Versatile Cascade Esterification Route to MQ Resins

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ABSTRACT: We describe a versatile cascade route for manufacturing MQ resins using alkoxysilanes (e.g., tetraethoxysilane (TEOS)) or equivalent oligomers (e.g., ethyl polysilicate (polyTEOS)), a carboxylic acid (typically acetic acid), and hexamethyldisiloxane (MM) as starting materials; a strong acid catalyst is also employed in the one-pot reaction. The siloxane resin synthesis is accompanied by esterification of the carboxylic acid to give ethyl acetate, which acts as an important solvent, making the process more controllable. Contrary to traditional sol–gel methods, no water is introduced in the experiments, but is generated in situ. The strategy offers several advantages, including reproducibility, high yields of siloxane resins with excellent batch-to-batch consistency and without gel formation, narrow dispersity, low Si-hydroxyl residues in the final products, and the ability of increasing the molecular weight by thermal treatment. The process utilizes the green chemistry concepts of lower pollutant formation and higher atom efficiency.

INTRODUCTION

MQ resins (M = Me₃SiO₁/₂, Q = SiO₄/₂) are attracting increasing attention because of their excellent heat resistance, flexibility over an extremely wide temperature range, film-forming properties, water resistance, and ability of acting as performance modifiers. Therefore, they are utilized in a broad range of applications including liquid silicone rubber, pressure-sensitive adhesive, light-emitting diode encapsulation, electronics, personal care, nanomaterials, and so on. MQ resins have been interested increasingly by the silicone industrial community and were rediscovered by academics in the report of Flagg and McCarthy in 2016.

Traditionally, the synthesis of siloxane resins involves hydrolysis/condensation processes that were invented and patented by Hyde for silsesquioxanes and by Daudt and Tyler for MQ resins. These processes and the properties of silsesquioxanes were reviewed by Baney et al. There are several disadvantages associated with traditional hydrolysis/condensation synthetic processes using chlorosilanes or organoalkoxysilanes as starting materials. Most problematically, the reactions occur too rapidly to permit effective control, and the formation of gels or insoluble white powders is a common outcome.

One modified strategy to avoid this problem, in part, involves a slower and more controlled hydrolysis typically carried out in an organic solvent/water biphasic system capable of dissolving chlorosilanes or organoalkoxysilanes as starting materials. Most problematically, the reactions occur too rapidly to permit effective control, and the formation of gels or insoluble white powders is a common outcome.

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= methyl, ethyl, and isopropyl). Although they were not concerned with the end state of the silicon compounds, the method shows precedent for this work. HCl is presumably the active acid catalyst. Milder acids are also effectively employed in the siloxane resin formation. Eisenberg et al. reported silsesquioxanes derived from formic acid and functional methoxysilanes, without acid catalyst; polycondensation was performed for a period of time from 2 days to 1 month. In an analogous process, Egorova et al. investigated in detail the mechanism and kinetics of the polycondensation of dimethoxymethylsilane with excess anhydrous deuterated acetic acid (CD₃COOD) as an active medium. They demonstrated that, in the absence of strong acids, esterification is the slowest step of the multistep process that leads to siloxanes, in this case, linear dimethylsilicone fluids. This process can be used to synthesize MQ copolymers, as reported by Vasil’ev et al., product formation using tetraethoxysilane (TEOS) ((SiOEt)₄), trimethoxymethoxysilane, and a large excess of acetic acid required 35 h at reflux with toluene as the solvent.

The rates of both transesterification and polysiloxane formation are accelerated when both weak and strong Brønsted acids are present in the reaction medium. Ivanova et al. reported that partial polycondensation of RSi(OMe)₃ (R = C₆H₅, CH₃) to give polycyclic structures with branched
Siloxane resins were synthesized concomitant with esterification to facilitate an understanding of the MQ synthesis process. These studies and related work by Muzafarov demonstrated that siloxane bond formation can be elicited by acidic transesterification processes.11 As noted, the reaction is slow in the absence of strong acids. The above processes described typically utilized excess acetic acid as an active medium. These reactions have failed to provide as high an induction period that could be substantially shortened by the addition of HCl or methanol.10

Initial experiments were undertaken with Si(OEt)4 to facilitate an understanding of the MQ synthesis process. Siloxane resins were synthesized concomitant with esterification of the carboxylic acid, generally using ~1 equiv of acetic acid/OEt group (Table 1). The results were compared to those obtained by traditional hydrolysis (Table 2). The “byproduct”-ethyl acetate—acted as a solvent such that the reaction is homogeneous throughout the reaction process. An exotherm was observed once the strong acidic catalyst was added (Figure 3). Siloxane resin products were obtained simply via neutralization, typically using Na2CO3 (aq), separation by filtration, and distillation of the ethyl acetate coproduct from the siloxane product. The process was completed by gentle heating to remove residual solvent.

A variety of strong acidic catalysts was tested, including strong acids such as trifluoromethanesulfonic acid, 98% sulfuric acid, p-toluenesulfonic acid, and some other acidic substances, including Lewis acid (FeCl3, AlCl3, SnCl2), acetyl chloride, trimethylchlorosilane, and tetrachlorosilane (Tables 3 and 4). Although the most effective catalyst was triflic acid based on the enhanced rate of reaction, and the lowest SiOH concentration (see below), the best balance of performance and cost was provided by sulfuric acid; similar products were observed (1 vs 2, Tables 1 and 3). Use of 98% H2SO4 at 2 wt % was found to balance the speed and efficiency of the reaction (Table 4).

Having demonstrated the key characteristics of the reaction with TEOS, analogous reactions were examined with its hydrolyzate, which comprises partly condensed TEOS (Q-oligomers, with one-half the OEt groups), requiring less acetic acid and producing less ethyl acetate; safety issues associated with TEOS are avoided. In addition, longer reaction times led to higher Mw products, but with accompanying higher dispersities. Otherwise, compared to TEOS, it was found that very similar reaction outcomes could be observed (9 vs 10; Tables 1 and 5). Surprisingly, small changes in the acid concentration, accompanied by transesterification, was rapid in the presence of HCl and an excess of acetic acid. The reaction has an induction period that could be substantially shortened by the addition of HCl or methanol.10

Table 1. Influence of Acidic Catalysts on the Esterification Reaction

| exp. | variable | reagents | catalyst | mol % | M/Q | HOAc/OEt | yield (%) | Mw | Mx | D_Mx |
|------|----------|----------|----------|-------|-----|---------|----------|-----|-----|------|
| 1    | catalyst | TEOS     | CF3SO3H  | 4.2   | 0.8 | 1.1     | 96.1     | 981 | 1416 | 1.44 |
| 2    | TEOS     | H2SO4    | 6.4      | 0.8   | 1.1 | 96.2    | 1657     | 2677 | 1.62 |
| 3    | [acid]   | TEOS     | H2SO4    | 2.1   | 0.8 | 1.1     | 98.6     | 1162 | 1646 | 1.41 |
| 4    |         | H2SO4    | 10.4     | 0.8   | 1.1 | 96.3    | 1380     | 1905 | 1.38 |
| 5    | M/Q     | polyTEOS | H2SO4    | 7.2   | 0.8 | 1.2     | 97.14    | 2338 | 4051 | 1.94 |
| 6    |         | polyTEOS | H2SO4    | 7.2   | 0.9 | 1.2     | 94.06    | 2229 | 3596 | 1.61 |
| 7    |         | polyTEOS | H2SO4    | 7.2   | 1.0 | 1.2     | 93.82    | 1855 | 2634 | 1.42 |
| 8    | reagent  | polyTEOS | H2SO4    | 1.5   | 0.8 | 1.1     | 96.5     | 1313 | 1848 | 1.41 |
| 9    |         | TEOS     | H2SO4    | 7.2   | 0.8 | 1.1     | 93.2     | 1247 | 1793 | 1.44 |
| 10   |         | polyTEOS | HCl      | 2.1   | 0.8 | NA      | 84.9     | 2660 | 4425 | 1.66 |
| 11   | hydrolysis | polyTEOS | HCl      | 6.3   | 0.8 | NA      | 84.9     | 2660 | 4425 | 1.66 |

With respect to TEOS. Determined by GPC. See also the Experimental Section for other formulae.

Table 2. Synthesis of MQ Silicone Resins by Hydrolysis

| exp. | M/Q ratio | yield (%) | Mw | Mx | D_Mx |
|------|-----------|-----------|-----|-----|------|
| 1    | 0.68      | 77.07     | 2782 | 5040 | 1.8116 |
| 2    | 0.80      | 84.89     | 2660 | 4425 | 1.6635 |
| 3    | 0.85      | 89.63     | 2257 | 3299 | 1.4617 |
| 4    | 0.90      | 90.67     | 1919 | 2601 | 1.3554 |
| 5    | 0.95      | 90.00     | 1875 | 2493 | 1.3296 |
| 6    | 1.00      | 89.07     | 1679 | 2164 | 1.2889 |
Table 3. Influence of Catalysts on the Esterification Reaction

| expt. | catalyst | dosage (g) | mmol | mol % vs TEOS | yield (%) | $T_{\text{max}}$ (°C)$^c$ | $M_n$,$^b$ | $M_w$,$^b$ | $D_M$ |
|-------|----------|------------|------|---------------|-----------|----------------|----------|----------|-------|
| 1     | 98% H$_2$SO$_4$ | 3.18       | 31.8 | 6.36          | 96.2      | 55                      | 1657     | 2677     | 1.6156 |
| 2     | CF$_3$SO$_2$H | 3.14       | 20.8 | 4.16          | 96.1      | 60                      | 981      | 1416     | 1.4434 |
| 3     | CH$_3$COCl   | 3.15       | 38.9 | 7.78          | 94.6      | 31                      | 1365     | 2279     | 1.6696 |
| 4     | Me$_2$SiCl   | 3.18       | 28.7 | 5.74          | 96.6      | 30                      | 2513     | 4475     | 1.7807 |
| 5     | FeCl$_3$     | 3.26       | 19.5 | 3.90          | 45.0      | 40                      | 2566     | 4686     | 1.8262 |
| 6     | cation-exchange resin$^*$ | 3.12 | 2.46 | 0.49 | 76.9 | 30 | 3966 | 32.323 | 8.1500 |

$^a$Maximum temperature of the reaction in the first hour. $^b$Determined by GPC using polystyrene (PS) standards. $^c$Refers to mol % H+. The catalyst was titrated and shown to provide 0.79 mequiv H+/g.

Table 4. Influence of H$_2$SO$_4$ Concentration on MQ Resin Characteristics

| expt. | H$_2$SO$_4$ (wt %) | yield (%) | $M_n$ | $M_w$ | $D_M$ |
|-------|-------------------|-----------|-------|-------|-------|
| TEOS (M/Q 0.8; HOAc/OEt 1.1:1) | | | | | |
| 1     | 0.1               | 102.3$^b$ | 1093  | 1968  | 1.80  |
| 2     | 1                 | 98.6      | 1162  | 1646  | 1.41  |
| 3     | 3                 | 95.5      | 1202  | 1532  | 1.27  |
| 4     | 5                 | 96.3      | 1380  | 1905  | 1.38  |
| 5     | 10                | 96.5      | 1382  | 1936  | 1.40  |
| PolyTEOS (M/Q 0.68; HOAc/OEt 0.75) | | | | | |
| 1     | 0.3               | 96.1      | 2227  | 7068  | 3.17  |
| 2     | 1                 | 92.5      | 3230  | 6370  | 1.97  |
| 3     | 2                 | 95.0      | 3388  | 5936  | 1.75  |

$^a$Determined by GPC. $^b$The excess material demonstrates that traces of alcohol reside in the product.

Table 5. Differences in Resins Formed from PolyTEOS or TEOS

| expt. | precursor | yield (%) | $M_n$ | $M_w$ | $D_M$ |
|-------|-----------|-----------|-------|-------|-------|
| 1     | polyTEOS  | 96.5      | 1313  | 1848  | 1.4075 |
| 2     | TEOS      | 93.2      | 1247  | 1793  | 1.4379 |

Table 6. Effect of Drying Time on Product Characteristics

| expt. | time (h) | temperature (°C) | yield (%) | $M_n$ | $M_w$ | $D_M$ |
|-------|----------|-----------------|-----------|-------|-------|-------|
| PolyTEOS (M/Q 0.8; HOAc/OEt 1.1:1) | | | | | | |
| 1     | 0        | 22              | 1032      | 1458  | 1.4128 |
| 2     | 3        | 22              | 1039      | 1511  | 1.4543 |
| 3     | 3        | 60              | 1090      | 1575  | 1.4450 |
| 4     | 3        | 80              | 1313      | 1970  | 1.5004 |
| 5     | 3        | 100             | 1849      | 2830  | 1.5306 |
| 6     | 3        | 120             | 2228      | 3702  | 1.6616 |
| 7     | 3        | 150             | 2499      | 4349  | 1.7403 |
| 8     | 3        | 180             | 2674      | 4810  | 1.7988 |

Calculation fraction by gas chromatography (GC) showed that MM was completely consumed in the reaction, which means that all MM is converted into MQ copolymers (Figure 6). This is too beneficial, as the distilled ethyl acetate stream is not contaminated by MM.

Characterization of the product MQ resins showed them to be quite different from products of hydrolysis (5–7 vs 11, Table 1). In particular, there was less residual SiOH (or SiOEt) in the resins produced by this cascade esterification, as shown by infrared analysis. Preliminary studies showed that the Si–OH concentration could be further reduced by gentle heating. For example, the low concentration of SiOH groups apparent from the signal near 3450 cm$^{-1}$ after drying at 60 °C for 3 h had nearly disappeared if instead the drying temperature was 120 °C for 3 h (Figure 7).

A second difference found with products from this process involved the molecular weight distributions. Lower M/Q ratios, unsurprisingly, led to higher $M_w$ materials (5–7, Tables 1 and 8). Samples dried at 60 °C exhibited a nearly unimodal distribution with $D_M$ near 1.4. By contrast, samples heated at 120 °C for 3 h showed a bimodal weight distribution almost without Si–OH residues but with a wider bimodal peak and $D_M$ of 1.6–1.8 (Table 6). Thus, practically, one can tune residual SiOH and $M_w$ profiles by the time/temperature of postreaction heat cure treatment.

The process showed excellent batch-to-batch reproducibility and consistency. Repetitions using sulfuric acid as the catalyst led to MQ resins with consistent yields and with almost the same molecular weight and $D_M$ (Table 9).

One common manifestation of the differences in MQ resins is their ability of adding tack to polymer elastomers or gels. A comparison with a commercial MQ resin showed distinct differences in tack provided at the same loading (Table 10).

**DISCUSSION**

The Fischer esterification of an alcohol with a carboxylic acid is a time-honored, reliable route to esters (Figure 2A). The
The efficiency of the process relies on a strong acid catalyst and a mechanism to distort the equilibrium to favor products. The use of excess alcohol or carboxylic acid can satisfy the latter requirement, but of course dehydration by distillation or by physical means has an analogous effect.

Slow release and consumption of water in situ are key to the efficient MQ resin synthesis observed (Figure 2B–F). Acid-catalyzed hydrolysis of alkoxysilanes produces a silanol and alcohol (Figure 2C); silanols are also formed from hydrolysis of Me3SiOSiMe3 (Figure 2B). Acid-catalyzed condensation of two silanols leads to disiloxanes and water (Figure 2E,F). The overall cascade progress is precisely controlled by the rate of liberation of water in situ.

It is noted that silicone polymers can be formed by redistribution polymerization under acidic conditions with MM and D4 ((Me2SiO)4). The redistribution process favors (more basic) M end groups compared to D units (Me2SiO). As a consequence, slow growth in molecular weight occurs as D units are inserted into the growing M-capped silicone chain (Figure 8A,B). In an analogous process, the hydrolysis and condensation of tetraalkoxysilanes lead initially to linear silica fibrils that, at high conversion, condense to form loose silica networks (Figure 8C–E); by contrast, under basic conditions, highly reticulated 3D structures form. We speculate that the formation of MQ resins using esterification follows analogous pathways. That is, Q units derived from TEOS slowly undergo hydrolysis and insertion into an M-rich structure, such that relatively low $M_w$ mostly linear oligomers are formed. A speculative model compound 1 is proposed in Figure 2F,G. Such a process would account for the narrow dispersity observed in the product; because little water is present at any given time, evolving products will have a relatively low concentration of SiOH groups remained (as shown by IR; Figure 7). This proposal is further supported by the ability of almost completely removing SiOH groups by gentle heating. This is likely the consequence of the condensation of the few free SiOH groups remaining after a significant amount of water had been driven off, as shown by IR (Figure 7).

### Table 7. Effect of Reaction Time on MQ Siloxan Resin Characteristics

| expt. time (h) | yield (%) | $M_n$ | $M_w$ | $D_M$ |
|---------------|-----------|-------|-------|-------|
| 1             | 93.23     | 2490  | 7898  | 3.1719 |
| 2             | 94.32     | 2622  | 5630  | 2.1472 |
| 3             | 90.00     | 2341  | 4846  | 2.0701 |
| 4             | 91.63     | 2483  | 4898  | 1.9012 |
| 5             | 90.06     | 2621  | 4979  | 1.8997 |
| 6             | 93.79     | 2591  | 4928  | 1.9020 |

Figure 5. Examples of changes in molecular weight with thermal treatment corresponding to Table 6. The legend refers to temperature (e.g., 22 = 22 °C) and time is in hours.

Figure 6. GC analysis showing no MM in the MQ resin product.
The many methods used to prepare MQ resins typically result in complex mixtures with high dispersity and high alkoxy and/or SiOH content. The described process, which hinges on the slow generation of water provided by esterification to give ester solvents, avoids these problems. In addition, the ester coproduct has commercial value. Almost no waste is generated in this chlorine-free reaction, particularly when compared to traditional reactions, which produce a complex mixture of

![Figure 7](image_url)

Figure 7. Infrared analysis of (A) MQ resin produced by hydrolysis and produced by the described method using TiOH as the catalyst; (B) a polyTEOS-derived resin dried under vacuum at low temperature (60 °C) or higher temperature (120 °C) for 3 h.

| Table 8. Synthesis of MQ Silicone Resins by Esterification at Different M/Q Ratios |
|-----------------------------------------------|----------------------------------|----------------|----------------|----------------|
| expt. | M/Q ratio | yield (%) | Mₙ | Mₘ | D_M |
|-------|----------|-----------|----|----|-----|
| 1     | 0.68     | 98.82     | 2387| 7682| 3.2183|
| 2     | 0.80     | 97.14     | 2338| 4051| 1.9423|
| 3     | 0.85     | 94.44     | 2205| 3710| 1.6825|
| 4     | 0.90     | 94.06     | 2229| 3596| 1.6133|
| 5     | 0.95     | 92.12     | 2081| 3113| 1.4959|
| 6     | 1.00     | 93.82     | 1855| 2634| 1.4199|

Table 9. Consistency of MQ Resin Production

| expt. | yield (%) | Mₙ | Mₘ | D_M |
|-------|-----------|----|----|-----|
| 1     | 92.5      | 3230| 6370| 1.97 |
| 2     | 94.8      | 2823| 5208| 1.85 |
| 3     | 93.7      | 3627| 7931| 2.07 |

*The standard deviation of the dispersities (n = 3) was 0.11.
solvents, acid, salts, and alcohol in wastewater. This alternative is completely greener.

Although this preparative method is still in the early stage of development, with respect to process optimization and also full molecular and property characterizations of the products, it offers many advantages over current processes. The main benefit is the narrower range of mixtures of the products, the ability of tuning the molecular weight in a programmed way, and the low SiOH content, which provides more stable products over time. In addition, the process offers significant environmental benefits and higher atom efficiency.

### CONCLUSIONS

MQ resins constitute an important class of materials used to broaden the properties and utility of silicone elastomers and gels. The use of a cascade esterification process of acetic acid with alcohols generated from tetraalkoxysilanes (and MM as the capping agent) only very slowly generates water in situ. As a consequence, MQ resins of low dispersity and of low SiOH and SiOR concentrations are produced. The $M_n$ is readily increased by gentle thermal treatment.

### EXPERIMENTAL SECTION

**Materials.** Tetraethoxysilane (tetraethyl orthosilicate, TEOS, >99%) and ethyl polysilicate (PolyTEOS) (>99%) were obtained from Guibao Technology; ferric chloride (FeCl₃) (≥97.0%) was from Sinopharm Chemical; trimethylchlorosilane (≥98.0%) was from Richjoint Chemical; trifluoromethanesulfonic acid (≥99.5%) was from Shanghai Huiquan Chemicals Co., Ltd.; acetic acid (≥99.5%) was from Richjoint Chemical; sulfuric acid (95.0–98.0%) was from Donghong Chemical; sodium carbonate anhydrous (>99.8%) and sodium sulfate anhydrous (≥99.0%) were from Tianjin Zhijuan Chemical; sulfuric acid cationic-exchange resin (0.79 mequiv/g Product Nankai 001 × 7) was from Tianjin Bohong Resin Company; and hexamethyldisiloxane (MM, >99%) and MQ Resin #803 were from Wacker. All chemicals were used as received unless otherwise stated. Deionized water was treated prepared using a reverse osmosis iron-exchange membrane (Polyamide Material, model: BW30HRLW-4040) from Dow Chemical.

**Methods.** Infrared spectra were recorded on Bruker Tensor 27 Fourier transform infrared spectrometer.

Molecular weight and polymer dispersity ($D_M$) were measured by gel permeation chromatography on Agilent 1260 GPC with an Agilent G1362RI detector and a PLgel 5 μm MIXED-D column. The column was packed with a styrene-divinylbenzene gel, and the samples were run in toluene with polystyrene (PS) as standard.

Gas chromatography was conducted on a GC 9890A from Shanghai Linghua Instrument Co., Ltd. using an SE-54 capillary column (30 m × 0.32 mm × 0.5 μm), a column temperature of 50 °C, an injector temperature of 145 °C, and an injection volume of 0.1 μL.

Elastomer samples containing MQ resins were prepared by taking the MQ resin (Table 1) in petroleum ether at a ratio of 1:3 and then mixing part A: telechelic vinyl–dimethyldisiloxane (42 parts) and platinum catalyst (0.05 parts, the MQ resin; Table 1). The solvents were removed at reduced pressure and then part B: SiH fluid (7 parts) was added and the reaction was mixed. A 2 mm thick slab was cured at 120 °C for 10 min.

Tack of MQ-filled elastomers was tested according to the Chinese standard GB/T 4852-2002 Test method for tack of pressure sensitive tapes by rolling ball using a Tack tester model: BLD-1007 Dongguan Bo Laide Equipment Co., Ltd. A slab of cured elastomer containing MQ resin (see Table 1 and details below) of dimensions 2 mm thick × 40 mm wide × 100 mm long was placed on the test bed (angled at 30°). Selected stainless steel balls of different diameters were allowed to accelerate along 100 mm of the rigid resin before contacting the elastomer film. The traveling distance from the first contact with the elastomer until the ball stopped moving was recorded.

**Synthesis of MQ Silicone Resins by Hydrolysis: PolyTEOS.** A general procedure is described for an M/Q ratio of 1:1. A mixture of polyTEOS (152.00 g, 1.0 mol), hexamethyldisiloxane (81.00 g, 0.50 mol), ethanol (15.00 g, 0.33 mol), toluene (56.4 g, 0.61 mol), and an acidic catalyst (36.5 wt % hydrochloric acid (6.33 g, 63 mmol)) was employed in a 1 L round-bottomed flask. Water (54.00 g, 3.0 mol) was slowly added dropwise with stirring over 90 min and then the mixture was heated to reflux (76 °C) for 4 h. After cooling to room temperature, the mixture was allowed to stand to obtain a silanol-rich toluene solution. Potassium hydroxide (0.26 g, 4.64 mmol) was added and the mixture was refluxed for 3 h; a small amount of 36.5 wt % hydrochloric acid was required to return the mixture to neutrality; residual ethanol and water were removed by distillation under vacuum (6.0 kPa) and dried with anhydrous sodium sulfate. After filtration, the solvent was removed from the MQ siloxane resin by vacuum distillation, leaving a white MQ siloxane resin powder (Table 2).

**Synthesis of MQ Siloxane Resins by Cascade Esterification: TEOS.** Influence of Strong Acid Catalysts on the Esterification Reaction: TEOS. A comparison was made of several potential acid catalysts for the esterification reaction starting from TEOS. The general procedure described below was followed, with the exception of the specific strong acid catalyst used (HOAc/TEOS mole ratio 4.4, M unit/Q unit mole feed ratio 0.8, catalyst amount 3.0 wt % based on TEOS; Tables 3 and 4). Reaction temperature curves (Figure 3) and molecular weight distributions of the samples by GPC were recorded (Figure 4).

The general procedure is described for the sulfuric acid catalyst. TEOS (104 g, 0.5 mol), hexamethyldisiloxane (32.4 g, mil., 0.20 mol), acetic acid (36.5 wt % hydrochloric acid (6.33 g, 63 mmol)) was employed in a 1 L round-bottomed flask. Water (54.00 g, 3.0 mol) was slowly added dropwise with stirring over 90 min and then the mixture was heated to reflux (76 °C) for 4 h. After cooling to room temperature, the mixture was allowed to stand to obtain a silanol-rich toluene solution. Potassium hydroxide (0.26 g, 4.64 mmol) was added and the mixture was refluxed for 3 h; a small amount of 36.5 wt % hydrochloric acid was required to return the mixture to neutrality; residual ethanol and water were removed by distillation under vacuum (6.0 kPa) and dried with anhydrous sodium sulfate. After filtration, the solvent was removed from the MQ siloxane resin by vacuum distillation, leaving a white MQ siloxane resin powder (Table 2).

### Table 10. Effect of MQ Resin on the Tack of an MQ-Filled Elastomer

| MQ resin wt % | this work | 803<sup>2</sup> |
|---------------|-----------|----------------|
| 0             | 10        | 20             |
| 8#            | 11        | 26             |
| 4#            | 6#        | 15             |

<sup>“Wacker #803, <sup>2</sup>Ball dimensions #4: 3.175; #8: 6.350; #15: 11.906; #26 20.638 mm.”</sup>

**Figure 8. Acid-catalyzed siloxane insertion reactions.**
0.2 mol), and acetic acid (132 g, 2.2 mol) were added to a 1 L three-neck round-bottomed flask equipped with high-speed mechanical stirring, a condensing reflux tube, and a thermometer. The mixture was warmed to 30 °C with stirring. The acidic catalyst, 98 wt % H₂SO₄ (3.18 g, 31.8 mmol), was added dropwise and the reaction mixture was stirred for 1 h without external heating. Then, the mixture was heated to 78 °C (reflux temperature for ethyl acetate) for 4 h. A Na₂CO₃ aqueous solution (12.0%, 304.72 g) was used to neutralize the mixture after allowing the mixture to cool to room temperature (with stirring); the MQ resin solution was collected by draining away the aqueous layer and then anhydrous sodium sulfate (10.07 g, 0.07 mol) was added to the organic phase to remove water. The resulting transparent, colorless solution was heated under a 6.0 kPa vacuum to remove the generated solvents by distillation and then left at 120 °C for 3 h to give the MQ resin as a solid white powder. When other catalysts were used, there was a distinct difference in the observed exotherms (Figure 3).

It can be seen (Table 3) that the efficiency of the reaction was high except for ferric chloride. The catalyst used affected the dispersity of the product. Me₃SiCl and ferric chloride led to broad dispersities, sulfuric acid and acetyl chloride led to bimodal distributions, whereas triflic acid led cleanly to a unimodal distribution of low D₅₀ (Table 3). Sulfuric acid was chosen for further studies.

**Effect of Catalyst Dosage (98% Concentrated Sulfuric Acid):**

**TEOS.** The general procedure for an M/Q ratio = 0.80, HOAc/OEt ratio = 1.1:1, 80 °C × 4 h is described. A mixture of TEOS (26.0 g, 0.125 mol), hexamethyldisiloxane (8.1 g, 0.05 mol), HOAc (33.0 mL, 0.55 mol), and 98% H₂SO₄ was added into a 250 mL round-bottomed flask. The reaction mixture was stirred at 30 °C for 60 min and then heated to 78 °C and allowed to react for 4 h. Each vessel was quenched with Na₂CO₃ aqueous solution (15.0 wt %, to pH = 7) after the reaction had cooled to room temperature. The MQ resin solution was collected by draining away the aqueous layer and then anhydrous sodium sulfate was added to the organic phase to remove water. The resulting transparent, colorless solution was heated under a 6.0 kPa vacuum to remove the generated solvents by distillation. The MQ resin solution in the organic phase was heated at 80 °C at 6.0 kPa for 3 h (Table 4).

**Effect of Silicon Starting Material on Transesterification Product Characteristics: TEOS vs PolyTEOS.** Analogous recipes were used to compare any differences in the MQ resin resins produced from TEOS or polyTEOS. As can be seen in Table 5, both polysilicate and TEOS produced similar primary resins under transesterification conditions.

**TEOS (52.00 g, 0.25 mol); MM (16.20 g, 0.1 mol); HOAc (66.00 g, 1.1 mol); H₃SO₄ (98%, 0.53 g, 5.3 mmol); 15% Na₂CO₃ (aq) (109.75 g); Na₂SO₄ (5.17 g); yield 93.2%.

PolyTEOS (37.50 g, 0.25 mol); MM (16.20 g, 0.1 mol); HOAc (33.00 g, 0.55 mol); H₃SO₄ (98%, 0.38 g, 3.8 mmol); 15% Na₂CO₃ (aq) (40.98 g); Na₂SO₄ (3.51); yield 96.5%.

**Effect of Drying Time on Product Characteristics: PolyTEOS (M/Q 0.8; HOAc/OEt 1:1:1).** PolyTEOS (225.00 g, 1.5 mol), MM (97.20 g, 0.6 mol), acetic acid (198.00 g, 3.3 mol), and sulfuric acid (3.31 g, 33.1 mmol) were used to establish whether removal of solvent played an important role in the final product structure. Eight thermal protocols were utilized, all of which involved drying under a vacuum of 6.0 kPa (Table 6). The samples were characterized by IR and GPC (Figures 5 and 7). Figure 7 demonstrates that the higher temperature process leads to materials that have, essentially completely, lost the SiOH groups, as shown by the loss of signal between 3100 and 3700 cm⁻¹ in the infrared spectrum. This is consistent both with loss of water or residual alcohols and with silanol condensation processes.

**Effect of Reaction Time on Product Characteristics: PolyTEOS.** M/Q ratio = 0.80, HOAc/OEt ratio = 1.1:1 (polyTEOS (225.00 g, 1.5 mol), MM (97.20 g, 0.6 mol), acetic acid (198.00 g, 3.3 mol), and sulfuric acid (3.29 g, 32.9 mmol)). The reactants were allowed to mix, which generated an exotherm in the case of sulfuric acid catalyst (Figure 3). After 60 min, heating was started; reflux of EtOAc occurred at 78 °C; reactions were allowed to proceed for an additional 1–5 h (t = 0 was designated as the onset of reflux). After cooling, the resulting mixture was neutralized with sodium carbonate aqueous solution (15.0 wt %, 326 mL). The MQ resin solution was collected by draining away the aqueous layer. After drying the organic phase over anhydrous sodium sulfate (51 g, 0.36 mol), the solution was filtered and solvents were removed with heating under reduced pressure (6.0 kPa) and then heated at elevated temperature. The resulting filtrate was dried at 150 °C under vacuum (6.0 kPa) to give the white powder (Table 7). The Mₜ did not substantially change over time, and there was a narrowing of the dispersity (D₅₀) over time.

**Capping Agent (MM) Residues in the Products: PolyTEOS.** GC analyses of the products were performed to establish whether residues of the reaction had been removed. As shown in Figure 6, no evidence of the capping agent (MM) or ethyl acetate could be detected in the product.

**Effect of M/Q Ratio on MQ Siloxane Resin Characteristics: PolyTEOS.** The general procedure is described for a M/Q ratio of 1:1. A mixture of polyTEOS (152.00 g, 1.0 mol), MM (81.00 g, 0.5 mol), acetic acid (144.00 g, 2.4 mol), and sulfuric acid (4.71 g, 47 mmol) was stirred for 1 h without external heating in a 1 L three-neck round-bottomed flask equipped with strong stirring, a condensing reflux tube, and a thermometer. The reaction mixture was heated at 78 °C (reflux temperature of EtOAc) for 4 h. After cooling, the resulting mixture was neutralized with sodium carbonate aqueous solution (15.0 wt %, 261.97 mL); the MQ resin solution was collected by draining away the aqueous layer. After drying the organic phase over anhydrous sodium sulfate (18.75 g, 0.13 mol), the solution was filtered and solvents were removed with heating under reduced pressure (6.0 kPa) and then heated at elevated temperature (150 °C) for 3 h to obtain the MQ siloxane resin (Table 8).

Note: polyTEOS is partly hydrolyzed TEOS that (upon drying) leads to 40 wt % SiO₂. Assuming the other 60% is ethanol, the nominal structure of the material is (HO),Si(OEt)₂ with an Mₜ of 152.

**Batch Consistency: TEOS.** Three repetitions of an identical reaction were made to examine batch consistency following the general procedure (Introduction section) described above: TEOS (6.24 g, 0.03 mol), hexamethyldisiloxane (1.65 g, 10.2 mmol), HOAc (5.26 mL, 0.092 mol), and 98% H₂SO₄ (33.9 μL, 62.4 mg, 0.64 mmol) were mixed in a 15 mL glass bottle. The solution was separated into three aliquots, in round-bottomed flasks of 4.4263, 4.4176, and 4.3240 g. Following three freeze–pump–thaw cycles to replace air with nitrogen, the reaction was stirred at 30 °C for 30 min, heated to 80 °C, and reacted for 4 h (in the same oil bath at the same time). Each vessel was quenched with Na₂CO₃ aqueous solution (20 wt %, 2.0 mL) after it cooled to room temperature. The MQ resin solution was collected by draining away the aqueous layer.
and then anhydrous sodium sulfate (10.07 g, 0.07 mol) was added to the organic phase to remove water. The resulting transparent, colorless solution was heated under a 6.0 kPa vacuum to remove the generated solvents by distillation. The MQ resin solutions in the organic phase were heated at 70 °C at 20 mmHg until a constant mass was reached. The obtained MQ resin was characterized by GPC (see Table 9).

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**Notes**
The authors declare no competing financial interest.

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