Preparation, Structure Characterization, and Thermal Performance of Phenyl-Modified MQ Silicone Resins

Xiaoqiu Xu, Chuan Wu, Baohua Zhang, Hong Dong

Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China

Correspondence to: C. Wu (E-mail: catalyst88@163.com) or H. Dong (E-mail: eyringer@163.com)

ABSTRACT: Methyl- and phenyl-modified MQ resins have been prepared by cohydrolysis and condensation-polymerization of the prepolymer of sodium silicate with $SiO_2/Na_2O = 3.33$ using the ethanol solution of hexamethyldisiloxane (MM), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (TMDVS), methyldiphenylethoxysilane (MDPES), dimethylphenylethoxysilane (DMPES), or their dimers. The influence of different end-capping agents on the composition and properties of the MQ resins has been investigated. Thermogravimetric analysis and differential scanning calorimetry results indicate that when the MQ resins are end capped with DMPES instead of MDPES, the resins were more easily purified and almost no high boiling point residuals were found in the phenyl MQ resins. The refractive indexes of the MQ resins were significantly affected by the phenyl group and their values could be adjusted by changing the amount of DMPES. The structures of the resins were characterized by ^{1}H-NMR and FT–IR spectroscopy. The M/Q ratios in the prepared MQ resins were calculated from the ^{1}H-NMR spectra or from elemental analysis or both. The M/Q values obtained agreed well with the changes of appearance and thermal stabilities of the MQ resins. The thermal stabilities of the MQ resins were greatly enhanced when DMPES was used. Phenyl-modified MQ resins were in the form of white powders due to the rigidity of the phenyl group while methyl MQ resins exhibited a range of appearances, from transparent liquids to white powders, with the reduction of M/Q values. The method developed to calculate the M/Q values is useful for the characterization of MQ resins and their derivatives. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4189–4200, 2013

INTRODUCTION

MQ type silicone resins are novel silicone materials widely used in many fields. For example, they can be used as the reinforcing materials for silicone rubbers to enhance their physical properties,[1] used as the tackifiers for silicone pressure-sensitive adhesives,[2] as well as a constituent of deforming agents.[3] In addition, MQ silicone resins play important roles in other fields such as surfactants, slow-release delivery agents, coatings, and additives.[4]

When MQ resins are used as the fillers for silicone rubbers, they can exhibit the same reinforcing effect produced by traditional fumed or precipitated silica but have little influence on the viscosity of the silicone rubbers. This advantage can significantly enhance the efficiency of the kneading process, in which the fillers are dispersed in the linear polysiloxane matrix through a robust mixing process to form a "uniform" component. The surface of the silica is covered with three kinds of silanols, namely the free (isolated) silanol, a geminal silanol, and a hydrogen-bonded silanol. Although the surface of MQ resins

inevitably contains small amounts of unreacted residual silanols, due to the steric hindrance of terminal groups, MQ resins are generally end capped with a range of terminal groups such as trimethylsiloxyl, dimethylvinylsiloxyl, and dimethylhydrogensiloxyl. Of these terminal groups, some active capping groups, such as dimethylvinylsiloxyl and dimethylhydrogensiloxyl, are more important since MQ resins can easily react with other reactive components by means of the hydrosilylation reaction. In this way, active MQ resins can be further modified or directly participate in the cross-linking reaction of the two-component liquid silicone rubber or silicone resin through the same hydrosilylation reaction. In addition to this kind of surface modification method, the structure of MQ resins will also be modified if chlorosilanes or alkoxysilanes, with two or three functionalities, are selected as the starting materials and subsequently cohydrolyze and polymerize with other components. Therefore, MQ resins can be more easily modified than fumed or precipitated silica fillers. Some derivatives of MQ resins with more sophisticated structures, such as MDQ, MTQ, MDT, or

even MDTQ, have been developed.[5–7] In these studies, much attention has been focused on the preparation of MQ derivatives terminated by dimethylvinylsiloxyl groups and their applications in reinforcing areas.[8,9] Once phenyl groups are attached to the side chain of the polysiloxane, the modified MQ silicone resins exhibit much better thermal stability, radiation resistance, and higher refractive index compared with other kinds of silicone resins.[10,11] Although phenyl group-modified silicone rubbers have been widely reported in silicone chemistry, there has been little research concerning the preparation and the structure characterization of phenyl-modified MQ type silicone resins. Kashiwagi et al.[12] prepared phenyl MQ resins by using a condensation reaction between the prepolymer of sodium silicate and end-capping agents containing the phenyl group. Another method was developed by Takanashi et al.,[13] who prepared phenyl MQ silicone resins by the hydrosilylation reaction of the presynthesized MQ silicone resins with methyl styrene. As it is difficult to remove all traces of catalyst from the reaction system, it is possible that the silicone rubber vulcanization process and the performance of the final products might be impeded by these residual materials.

In this article, phenyl-modified MQ resins, with an active dimethylvinylsiloxyl group, are prepared from the prepolymer of sodium silicate and end capped with the methyldiphenylsiloxyl or dimethylphenylsiloxyl group resulting from the hydrolysis of methyldiphenylethoxysilane (MDPES) or dimethylphenylethoxysilane (DMPES). Various factors affecting the properties of the MQ resins are investigated in detail. The MQ resins obtained are characterized by FT–IR and ^{1}H-NMR spectroscopy. A method to determine the M/Q value of the MQ resins has been developed and compared with the results derived from the thermogravimetric analysis (TGA) tests. In addition, the influence of M/Q values on the thermal performance of simple MQ resins and the phenyl group-modified MQ resins are also discussed.

EXPERIMENTAL SECTIONS

Materials

Both MM and TMDVS are industrial grade and were purchased from Zhejiang Sanmen Qianhong Industries Co. Ltd. (China). MDPES and DMPES were obtained from Aldrich Chemical Co. Inc. (USA) and used without further purification. Sodium silicate with $SiO_2/ Na_2O = 3.33$ was purchased from Hangzhou Fenghuang Chemical Co. Ltd. (China). 1, 4-dioxane, anhydrous ethanol, anhydrous calcium chloride, toluene, and hydrochloric acid were analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd. (China).

Preparation of MQ Resins

MQ resins and the phenyl group-modified MQ silicone resins are prepared by cohydrolysis and condensation polymerization reactions between the silanol prepolymers resulting from the hydrolysis of sodium silicate and the silanols generated from the hydrolysis of the various end-capping agents, as illustrated in Scheme 1(a–h). Scheme 1(a) is the hydrolysis of sodium silicate, Scheme 1(b) shows the growth of silanol prepolymers and the formation of a core of 3D Q units ($SiO_{4/2}$). Scheme 1(c–f) shows the formation of monofunctional silanols arising from the hydrolysis of the corresponding monomers or disiloxanes.

The formation of methyldiphenylsiloxyl- or dimethylphenylsiloxyl-terminated MQ silicone resins is illustrated in Scheme 1(g) and 1(h). In these stages, the prepolymers are end capped with monofunctional silanols and the core of the 3D Q units is eventually surrounded by a shell of M units.

A typical process for preparation of MQ resins or the phenyl group-modified MQ resins is as follows. An appropriate amount of concentrated hydrochloric acid and deionized water is added to a three-necked flask and the temperature held constant at 35°C. A mixture of sodium silicate and water is quickly added to the flask with vigorous agitation for 1 min. To avoid gelation, the reaction temperature must be held below 40°C. Subsequently, an ethanol solution of mixtures of the required amounts of MM, TMDVS, MDPES, or DMPES or their dimers, such as TMDPS and DMTPS, is added to the flask and allowed to react for 30 min. Appropriate amounts of toluene or MM extractant are then added to the flask and the temperature is raised to 70°C and held for 2 h. After cooling to room temperature, the mixtures are washed repeatedly with deionized water to neutral pH. The organic phase is further collected and dehydrated completely using anhydrous calcium chloride. After filtration and removing toluene or MM by evaporation, the MQ silicone resins were obtained. Following these procedures, a series of samples with different structures and properties were prepared by changing the composition of the raw materials. Detailed experimental conditions are listed in Table I.

Measurements

The structure of the synthesized MQ resins was verified by ^{1}H-NMR and FT–IR spectroscopy. The relative molecular weights and the distribution of molecular weights of the MQ resins were determined by gel-permeation chromatography (GPC). The refractive index of the MQ silicone resins were measured using an Abbe refractometer. The composition and structure of the residuals in the MQ silicone resins were analyzed by gas chromatography–mass spectroscopy (GC–MS) and single-crystal X-ray diffraction (SXD), respectively. The influence of the residuals on the thermal stability of the MQ silicone resins was determined using differential scanning calorimetry (DSC). The heat resistance of the MQ resins was characterized by TGA. The molar contents of the phenyl and vinyl groups in the MQ resins were calculated from the ^{1}H-NMR spectra using an additional, known amount of 1, 4-dioxane as the reference (internal standard).

^{1}H-NMR spectra of the MQ silicone resins were obtained with an AVANCE AV400 MHz spectrometer (Bruker, Germany). The relative molecular weights and the distribution of molecular weights were determined by GPC (Waters 1525, Germany) with toluene as the eluent and polystyrene samples as standards. The concentrations of small molecules retained in the MQ silicone resins were determined by a GC–MS TRANCE DSQ (Thermo Finnigan, USA) equipped with an Agilent HP-5 chromatographic column (30 m × 0.25 mm × 0.25 μm). Their structures were determined using an Apex Duo Single-Crystal X-ray Diffractometer (Bruker, Germany) at 296.2 K using Mo Kα radiation ($\lambda = 0.71073$ Å). TGA as carried out using a TG209C

Scheme 1. Schematic diagram for synthesis of MQ resins and the phenyl group-modified MQ silicone resins.

apparatus (Germany), in which samples are heated from ambient temperature to 800°C at a rate of 10°C/min^{-1} in a dynamic nitrogen atmosphere. The DSC measurements were conducted using a Q100 differential scanning calorimeter (TA instruments). The refractive index of the MQ silicone resins was measured using a 2WA-J Abbe refractometer (Shanghai CSOIF Co., Ltd. China).

Determination of M/Q Value

As one of the most important structure parameters, the value of M/Q, needs to be accurately calculated since the configurations, appearance and physical properties (such as density, transmittance, viscosity, softening point, and tackability), and the hydrophilic and lipophilic properties of the silicone resins change with M/Q value. In addition, the physical properties of

the composites reinforced by MQ resin fillers are greatly affected by the structure of the MQ resins. Various attempts have been described in the literature to accurately determine the M/Q ratio in MQ type silicone resins.[14] However, the results are still unsatisfactory. In TGA experiments, Wei[15] completely calcinated the MQ resin to constant weight, and then believed that only inorganic components composed of Si—O—Si remained. He calculated M/Q values from these results and provided a method to characterize the structure of the MQ silicone resins. It is usually believed that during the thermal decomposition process of organosilicones in an inert atmosphere, the organic groups decompose first.[16] Subsequently, the unpaired electrons of oxygen atoms in the polymer molecule bonded to the unoccupied 3d orbital of adjacent silicon atoms. Through the breakage and rearrangement of the

Table I. Preparation of MQ and Phenyl-Modified MQ Resins

Entry	Sodium silicate solution		HCl solution		End-capping agents				Extractant (g^{-1})	Product (g^{-1})
	Sodium silicate (g^{-1})	H_2O (g^{-1})	HCl (g^{-1})	H_2O (g^{-1})	MM (g^{-1})	DMPES (g^{-1})	TMDVS (g^{-1})	EtOH (g^{-1})		
0	42.8	98.1	105.0	168.8	12.7	90.0[a]	3.0	210.2	210[d]	42.3
1a	71.8	82.0	87.5	140.0	87.4	0	0	175.0	175.0[c]	26.7
1b	71.2	81.8	87.5	140.0	79.4	0	10.0	175.0	175.0[c]	28.4
1c	213.5	245.0	262.5	420.0	210.5	0	60.0	525.0	525.0[c]	105
1d	71.4	82.5	87.5	40.0	67.2	0	33.0	175.0	175.0[c]	30.2
1e	10.7	12.3	13.1	21.0	7.2	6.0[b]	3.0	26.3	26.3[c]	3.6
1f	10.7	12.3	13.1	21.0	7.9	6.0	1.8	27.0	26.3[c]	3.4
1g	85.4	98.0	105.0	168.0	63.8	24.3	4.8	214.1	210.0[c]	33.8
1h	10.4	12.1	14.0	21.4	0	26.9	11.8	26.1	26.3[b]	4.2
2a	43.0	57.7	45.0	80.0	130.0	0	0	95.0	90.0[d]	14.5
2b	43.1	58.1	45.0	80.0	90.0	0	0	40.3	90.0[d]	13.8
2c	18.3	42.0	45.0	120.0	129.0	0	0	90.0	90.0[d]	7.3
2d	12.2	28.0	30.0	80.0	105.1	0	0	60.0	60.0[d]	5.2
2e	6.1	14.0	15.0	40.0	13.4	0	0	30.0	30.0[d]	2.1
2f	6.1	14.0	15.0	40.0	43.0	0	0	30.0	30.0[d]	2.0
3a	10.4	12.1	14.0	21.9	10.0	5.6	3.0	26.1	26.3[c]	3.4
3b	85.9	98.4	105.0	168.0	67.8	48.1	24.3	214.1	210.0[c]	35.2
3c	10.7	12.4	13.1	21.0	0	14.8	3.0	26.1	26.3[c]	4.0
3d	10.7	12.3	13.2	21.6	9.6	23.0	3.0	27.0	26.3[c]	3.8
3e	10.6	12.2	13.1	21.5	3.5	26.5	3.0	26.1	26.3[c]	3.8

[a]The end-capping agent is MDPES, [b]The extractant is MM, [c]The extractant is toluene, [d]The end-capping agent is TMDPS.

Si—O—Si bond or via other mechanisms such as pyrolysis and cyclization, a number of volatile organic compounds were produced, which evaporated at higher temperature.[17,18] Under these circumstances, the content of silicon and oxygen in the weight residuals decreases and the values of the calculated M/Q ratio are quite questionable. Consequently, the M/Q value cannot be accurately determined from TGA results. Another attempt was made by Yin,[19] who estimated the M/Q value in methyl MQ resin directly by integrating the ^{29}Si-NMR spectra of the MQ resin without subtracting the interference signal that arises from the NMR tubes. However, this method is also questionable. To quantitatively analyze the structure of products from ^{29}Si NMR spectra, the interference signal from the glass sample tube and the probe must be removed, either by a modified "Hahn spin echo" sequence[20] or by adding the paramagnetic relaxation agent $Cr(acac)_3$ to decrease relaxation times sufficiently.[21] In addition to these two attempts, the M/Q value has been calculated directly from the initial feed ratio of each component.[22] Clearly, the value of the M/Q ratio determined by this method is quite unreasonable because not all the chemicals will be completely consumed in the hydrolysis and condensation-polymerization reactions.

In this work, we describe an accurate expression for the M/Q value based on the total content of carbon and hydrogen in the resin.

$Me_3SiO_{1/2}$-Terminated MQ Resins. $Me_3SiO_{1/2}$-terminated MQ resins have the following structure.

$$[Me_3SiO_{1/2}]_n[SiO_{4/2}]_m \quad (1)$$
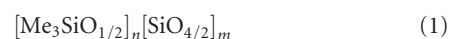
The total mass percentage of carbon and hydrogen contained in this MQ resin, represented by the symbol G, is calculated using eq. (2).

$$G = 45n/(81n + 60m) \quad (2)$$

where $45n$, $81n$, and $60m$ stand for the total mass weight of all the methyl groups, the total mass weight of the end-capping unit M and the total mass weight of all the Q segments in the resin, respectively.

Equation (3) can be derived from eq. (2) as follows:

$$G = \frac{45}{81 + 60m/n} \quad (3)$$

where m/n represents the molar ratio between the Q and M segments, whose reciprocal value is the M/Q value.

The total mass percentage G of both carbon and hydrogen can be determined either from elemental analysis or from the ^{1}H-NMR spectrum. To quantitatively determine the absolute content of all the methyl groups from the ^{1}H-NMR spectra, a
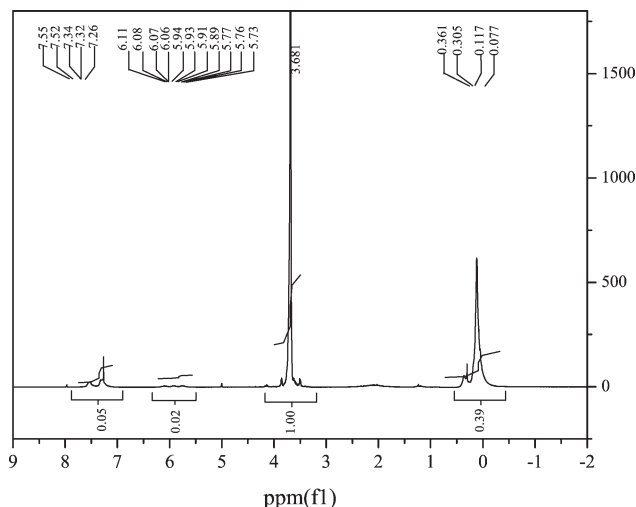
Figure 1. ^{1}H-NMR spectrum of $Me_2PhSiO_{1/2}$-terminated MQ resin (Entry 3c). The sample is consisted of 0.0145 g phenyl-modified MQ resin (Entry 3c) and 0.0219 g 1,4-dioxane with $\delta = 3.681$ ppm.

certain amount of 1, 4-dioxane is added to the CDCl$_3$ solution of a known amount of MQ resin as an internal standard. The chemical shifts of protons attributed to the methyl groups in the MQ resin and methylene (—CH$_2$—) groups in the internal standard 1, 4-dioxane are easily determined. Therefore, the content of methyl groups in the sample can be quantitatively determined using the relationship between the integrated area and the number of protons,[23] and thus the M/Q value of the MQ resin can be computed.

$Me_2PhSiO_{1/2}$-Terminated MQ Resins. Like $Me_3SiO_{1/2}$-terminated MQ resins, the molecular structure of phenyl MQ resins prepared can be expressed as follows.

$$[Me_3SiO_{1/2}]_a[Me_2ViSiO_{1/2}]_b[Me_2PhSiO_{1/2}]_c[SiO_{4/2}]_m \quad (4)$$

Since the chemical shifts of the methyl protons in the $Me_3SiO_{1/2}$, $Me_2ViSiO_{1/2}$, and $Me_2PhSiO_{1/2}$ segments overlap each other in the region 0 to about 0.36 ppm in the ^{1}H-NMR spectra (Figure 1), clear identification of these functional groups is very difficult. However, the chemical shifts of the phenyl protons in the $Me_2PhSiO_{1/2}$ segment and vinyl protons in the $Me_2ViSiO_{1/2}$ segment can be clearly resolved. The former is located in the range 7.24 to 7.55 ppm and the latter at about 6.0 ppm. Therefore, the phenyl and vinyl contents can be determined by using the method described in "$Me_3SiO_{1/2}$-Terminated MQ Resins" section. The total content of all the methyl groups in the phenyl-modified MQ resins can also be calculated by integrating the peak area of all the protons in the range 0 to 0.36 ppm. When ignoring the influence of Si—OH and other kinds of residuals on the value of M/Q, the methyl content in the $Me_3SiO_{1/2}$ segment can be calculated by subtracting the methyl contents in both $Me_2ViSiO_{1/2}$- and $Me_2PhSiO_{1/2}$ segments from the total content calculated previously. By determining the stoichiometric ratios between the methyl, phenyl, and vinyl groups in the $Me_2ViSiO_{1/2}$ or $Me_2PhSiO_{1/2}$ segment, the methyl content in both segments

can be determined. Therefore, the values of a, b, c in the molecular structure of the phenyl MQ resin (eq. (4)) can be determined and thus the mass of all the M segments can also be calculated. The mass of the Q segment is calculated by subtracting the mass of all the M segments from the sample weight and, finally, the value of m can be determined. Therefore, the M/Q value in the phenyl MQ resin can be expressed by eq. (5).

$$M/Q = \frac{a+b+c}{m} \quad (5)$$

RESULTS AND DISCUSSION

Preparation of Phenyl-Modified MQ Resins
$MePh_2SiO_{1/2}$-Terminated MQ Resins. The methyldiphenylsiloxyl group has two phenyl groups and the refractive index of MQ resins is greatly influenced by the content of the phenyl group incorporated in their molecules. First, an MQ resin modified by a phenyl group is prepared using a mixture of MM, MDPES, and TMDVS as the end-capping agents (Table I, Entry 0) and characterized by DSC and TGA to provide primary evaluation of performance. The DSC curve of this sample in Figure 2 clearly shows a sharp endothermic peak between 49°C and 50°C. The softening temperature of MQ silicone resins is often far higher than this temperature, which implies that some high-boiling residues might be retained in the MQ resin. To identify the impurities and determine how these impurities are generated, a sample of $MePh_2SiO_{1/2}$-terminated MQ silicone resin was analyzed using a GC–MS. An obvious peak was found in the GC spectrum with a retention time of 18.79 min [Figure 3(a)]. The corresponding mass spectrum, shown in Figure 3(b), indicates m/z values 410(M$^+$, 13.9), 396(32.9), 318(29.0), 317(100), 195 (74.3), 151(72.7). To further determine the structure of this impurity, another control experiment was carried out in which an ethanol solution of MDPES was added to a mixture of concentrated hydrochloric acid and deionized water. The reaction was then allowed to proceed as described in "Preparation of MQ Resins" section. The solid obtained was collected by filtration and purified by
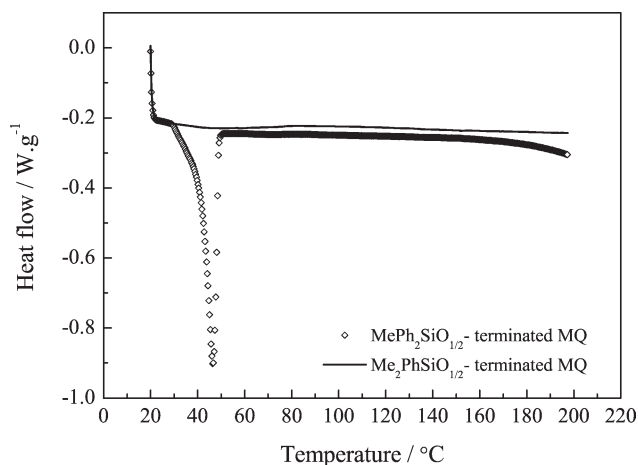

Figure 2. The DSC curve of $MePh_2SiO_{1/2}$- and $Me_2PhSiO_{1/2}$-terminated MQ resin (Entry 0 versus 3c).
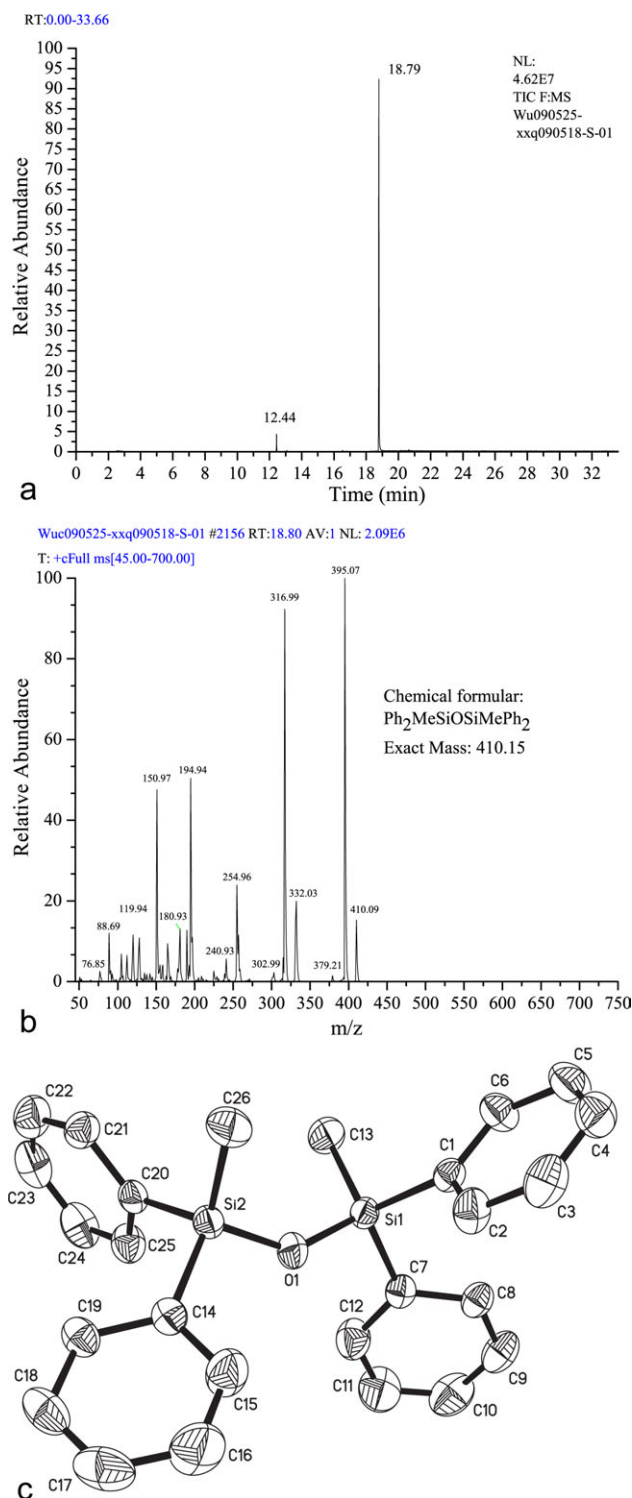
Figure 3. (**a**) GC spectrum of methyldiphenylsiloxyl-terminated MQ resin (Entry 0). (**b**) Mass spectrum of methyldiphenylsiloxyl-terminated MQ resin (Entry 0). (**c**) The single crystal structure of 1, 3-dimethyl-1, 1, 3, 3-tetraphenyldisiloxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recrystallization with dehydrated ethanol. The solid sample was then dissolved again in dehydrated ethanol and single crystals grown slowly at room temperature. After 2 weeks, some needle-

shaped crystals were collected and studied by SXD. A 3D image of the measured single crystal is presented in Figure 3(c) and shows that the impurity retained in the $MePh_2SiO_{1/2}$-terminated MQ resins is 1, 3-dimethyl-1, 1, 3, 3-tetraphenyldisiloxane (DMTPDS). The melting point of this compound is about $50°C$,[24] which is in good agreement with the sharp endothermic peak revealed by the DSC curve.

The formation of this DMTPDS impurity might be related to the self-condensation of methyldiphenylsilanol molecules, as illustrated in Scheme 2. During the hydrolysis of MDPES performed under acid conditions, the methyldiphenylsilanols generated not only react and condense with the Si—OH of the prepolymer of sodium silicate, but can also self-condense to form DMTPDS. The normal boiling point of this impurity is very high ($418°C/740–760$ mmHg)[24] and it is difficult to remove it from the MQ product in subsequent operations. Therefore, a large amount of DMTPDS accumulates in this stage. As well as DMTPDS, other impurities, such as $MePh_2SiO-SiMe_3$, $MePh_2SiOSiViMe_2$, and $Me_3SiOSiViMe_2$ are also detected by GC–MS. The possible mechanisms for their formation might be related to reciprocal condensation reactions taking place between different end-capping agents. Obviously, the reaction mechanisms involved in the preparation of the MQ silicone resins are far more complicated and their properties can be affected by a number of factors.

In Figure 4 and Table II, the TGA curve of $MePh_2SiO_{1/2}$-terminated MQ resin indicates that it exhibits rather poor heat resistance, due to the influence of the remnants. The temperatures for the 5.0% (T_5), 10.0% (T_{10}), and 15.0% (T_{15}) weight loss are 224.6, 246.0, and 258.1°C, respectively, and the weight remaining at 800°C (also called the ceramic yield) is only 34.4%.

$Me_2PhSiO_{1/2}$-Terminated MQ Resins. Since high boiling point residuals, such as DMTPDS, are difficult to remove by any of the known methods, such as vacuum distillation, column separation, and extraction separation, and such residuals greatly affect the performances of phenyl-modified MQ resins, MDPES, the source of DMTPDS, needs to be replaced by other lower boiling point, or more easily removed end-capping agents. Therefore, DMPES or its dimer, TMDPDS, was used as the end-capping agent to give a series of phenyl group-modified MQ silicone resins, with different phenyl content, as shown in Table I. Entries 1e–1h and 3a–3e were prepared using the same procedure described above. Under these circumstances, although some byproducts, such as $Me_3SiOSiViMe_2$ and $Me_2PhSiOSiPhMe_2$, are still generated through reciprocal condensations between each kind of end-capping agents, these impurities can be completely removed, since they have low boiling points relative to the impurities obtained using MDPES. For example, for DMPES, the most difficult volatile impurity is TMDPDS. Because the saturated temperature of this compound is 292°C, at pressures ranging from 740 to 750 mmHg,[24] all the impurities can be completely removed by high vacuum distillation at elevated temperatures. Consequently, the influence of the impurities on the performance of MQ silicone resins can be greatly suppressed.

The TGA data for the $Me_2PhSiO_{1/2}$-terminated MQ resin are presented in Figure 4 and Table II, showing clearly its heat-
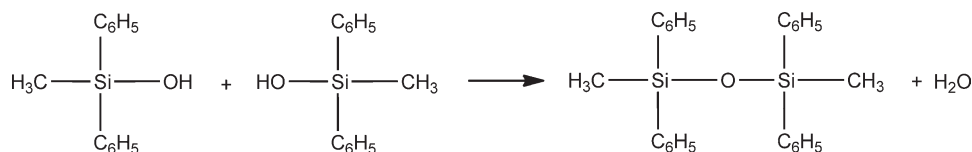
Scheme 2. Self-condensation of methyldiphenylsilanol.

resistant properties. Values of T_5, T_{10}, and T_{15} for this resin are 401.0, 478.9, and 513.1°C, respectively, and the ceramic yield at 800°C is as high as 72.8%. Comparing this with the TGA data for methyl phenyl silicone resin, reported by Wu and his colleagues,[25] the ceramic yield at 800°C for the $Me_2PhSiO_{1/2}$-terminated MQ resin is close to that of the methyl phenyl silicone resin. This comparison also confirms that almost no impurities are contained in the phenyl-modified MQ resins.

The DSC curve of the $Me_2PhSiO_{1/2}$-terminated MQ resin (Table I, Entry 3c) is also plotted in Figure 2 and compared with that of the $MePh_2SiO_{1/2}$-terminated MQ resin (Table I, Entry 0). No obvious endothermic peak can be observed when the temperatures are below 200°C, which indicates that no small molecular remnants can be detected in the MQ resins and the influence of impurities on the properties of the phenyl-modified MQ silicone resins can be neglected.

A typical FT–IR spectrum for the $Me_2PhSiO_{1/2}$-terminated MQ silicone resin sample (Table V, Entry 3c) is presented in Figure 5. The peak at 3433 cm^{-1} is the absorption of Si–OH, 3071 cm^{-1} is the C–H stretching vibration absorption in the phenyl group, 2962 cm^{-1} is the C–H absorption in the methyl group, 1428 and 1120 cm^{-1} are stretching vibrations of the benzene ring and 1599 cm^{-1} is the C=C stretching vibration in the vinyl group. The peak at 1085 cm^{-1} is the typical Si–O–Si stretching vibration and 1256 and 830 cm^{-1} are characteristic absorption peaks for the $Me_3SiO_{1/2}$ segment in the MQ resin. The FT–IR analysis therefore verifies the structure of the phenyl-modified MQ resins.

Refractive Index
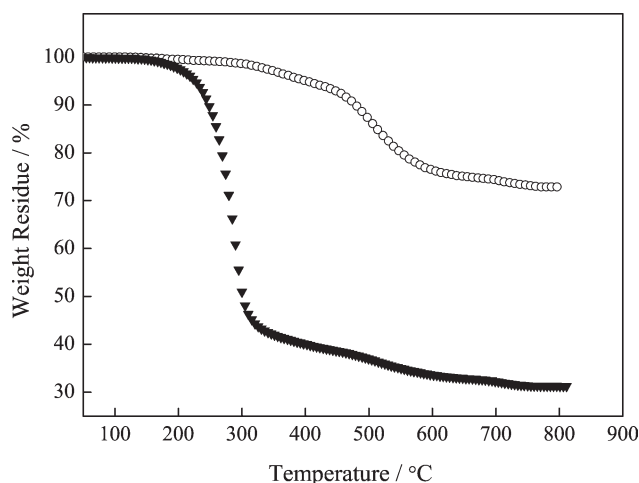
According to the Lorentz–Lorentz equation,[26] the specific refraction of a polymer, which is independent of temperature and pressure, is defined as:

$$r_D = \frac{1}{\rho} \times \frac{n^2 - 1}{n^2 + 2} \qquad (6)$$

where n is the refractive index and ρ is the density of the polymer.

The MQ silicone resin is a kind of cage-like oligosiloxane with a core-shell structure. The core is composed of silica aggregates, while its shell consists of every kind of terminal siloxy group. For polymers that have such a core-shell structure, the specific refraction is given by

$$r_D = \phi_1 r_{D1} + \phi_2 r_{D2} \qquad (7)$$

where ϕ_1 and ϕ_2 are the volume fractions of the core and shell component, respectively, r_{D1} and r_{D2} are the specific refractions of each component.

The molar refraction R is defined as the product of the specific refraction and the molecular weight.

$$R = M \times r_D \qquad (8)$$

The refractive indexes of methyl MQ and phenyl-modified MQ silicone resins are presented in Table III. When the phenyl group is absent from the MQ resins, the refractive index of the resins increases slightly with the vinyl content (Table III, Entries 1a to 1d), which indicates that the vinyl group has little influence on the refractive index of MQ resins. Since the molar refraction is a more or less additive property of the groups or elements comprising the compound, and values of the molar refraction of the methyl and vinyl groups are 5.718 and 5.033,[27] respectively, the values for MQ resins will not be significantly affected by incorporation of the vinyl group. Nevertheless, the vinyl group is still indispensable, since vinyl-modified MQ resins can chemically bond with the Si—H bond contained in the

Figure 4. TGA curve of $MePh_2SiO_{1/2}$- and $Me_2PhSiO_{1/2}$-terminated MQ resin. (○), Entry 3c, $Me_2PhSiO_{1/2}$- terminated MQ resin; (▼), Entry 0, $MePh_2SiO_{1/2}$-terminated MQ resin.

Table II. TGA in Nitrogen for Silicone Resin

Silicone resin	T_5 (°C)	T_{10} (°C)	T_{15} (°C)	Residual weight (%)
0[a]	224.6	246.0	258.1	34.4
3c[b]	401.0	478.9	513.1	72.8
c[c]	424.5	503.4	552.1	74.4

[a](0) $MePh_2SiO_{1/2}$- terminated MQ resin, [b](3c) $Me_2PhSiO_{1/2}$- terminated MQ resin, [c](c) methylphenylsilicone resin.[25]
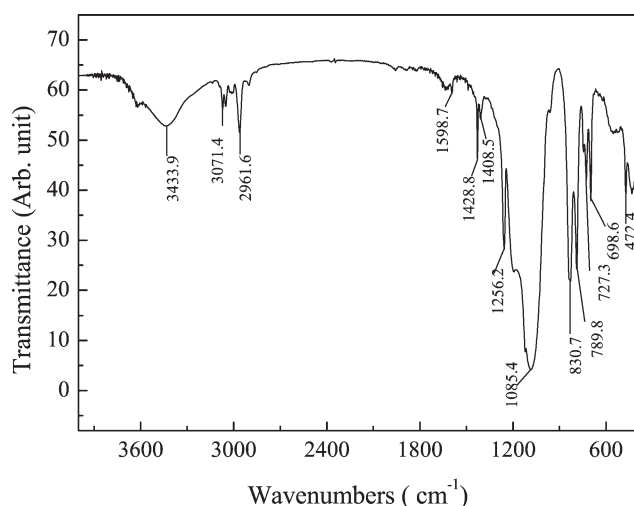
Figure 5. FT–IR spectrum of $Me_2PhSiO_{1/2}$- terminated MQ resin (Entry 3c).

cross-linking agent by means of the hydrosilylation reaction. When MQ resins are used as reinforcing fillers in a polysiloxane matrix, the physical properties of the prepared composites are greatly affected by the number of vinyl groups in the MQ structure, since the cross-linking density of such composites is closely related to this value.

By comparing the results for entries 1e to 1h, shown in Table III, it can be seen that the refractive index of the phenyl MQ silicone resins increases significantly with phenyl content, a similar result to that reported by Graham et al.[28] They considered the high polarizability of the phenyl group (p-bonding electrons) as the probable reason for this increase. In fact, the molar refraction of the phenyl group is as high as 25.463, ranking second among all the known atomic and group molar refractions and only inferior to that of the naphthyl group.[27] Therefore, according to the Lorentz–Lorentz equation, the refractive index of phenyl-modified MQ resins increases with the volume fraction of the phenyl group introduced in the shell

Table III. Properties of MQ and Phenyl-Modified MQ Resins

Entry	Vinyl content (wt %)	Phenyl content (wt %)	n_D^{25}	M_n (g mol⁻¹)	MWD
1a	0	0	1.4231	2.12×10^3	1.41
1b	0.92	0	1.4243	2.08×10^3	1.52
1c	1.89	0	1.4255	2.11×10^3	1.45
1d	5.67	0	1.4307	2.17×10^3	1.48
1e	3.24	4.16	1.4397	1.79×10^3	2.65
1f	1.65	13.57	1.4529	2.89×10^3	2.10
1g	0.86	23.91	1.4839	4.99×10^3	1.95
1h	3.01	29.95	1.4990	7.12×10^3	2.13

The vinyl and phenyl content in MQ resin were determined from ^{1}H-NMR spectrum by internal standard method.
The refractive index n_D^{25} was determined by extrapolation method from different concentrations of MQ resin in toluene solution.

structure of the resins. In the present study, when the mass fraction of the phenyl group is 29.95%, the refractive index of the MQ resins reaches 1.4990 (Table III, Entry 1h).

As discussed above, the introduction of the phenyl group helps to increase the refractive index of a compound or polymer, which is crucial to the design and preparation of high refractive index encapsulant materials, because the light extraction efficiency of high power light emitting diode (LED) is greatly affected by the difference in refractive index between the chip and the encapsulants. With any increase in the refractive index of the encapsulants, the difference in refractive index between the chip and the encapsulants decreases. In these circumstances, the critical angle for total internal reflection decreases and the light extraction efficiency of the LED devices is improved.

Relative Molecular Weight and Molecular Weight Distribution
The influence of various kinds of end-capping agents on the molecular structure of MQ resins is listed in Table III. It appears that if no phenyl group is introduced, the relative molecular weights and molecular weight distribution (MWD) values for the MQ silicone resins change little with vinyl contents (Table III, Entries 1a to 1d). These samples have almost the same M_n values (about 2.12×10^3 g.mol⁻¹) and MWD values (about 1.45). Once the phenyl group is introduced (Table III, Entries 1e to 1h) in the form of the $Me_2PhSiO_{1/2}$-terminal group, the relative molecular weights and MWD values increase with phenyl content. For instance, when the mass fraction of the phenyl group increases from 4.16% to 29.95%, the relative molecular weights increase from 1.79×10^3 to 7.12×10^3 g.mol⁻¹, together with an increase of MWD value of up to about 2.0. These results indicate that the degree of end-capping reactions is greatly affected by the kind and the amount of monofunctional species that serve as the terminal groups.

In the second stage of the preparation of MQ resins, the two adjacent Si–OH groups belonging to either the same or different kinds of silanol prepolymers condense with each other, catalyzed by HCl. As illustrated in Scheme 1(b), the chain growth reaction of the MQ resin is mainly promoted by the self-condensation of silanol prepolymers stemming from the hydrolysis of sodium silicate. After the chain growth, the end-capping reaction occurs between the residual silanols of the SiO_2 core and the monofunctional silanols arising from various kinds of end-capping agents. In fact, there is more than one residual silanol attached to each silicon atom of the outermost layer of the SiO_2 core. The condensation and polymerization reactions between these residual silanols continue until they are completely consumed by the end-capping reactions, which lead to a further increase in the molecular weight of the MQ resins. By comparison with the $Me_3SiO_{1/2}$- and $Me_2ViSiO_{1/2}$-group, the $Me_2PhSiO_{1/2}$-group exhibits greater steric hindrance, due to the bulky phenyl group, which impedes the condensation reaction between the $Me_2PhSiO_{1/2}$-group and the silanol prepolymers. Under these circumstances, the silanol prepolymers are unlikely to be promptly and completely terminated by $Me_2PhSiO_{1/2}$- or other terminal groups. Therefore, they can continue to react and condense with each other to form the next generation of SiO_2 core prepolymers, resulting in MQ resins with higher

Table IV. M/Q Value of Methyl MQ Resins and their Thermal Performances

Entry	G%[a]	M/Q[b]	G%[c]	M/Q[d]	Appearances	T_5[e] (°C)	T_{10}[f] (°C)	T_{15}[g] (°C)	MRDT[h] (°C)	MRD[i] (K^{-1})	Residual weight (%)
2a	33.82	1.15	33.05	1.09	Transparent liquid	162.8	204.5	228.5	266.7	0.446	12.50
2b	31.54	0.97	31.18	0.95	Transparent semisolid	212.2	236.5	252.8	313.4	0.422	22.77
2c	30.48	0.89	30.54	0.90	Transparent solid; melt while heating	186.8	227.7	265.6	337.6	0.310	36.95
2d	28.8	0.80	29.76	0.85	White powders	275.1	298.5	324.7	346.3	0.279	48.60
2e	28.78	0.80	28.89	0.81	White powders	292.1	330.9	356.5	402.6	0.275	49.57
2f	28.34	0.72	27.32	0.76	White powders	276.0	319.3	351.9	422.4	0.145	50.62

[a]This value was obtained from element analysis, [b]M/Q value calculated from element analysis, [c]This value was obtained from NMR spectrum, [d]M/Q value calculated from NMR spectrum, [e]Temperature for 5% weight loss, [f]Temperature for 10% weight loss, [g]Temperature for 15% weight loss, [h]The temperature for the maximum rate of decomposition, [i]Maximum rate of decomposition.

molecular weight. On the other hand, there are some unreacted silanols in MQ species that have already been incorporated with different amounts of Me$_2$PhSiO$_{1/2}$-groups and these silanols can take part in the further condensation polymerization reactions. However, their reactivities are greatly affected by the steric effect of the bulky phenyl group. The more phenyl groups are introduced into the MQ resins, the slower the reactivity becomes. Therefore, the difference in the reactivity of different phenyl-modified MQ prepolymers leads to a broader distribution of molecular weight in the phenyl-modified MQ resins. This effect becomes more significant with increasing phenyl content.

The Influence of M/Q Value on Properties of Methyl MQ Resins

Appearance. Six kinds of MQ resins, with different M/Q values, were prepared by changing the feeding ratio between the end-capping agents and sodium silicate. Each of the six samples was subsequently analyzed by elemental analysis and ^{1}H-NMR spectroscopy to determine the M/Q values using eq. (3). The appearance and the calculated M/Q values are listed in Table IV.

It can be seen from Table IV that the appearance of the MQ resins changes significantly with the variation in M/Q values. Although the M/Q values calculated by these two methods are not completely equal, both of them exhibit the same trends since both decrease simultaneously with the decrease in total content of carbon and hydrogen. For example, when the M/Q values computed by elemental analysis decrease from the 1.15 to 0.72, the M/Q values computed from the NMR spectra data exhibit the same trend, decreasing from 1.09 to 0.76. Meanwhile, the appearance of the MQ resins changes from transparent liquid to transparent semisolid (Table IV, Entries 2a to 2c) to white powders for M/Q values lower than 0.89 (Table IV, Entries 2d to 2f). Clearly, the trends in M/Q values determined by these two methods are in good agreement with the morphological changes in the MQ resins, and the results also match well with those reported in the literature.[29]

Thermal Performance. To investigate the influence of the M/Q value on the thermal performance of MQ silicone resins, the TGA curves of the six MQ resins were measured in an inert atmosphere and are presented in Figure 6. Values of T_5, T_{10}, and T_{15}, the temperature of the maximum rate of decomposi-

tion (MRDT), the maximum rate of decomposition (MRD), and the ceramic yield at 800°C were calculated from the TGA or DTG curves. These are listed in Table IV and shown graphically in Figure 7.

Clearly, the values of T_5, T_{10}, and T_{15} for the six methyl MQ resins generally increase with the decrease in M/Q values since the moieties of the organic groups in the silicone resins decrease at the same time. Some minor inconsistencies appear in the overall trend listed in Table IV and may be related to impurities such as the residual silanols and adsorbed water contained in the sample. As the TGA temperature increases, these silanols react and condense with each other. When the TGA temperature further increases, the generated or adsorbed water or both evaporate is released in the form of volatile components. With increase of temperature, the influence of these impurities gradually diminishes. As shown in Figure 7, the values of MRDT and the ceramic yield at 800°C increase with the decrease in M/Q values and meanwhile, the values of MRD at MRDT decrease with the decrease in M/Q values. This indicates that the thermal decomposition rate of the methyl MQ silicone resins slows down with the reduction of the size of the organic group
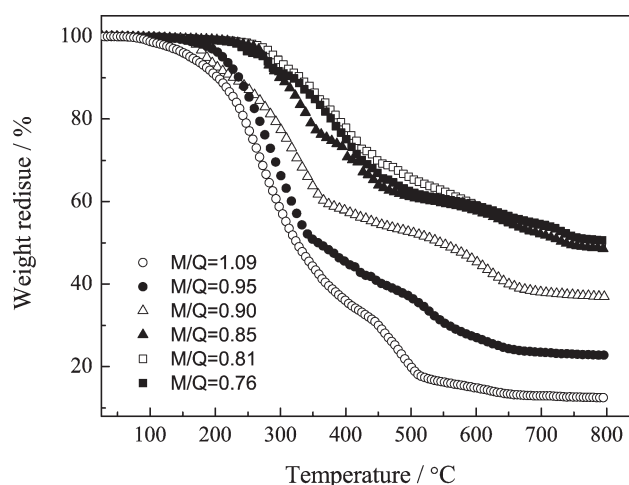

Figure 6. TGA curve of Me$_3$SiO$_{1/2}$- terminated MQ resin with different M/Q ratios. (■), M/Q = 0.76; (□), M/Q = 0.81; (▲), M/Q = 0.85; (△), M/Q = 0.90; (●), M/Q = 0.95; (○), M/Q = 1.09.
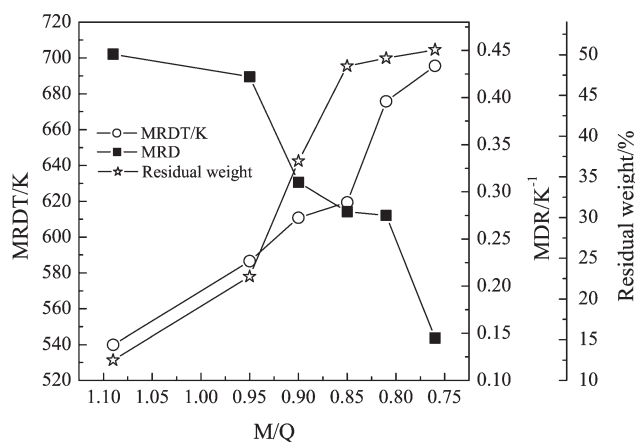
Figure 7. The influence of M/Q ratio on MRDT, MRD and residual weight for $Me_3SiO_{1/2}$-terminated MQ silicone resins. (○)MRDT; (■) MRD; (☆) residual weight. (M/Q values are determined from ^{1}H-NMR).

moiety. In fact, MQ resins prepared in the experimental conditions shown in "Preparation of MQ Resins" section are not crosslinked at all, which can be verified by the solubility test, where all the MQ resins can be completely dissolved in toluene to form clear solutions. As discussed above, some silanols can exist quite stably in MQ resins even when more severe experimental conditions are adopted. Therefore, in addition to the degradation reaction of MQ resins taking place in the TGA test at elevated temperatures, a cross-linking reaction also occurs at the same time. With the decrease in M/Q ratio, there is a decrease in the amount of the end-capping groups attached to the surface of the MQ resins, so more and more unterminated silanols stay in the system. With increase of temperatures, these active silanols react and condense with each other, which lead to the crosslinking of the MQ resins. The crosslinking density of the resins is highly dependent on the amount of residual silanols. As reported previously,[30–33] the thermal stability of polysiloxane increases with the increase in the crosslinking density. Therefore, with the increase in the amount of Q ($SiO_{4/2}$) segment, an improvement in the thermal stability of MQ resins is obtained.

In the present study, when the M/Q value decreases from 1.09 to 0.76, the MRDT values increase from 266.7°C to 422.4°C, together with an increase of ceramic yield at 800°C from 12.50% to 50.62% and a decrease of MRD value from 0.446 to 0.145

Figure 8. TGA curve of $Me_2PhSiO_{1/2}$-terminated MQ resin with different M/Q ratios. (★), M/Q = 0.78; (◇), M/Q = 0.85; (□), M/Q = 0.89; (○), M/Q = 1.07; (▲), M/Q = 1.13.

K^{-1}. These experimental data prove that the M/Q values determined by these two methods are a good indication of changes in the thermal stabilities of MQ resins.

The Influence of M/Q Value on Properties of Phenyl-Modified MQ Resins

Appearance. To investigate the influence of the M/Q value on the structure and properties of MQ resins, five kinds of Me_2Ph-$SiO_{1/2}$-terminated MQ resins with different phenyl content were prepared by alternating the amount of DMPES in the mixture of end-capping agents while holding the ratio of M to Q in feedstock at a constant value of about 4.15 (Table I, Entries 3a to 3e). The M/Q values of the obtained phenyl MQ silicone resins were calculated as described above and the results are listed in Table V, together with the phenyl contents calculated from the ^{1}H-NMR spectra. As can be seen from Table V, all the phenyl-modified MQ resins are white powders, which is a result of the rigidity of the phenyl group introduced into the MQ molecule. Unlike methyl MQ resins, it is not possible to estimate the range of M/Q values of these phenyl-modified MQ resins based on their appearance.

Thermal Performance. As shown in Table V and Figures 8 and 9, the influence of M/Q values on thermal stability of the

Table V. M/Q Value of Phenyl MQ Resins and their Thermal Performances

Entry	Phenyl content / wt%	Appearances	M/Q[a]	T_5[b] (°C)	T_{10}[c] (°C)	T_{15}[d] (°C)	MRDT[e] (°C)	MRD[f] (K^{-1})	Residual weight (%)
3a	10.51	White powders	1.12	348.5	420.3	453.8	471.3	0.198	64.6
3b	14.09	White powders	1.07	356.0	454.0	481.5	476.7	0.247	66.9
3c	16.05	White powders	0.89	401.0	478.9	513.1	502.5	0.160	72.8
3d	21.25	White powders	0.85	378.6	496.1	540.4	535.7	0.141	76.4
3e	28.55	White powders	0.78	379.9	491.2	566.6	558.9	0.087	77.7

[a]M/Q value calculated from NMR spectrum, [b]Temperature for 5% weight loss, [c]Temperature for 10% weight loss, [d]Temperature for 15% weight loss, [e]The temperature for the maximum rate of decomposition, [f]Maximum rate of decomposition.
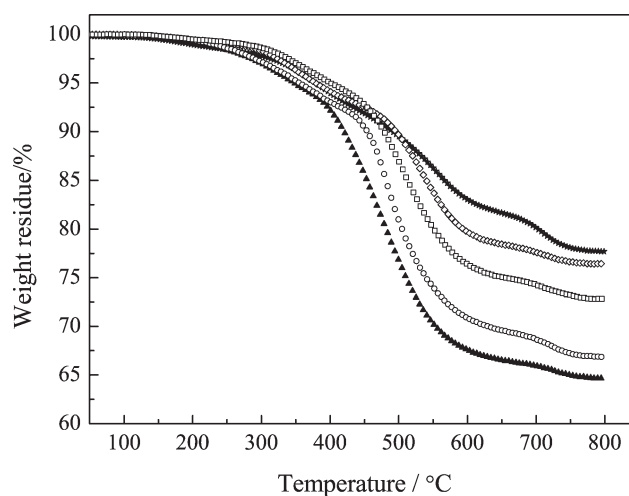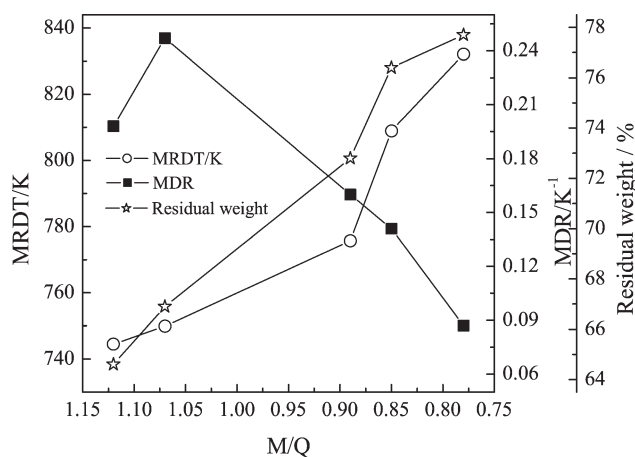
Figure 9. The influence of M/Q ratio on MRDT, MRD and residual weight for $Me_2PhSiO_{1/2}$- terminated MQ silicone resins. (○)MRDT; (■) MRD; (☆) residual weight (M/Q values are determined from ^{1}H-NMR).

phenyl-modified MQ resins exhibits a similar trend as those reported for methyl MQ resins, namely, that the thermal stability of the phenyl-modified MQ resins also improves with the decrease in M/Q ratios. The values of T_5, T_{10}, and T_{15} for five phenyl-modified MQ resins change in almost the same manner as those of the methyl MQ resins. With the decrease in M/Q values, the values of T_5, T_{10}, T_{15}, and MRDT, as well as the ceramic yield at 800°C, gradually increase. However, the values of MRD decrease with the decrease in M/Q values. When the M/Q values decrease from 1.12 to 0.78, the values of the MRDT increase from 471.3°C to 558.9°C. Meanwhile, the ceramic yields at 800°C increase from 64.6% to 77.7%, together with a decrease of MRD values from 0.247 to 0.087 K^{-1}. Comparing different methyl MQ resins with equivalent M/Q values, it can be concluded that the phenyl-modified MQ resins are far more resistant to thermal oxidation than methyl MQ resins. In fact, most silicone resins for high temperature applications have a combination of methyl and phenyl substituents to achieve the required balance of heat stability, flexibility, and compatibility with organic resins. The influence of the phenyl group on the thermal stability of polysiloxanes has frequently been referenced and the strengthening of the siloxane bond by increased participation of the lone pair electrons on oxygen is believed to be responsible for this effect.[34]

CONCLUSIONS

Phenyl MQ resins can be prepared by hydrolysis of sodium silicate solution in the presence of HCl solution and then end capped with DMPES, MM, or TMDVS. Low molecular weight residues were not detected in the phenyl MQ resins when MDPES was substituted by DMPES and used as the end-capping agent. MQ resins with different phenyl content can be obtained by changing the ratio between DMPES and the other end-capping agents. The relative molecular weight of MQ resins increases with phenyl content and their MWD values were much higher than those of $Me_3SiO_{1/2}$-terminated MQ resins. The structure of the MQ resins was characterized by ^{1}H-NMR and FT–IR spectra. The M/Q values in $Me_3SiO_{1/2}$-terminated

MQ resins can be determined either from elemental analysis or from ^{1}H-NMR spectra, and both were in good agreement with the changes of appearance and thermal stabilities of the resins. The M/Q ratio in phenyl-modified MQ resins could not be determined by elemental analysis, because the content of C and H in each end-capping segment could not be clearly resolved. Based on the analysis of each kind of proton in the phenyl-modified MQ resins and with the help of the addition of a quantitative amount of 1, 4-dioxane, the values of M/Q could be determined. With the decrease in M/Q values, the thermal stabilities of the phenyl MQ resins increased. Compared with methyl MQ resins, the thermal stabilities of phenyl MQ resins were significantly enhanced.

REFERENCES

1. Huang, W.; Huang, Y.; Zhao, H. T.; Yu, Y. Z. *China Synth. Rubber Ind.* **2000**, *23*, 170.

2. Lin, S. B.; Kerr S. R. *US Pat. 5*, **1997**, *602*, 214.

3. Woodward, K. J. *US Pat. 0*, **1986**, *179*, 598.

4. Harashima, A.; Kondo, H.; Nakagawa, O. *Eur. Pat. 0*, **1992**, *516*, 109B1.

5. Taiko, K.; Hirai. *Jpn. Pat.* **2008**, *127*, 517.

6. Yoshida, M.; Uehara, K.; Nanba, T. *Jpn. Pat.* **1996**, *143*, 426.

7. Yoshida, M.; Uehara, K.; Nanba, T. *Jpn. Pat.* **1996**, *143*, 429.

8. Qi, Y. X.; Zhao, S. G.; Jiang, W. F.; Wang, X. B. *Shandong Chem. Ind.* **2005**, *34*, 3.

9. Huang, W.; Huang, Y.; Yu, Y. Z. *Chinese J. Polym. Sci.* **1999**, *17*, 429.

10. Zosel, A. *Int. J. Adhes. Adhes.* **1998**, *18*, 265.

11. Liu, X. L.; Lu, W. B.; Li, J. H.; Zhang, R. J. *Silicone Mater.* **2010**, *24*, 293.

12. Kashiwagi, T.; Shiobara, T. *US Pat. 0*, **2005**, *067*, 494.

13. Takanashi, M. *Jpn. Pat.* **2006**, *335*, 845.

14. Li, Y.; Hu, X. S.; Lin, X. D.; Zeng, X. R. *China Adhes.* **2010**, *19*, 36.

15. Wei, P. Study on Preparation and Modification of Addition-cured Room Temperature Vulcanization Silicone Rubber. Master Degree Thesis, Wuhan University of Technology, **2007**.

16. Wu, Q. B.; Qing, S. G.; Xiong, T.; Wang, F.; Lu, W. Z.; Luo, Z. K. *Guangdong Chem. Ind.* **2009**, *36*, 23.

17. Thomas, T. H.; Kendrick, T. C. *J. Polym. Sci. Part B: Polym. Phys.* **1969**, *7*, 537.

18. Michalczyk, M. J.; Farneth, W. E.; Vega, A. *J. Chem. Mater.* **1993**, *5*, 1687.

19. Yin, Z. H.; Pan, H. M.; Wu, W. Q.; Li, J. Z.; Chen, J. G.. *China Adhes.* **2002**, *11*, 21.

20. Sanders, J.K.M.; Hunter, B.K. Modem NMR Spectroscopy: A Guide for Chemists; Oxford University Press: New York, **1987**, p 65.

21. Robert, J. H. *J. Non-Cryst. Solids* **1996**, *195*, 1.

22. Yin, Z. H.; Pan, H. M.; Wu, W. Q.; Li, J. Z. *China Adhes.* **2003**, *12*, 16.

23. Gomez, M. V.; Guerra, J.; Velders, A. H.; Crooks R. M. *J. Am. Chem. Soc.* **2009**, *131*, 341.

24. Daudt, W. H.; Hyde, J. F. *J. Am. Chem. Soc.* **1952**, *74*, 386.

25. Wu, C.-B.; Jin, Y.-H.; Li, W.; Gao, D.-H.; Jia, M.-Q. *High Perform. Polym.* **2010**, *22*, 959.

26. Van Krevelen, D. W. Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions. Completely revised; 3rd ed; Elsevier: Amsterdam, **1997**.

27. Speight, J. G. Lange's Handbook of Chemistry; 16th ed.; McGraw-Hill: New York, **2005**, pp 2.288.

28. Graham, R. A.; Krolikowska, R. M.; Samoc, A. J. *Non-Cryst. Solids* **2000**, *265*, 210.

29. Suzuki, T.; Sakae, Y.; Kushibiki, N.; Mita, I. *Chem. Mater.* **1994**, *6*, 692.

30. Redondo, S. U. A.; Radovanovic, E.; Torriani, I. L.; Yoshida, I. V. P. *Polymer* **2001**, *42*, 1319.

31. José, N. M.; Prado, L. A. S. A.; Yoshida, I. V. P. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 4281.

32. José, N. M.; Prado, L. A. S. A.; Schiavon, M. A.; Redondo, S. U. A.; Yoshida, I. V. P. *J. Polym. Sci. Part B: Polym. Phys.* **2007**, *45*, 299.

33. Prado, L. A. S. A.; Sforça, M. L.; de Oliveira, A. G.; Yoshida, I. V. P. *Eur. Polym. J.* **2008**, *44*, 3080.

34. Poole, C. F. The Essence of Chromatography; Amsterdam: Elsevier, **2002**, pp 95.