small, and the reaction would lead to gel formation.

Figure 2 shows the relationship of the unit ratio M/Q of the product to the mole ratio in the feed for the preparation using ethyl silicate-40 as the starting material. It can be seen that almost all the M units are built into the product when the M/Q ratio of the feed is less than 1. However, when the M/Q mole ratio in the feed is greater than 1, the M/Q ratio of the product is no longer equal to that in the feed, and the difference becomes more and more significant as the M/Q ratio in the feed increases.

Similar results were obtained using tetraethoxysilane as the starting material, as shown in Fig. 3. It can be seen that the first silanol group of the Q unit is capped quite easily, and the capping of the functional groups on the Q unit becomes obviously more difficult when an M unit is already attached on it. This can be attributed to the steric hindrance of the bulky trimethylsilyl group.

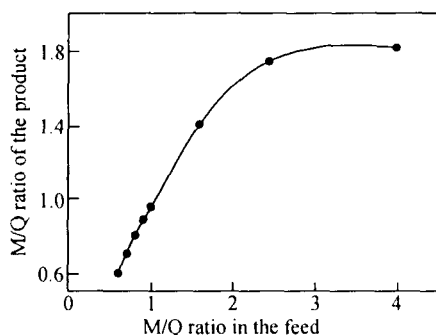


Fig. 2 A plot of unit ratio of the product versus the unit ratio of the feed for hydrolytic condensation of Ethyl Silicate-40 and HMD $[\text{H}_2\text{O}]/[\text{ethoxy group}]=0.8$, the concentration of hydrochloric acid was 0.078 mol/L

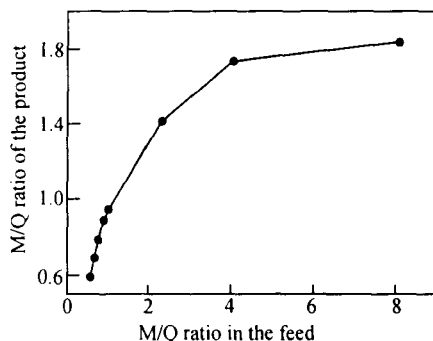


Fig. 3 A plot of unit ratio of the product versus the unit ratio of the feed for hydrolytic condensation of tetraethoxysilane and HMD $[\text{H}_2\text{O}]/[\text{ethoxy group}]=1$, the concentration of hydrochloric acid was 0.078 mol/L

Effect of the Concentration of Hydrochloric Acid on the Unit Ratio

The effect of pH value of the media on the hydrolysis and the condensation of alkoxy silanes is known^[18]. For the synthesis of MQ silicone resins the presence of a strong acid is essential when HMD is used as the source of the M unit because HMD has to be cleaved by the acid through Reaction (4) in order that the capping reactions can take place.

Figure 4 shows the effect of hydrochloric acid concentration on the unit ratio of MQ resins. It can be seen that when the feed M/Q ratio is low, all M units are built into the resin, and the hydrochloric acid concentration does not affect the unit ratio of the product.

When the feed ratio is high, however, the effect of the hydrochloric acid becomes significant. An increase in the hydrochloric acid concentration favors the capping of the M unit. The effect levels off as the hydrochloric acid concentration is higher than 0.075 mol/L. Therefore, MQ resins of high M/Q ratio cannot be obtained by increasing the hydrochloric acid concentration.

Synthesis of MQ Resins Using Sulfuric Acid as Catalyst

It was found that when an aqueous solution of sulfuric acid was used instead of hydrochloric acid for the preparation of the MQ silicone resins, the results were very similar to what described in the previous paragraph.

In order to prepare the MQ resins with high M/Q ratio concentrated sulfuric acid was used as a catalyst. In the preparations the amount of sulfuric acid was 5.6% of the weight of water, and the charge of water was calculated according to the mole number of the ethoxy group to be hydrolyzed. The reverse hydrolytic process occurred smoothly. Gel formation was avoided completely and thus the MQ silicone resins with high M/Q ratio were prepared successfully with very high yield.

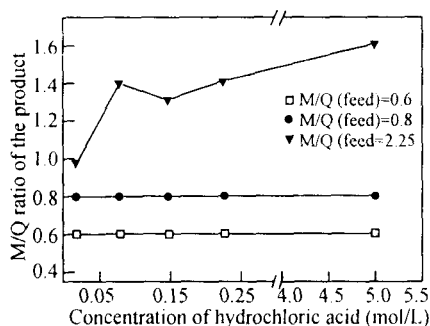


Fig. 4 Effect of the concentration of hydrochloric acid on the unit ratio of MQ resins

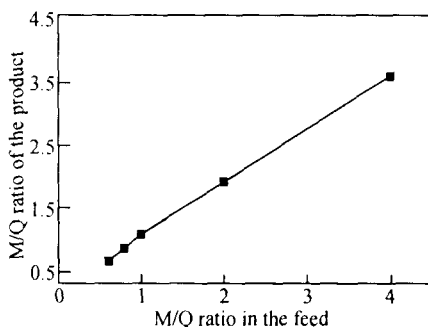


Fig. 5 A plot of unit ratio of the product versus the unit ratio of the feed for hydrolytic condensation of TEOS and HMD, $[H_2O]/[ethoxy\ group]=1$

A plot of the M/Q ratio of the product versus the unit ratio in the feed (Fig. 5) was substantially different from that where an aqueous solution of hydrochloric acid was used to catalyze the reactions. It can be seen that the M/Q ratio is very close to that in the feed even if the unit ratio is as high as 4. The result can be explained as follows. Because the concentration of water in the system was kept quite low during the reaction, the rate of hydrolysis reaction of TEOS was low. On the other hand, the cleavage rate of Si—O—Si bond catalyzed by concentrated sulfuric acid was much higher than that of hydrochloric acid^[19, 20]. So the capping reaction was sped up greatly in comparison with the self-condensation reaction of the hydrolysate of TEOS.

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