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Synthesis of High Molecular Weight Vinylphenyl-Containing MQ Silicone Resin via Hydrosilylation Reaction

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Abstract: To overcome the inherent limitation that the preparation of high molecular weight MQ copolymers ($M_w \geq 30,000$ g/mol) via the hydrolysis and condensation of silicate salts generally results in an intractable gel, vinylphenyl-containing MQ silicone resin with a high molecular weight was designed and synthesized through the hydrosilylation reaction of vinyl-containing MQ silicone resin and linear poly(diphenylsiloxane) with two terminal Si–H bonds. The weight average molecular weight of these modified copolymers reported here is at least $30,000$ dal·mol^{−1}. These polymers have favorable thermal stability and a higher refractive index than that of the base resin due to the formation of novel regular macromolecular structures and the introduction of phenyl groups. These inorganic/organic hybrid materials could be used as a potential component for temperature-resistance electronics adhesive, heat-resistant coatings and high-performance liquid silicone rubber. Moreover, the proposed process also provides a possibility to choose higher molecular weight MQ silicones according to application requirements.

Keywords: MQ silicone resin; modified; hydrosilylation; high molecular weight

1. Introduction

MQ-type silicone resins are polymers consisting of mono-functional siloxane ($R_3SiO_{1/2}$, the M units) and tetra-functional siloxane ($SiO_{4/2}$, the Q units) [1,2], wherein R is a functional or nonfunctional organic group, such as hydrogen, vinyl, methyl, aryl and some related organic or inorganic groups. These are thus called hydrogen-containing MQ silicone resin, vinyl-containing MQ silicone resin, methyl-containing MQ silicone resin and so on.

Since it was first synthesized by Herbert and his co-workers in the early 1950s [3], MQ-type silicone resins have attracted great attention in commercial applications owing to their special structures and properties. For example, they are used as a tackifier for silicone pressure-sensitive adhesives [4], as silicone hot melt adhesive additives [5], as the reinforced fillers of liquid silicone rubber [6], as the reinforced agent for heat-resistant coatings [7], etc. Silicone pressure-sensitive adhesives using high molecular weight MQ silicone resin (weight average molecular weight, $M_w \geq 30,000$ g/mol) as a tackifier

possesses a stronger holding power than that of adhesives using low molecular weight MQ silicone resin (weight average molecular weight, $M_w \leq 8000$ g/mol) with a similar structure [8]. In addition, MQ silicone resin is an essential part of silicone hot melt adhesive [9], as it can effectively improve the mechanical and adhesive properties. Generally, high molecular weight MQ silicone resin has a more obvious improving effect than low molecular weight silicone resin [7]. Therefore, it makes sense to prepare high molecular weight MQ silicone resin. However, a polymer with greater molecular weight does not always cause a better application result. For example, using an MQ resin with an exorbitant molecular weight as a tackifier for silicone pressure-sensitive adhesive will lead to the decrease of the initial adhesion of the adhesive. This does not influence the importance of this polymer, however, because it can be possible to choose higher molecular weight MQ silicones according to application requirements.

MQ silicone resins are frequently synthesized through hydrolysis/condensation reactions of tetraethoxysilane [10–12] or silicate salts [13,14], followed by end capping reactions with mono-functional siloxane. Their weight average molecular weight and number average molecular weight have been controlled to about 30,000 and 7000 g/mol separately for the inherent limitation of this reaction, as attempts to synthesize higher molecular weight copolymers by reducing the value of the M/Q ratio have usually resulted in the formation of an intractable gel [15]. Huang [16] prepared MQ silicone resins with a number average molecular weight of about 6000 g/mol through the hydrolytic condensation of ethyl polysilicate and hexamethyldisiloxane in 1998. Xu [17] prepared methylphenyl-modified MQ silicone resins with a number average molecular weight of about 7000 g/mol through co-hydrolysis and the condensation polymerization of sodium silicate, hexamethyldisiloxane (MM), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane and methyldiphenylethoxy silane in 2013. Though Flagg [18] prepared MQ silicone resins with a weight average molecular weight of more than 30,000 g/mol, there remained problems with difficult-to-avoid sol growth and complete gel formation. Meanwhile, the weight average molecular weight of MQ resins has not yet exceeded 100,000 g/mol.

The introduction of phenyl can improve the heat resistance and refractive index of MQ silicone resin, which further enlarges its application possibilities [19]. To address the abovementioned issues, an approach to synthesize high molecular weight phenyl-modified MQ silicone resin (VPMQ) through the hydrosilylation reaction of low molecular weight vinyl-containing MQ silicone resin (VMQ) and linear poly(diphenylsiloxane) with two terminal Si–H bonds (PDPS) was reported. Simultaneously, a series of different molecular weight VPMQ polymers were prepared by changing the molar ratio of Si–H/Si–CH=CH₂ under appropriate conditions. The structure, molecular weight, optical properties and thermal stability properties of these silicone resins were investigated. Overall, this studies aimed to obtain VPMQ material with a high molecular weight and good optical and thermal stability, thus further improving its application value.

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, AR), 1,1,3,3-tetramethyl divinyl disiloxane (TMDVS, AR) and hexamethyldisiloxane (MM, AR) were purchased from Shanghai Hansi Chemical industry Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl, AR), ethanol (C₂H₅OH, AR) and toluene (98 wt %, AR) were provided by Tianjin Baishi Chemical industry Co., Ltd. (Tianjin, China). Linear poly(diphenylsiloxane) with two terminal Si–H bonds (PDPS, hydrogen content: 0.25 wt %, AR) was supplied by Iota Silicone Oil Co., Ltd. (Anhui, China). Chloroplatinic acid (H₂PtCl₆, 5000 mg/Kg, AR) was purchased from Tianjin Maisike Chemical Industry Co., Ltd. (Tianjin, China). Carbon tetrachloride (CCl₄, ≥95 wt %, AR), iodine bromide (IBr, 98 wt %, AR), potassium iodide (KI, 100 g/L, AR), sodium thiosulfate (Na₂S₂O₃, 0.1 mol/L, AR) and starch solution (1.0 wt %, AR) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China).

2.2. Synthesis of the VMQ

The VMQ was prepared by the hydrolysis/condensation reactions of TEOS, TMDVS and MM, according to a literature procedure reported by Xiang et al. with a small amendment [20]. Distilled water (40.0 mL), HCl (6.0 mL), toluene (50.0 mL), ethanol (10.0 mL), TMDVS (8.19 g, 0.05 mol) and MM (37.3 g, 0.2 mol) were added to a 500 mL three-necked flask. The mixture was stirred for 30 min at room temperature and then the TEOS (104.2 g, 0.5 mol) was added to the flask drop by drop. Stirring continued at 60 °C for 3 h. After that, 100 mL toluene was used to extract the products and deionized water was used to wash the products until pH = 7 was reached. Finally, the polymer–toluene solution was distilled at 110 °C for 1 h to obtain the VMQ polymers. The mass fraction of vinyl of the VMQ was measured and the results showed a vinyl content of 1.8%.

2.3. Synthesis of the VPMQ

Taking the synthesis of VPMQ-1 as an example: VMQ (30.0 g), toluene (6.0 mL), PDPS (1.60 g) and the hydrosilylation catalyst H_2PtCl_6 (0.06 g) were added to a 250 mL three-necked flask. The mixture was stirred for 5 h at 70 °C; then, the toluene and low molecular byproducts were distilled at 110 °C for 2 h to obtain the VPMQ polymer (Figure 1, Table 1).

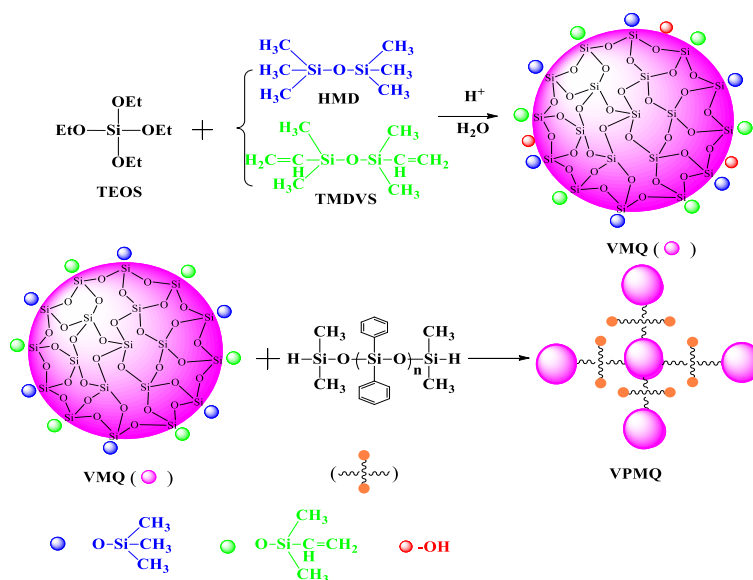


Figure 1. Synthesis routine of the VPMQ.

2.4. Characterizations and Measurements

Content of vinyl groups in the VMQ: The mass fraction of vinyl groups in the VMQ was measured by iodimetry according to a previously reported procedure [21]. First, the VMQ sample was dissolved into a 250 mL iodine flask containing 20 mL of CCl_4 solution. This was shaken evenly. Second, 10 mL of IBr was added to the iodine flask, which was shaken evenly again. The reaction was allowed to continue in the dark for 1 h. Thirdly, 5 mL of KI solution was added to the iodine flask, which was shaken for about 5 min. After that, 40 mL of distilled water was added. Fourth, the solution was titrated with 0.1 mol/L of $\text{Na}_2\text{S}_2\text{O}_3$ until it became light yellow. Then, 2.0 mL of a starch solution was added. The solution continued to be titrated until the blue coloration disappeared. The mass fraction of vinyl groups in the VMQ was determined by the following equation:

$$\omega = \frac{27 \times 0.5 \times 0.001 \times C_{\text{Na}_2\text{S}_2\text{O}_3} \times (V_0 - V_1)}{M} \quad (1)$$

where ω is the mass fraction of the vinyl groups in the VMQ (%); $C_{\text{Na}_2\text{S}_2\text{O}_3}$ is the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (mol/L); V_0 is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ consumed by the blank experiment; V_1 is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ consumed by the experimental group.

Physical state in toluene: About 1.00 g of every polymer sample was put into 10 μL of toluene solvent to observe its physical state in toluene, and the solubility or dispersibility of the polymers was evaluated by observing the appearance of the mixture.

FT-IR: The structure of VMQ and VPMQ samples was characterized by VERTEX70 Fourier transform infrared (FT-IR) spectra (Shimadzu, Japan) combined with the HF-7 detachable liquid pool (Bruker, Karlsruhe, Germany) with a capacity of 1 mL. All the samples were formulated with a mass concentration of 5 wt % by dissolving 0.20 g of the samples into 39.80 g of CCl_4 solution. Every sample was scanned from 400 to 4000 cm^{-1} and averaged over 16 times.

^1H -NMR: The structure of the VMQ and VPMQs was characterized at 25 $^\circ\text{C}$ with an Av500 Hydrogen Nuclear Magnetic Resonance Spectrometer (Bruker, Germany) at a frequency of 500 MHz. Deuterated chloroform (CDCl_3) was used as the solvent and tetramethylsilane (TMS) as an internal standard.

^{29}Si NMR: The ^{29}Si NMR analysis of the VMQ and VPMQ samples was carried out on Bruker AVANCE AV 400 MHz spectrometer (Bruker, Germany) at room temperature, and CDCl_3 was used as a solvent.

Gel permeation chromatography (GPC): Molecular weights and molecular weight distributions of all the samples were determined by GPC using an Angilent 1260 infinity LC system (Angilent, America) equipped with two PLgel MixedC columns and one PLgel Mixed-D column as well as a refractive index detector. The operation was performed at 25 ± 1 $^\circ\text{C}$, using HPLC grade THF as the eluent with a flow rate of 1 mL/min. Polystyrenes were used as the molecular weight standards.

Differential scanning calorimetry (DSC): The Glass transition temperature (T_g) of the samples were investigated by Q2000 Differential scanning calorimetry (TA Instruments, Wilmington, American). The temperature was increased from -100 $^\circ\text{C}$ to 240 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$.

Thermogravimetric analysis (TGA): Thermogravimetric analysis measurement was carried out on a Mettler Toledo TG thermal analyzer (Mettler Toledo AG, Columbus, OH, USA) at a flow rate of 20 mL/min in nitrogen. The samples were heated from 40 to 800 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$.

Refractive index measurement: The refractive indexes of the samples were measured using a 2WA-J Abbe refractometer (Shanghai CSOIF Co., Ltd., Shanghai, China). Before measuring, the samples were dissolved in carbon tetrachloride.

3. Results and Discussion

3.1. Structural Analysis

The molecular weight of MQ silicone resin is mainly determined by the molar ratio of M units to Q units [20]. In the experiment, we attempted to directly prepare high molecular weight MQ silicone resin through the hydrolysis/condensation reactions of TEOS (Q units), TMDVS ($^{\text{vi}}$ M units) and MM (M units) by decreasing the ratio of M units to Q units. Unfortunately, this attempt failed. This was because too small of a molar ratio of M/Q causes the formation of highly reactive Q units, which are difficult to control and inevitably produce a gel [22]. On the contrary, MQ silicone resins with high molecular weight prepared via a hydrosilylation reaction of low molecular weight MQ silicone resin and PDPS are easy to control due to their mild reaction condition. Meanwhile, PDPS was simply used as a linear molecular bridge to link the low molecular weight of VMQ to make the high molecular weight VPMQ polymers in this reaction; it has almost no effect on the ratio of M/Q unit in MQ silicone. Therefore, it increases the molecular weight of MQ silicone resin and does not result in gelation at an appropriate addition amount.

The content of vinyl groups, average molecular weight and polydispersity index of VMQ were measured first. The results showed that the mass fraction of vinyl groups in VMQ was 1.8%, while the

average molecular weight and polydispersity index values were 4801 dal/mol and 1.87, respectively. Then, VPMQ with high molecular weight was synthesized through the hydrosilylation reaction of VMQ and PDPS. These novel polymers have structures similar but not identical to MDQ silicone resin, because difunctional siloxanes (D, $R_2SiO_{2/2}$) were introduced into the polymer but not all the silicon atoms are connected by Si–O–Si bonds. Even so, such polymers can still be considered as MQ-type silicone resins because less than 20% of the resin molecules are comprised of D units [23]. To analyze the structure and properties of these copolymers, a series of VPMQ samples was synthesized by changing the molar ratio of Si–H/Si–CH=CH₂. The amount of each feed material is listed in Table 1. As can be seen, the physical state of these polymers changed from a viscous liquid to a semisolid when moving from VPMQ-1 to VPMQ-5, and the physical state of their dispersions in toluene varied from a clear liquid to a gel when moving from VPMQ-1 to VPMQ-5. The presence of the clear liquid state in toluene solvent indicates that the VPMQ materials have good dispersibility, while the presence of the gelatinous liquid state indicates that the polymer has poor dispersibility and little application value.

Table 1. The formulations of VPMQ polymers.

| Entry | Si–H/ Si–CH=CH ₂ | VMQ (g) | PDPS (g) | H ₂ PtCl ₆ (g) | Toluene (g) | Physical State | Dispersion in Toluene |
|--------|--------------------------------|------------|-------------|---|----------------|----------------|--------------------------|
| VPMQ-1 | 0.2/1 | 30.00 | 1.60 | 0.06 | 6.0 | viscous liquid | clear |
| VPMQ-2 | 0.4/1 | 30.00 | 3.20 | 0.06 | 6.0 | viscous liquid | clear |
| VPMQ-3 | 0.6/1 | 30.00 | 4.80 | 0.06 | 6.0 | viscous liquid | clear |
| VPMQ-4 | 0.8/1 | 30.00 | 6.00 | 0.07 | 6.0 | semisolid | clear |
| VPMQ-5 | 1.0/1 | 30.00 | 7.20 | 0.07 | 6.0 | semisolid | gelatinous |

The FT-IR spectra of VMQ, PDPS and VPMQ are shown in Figure 2a. In the curve of the VMQ, the strong absorption peak at 3450 cm^{−1} is assigned to the H-bonded silanol (Si–OH) group [24]. The peaks at 2960 and 2910 cm^{−1} are attributed to the stretching vibration absorption of C–H in –CH₃, and the peak at 1260 cm^{−1} is ascribed to the scissoring vibration absorption of Si–CH₃. The peaks at 1600 and 1410 cm^{−1} correspond to the stretch vibration absorption of C–H in Si–CH=CH₂. In addition, the broad absorption peak at 1100–1080 cm^{−1} is attributed to the stretching vibration absorption of Si–O–Si [25,26]. In the curve of PDPS, the peak at about 3080 cm^{−1} is assigned to the stretching vibration of the C–H group in Si–C₆H₅, and the sharp peaks at 1591 and 1430 cm^{−1} correspond to the C–C stretching vibration of Si–C₆H₅. Simultaneously, the characteristic peaks at 800, 756 and 702 cm^{−1} are associated with the ring deformation vibration and C–H deformation vibration of the phenyl group, respectively. Moreover, it is relatively easy to observe the strong signal of Si–H at 2134 cm^{−1}. In terms of the VPMQ, the characteristic absorption peaks of the C–H group on Si–C₆H₅ also appear at 3080, 800, 756 and 702 cm^{−1} [27]. Furthermore, the symmetric stretching vibrations of C–H on Si–CH₂–CH₂–Si bridges formed during the hydrosilylation reaction appear at 2870 cm^{−1} [28], and the characteristic absorption peak at 1010 cm^{−1} attributed to Si–O–Si introduced by PDPS can be seen. Moreover, the characteristic absorption peak of Si–CH=CH₂ at 1600 cm^{−1} is significantly weakened, and the absorption peak of Si–H at 2134 cm^{−1} is absent. Based on the above analysis, it can be concluded that the VPMQ polymer was synthesized successfully.

In addition, to further investigate the extent of the reaction, the characteristic absorption peak at 1600 cm^{−1} for Si–CH=CH₂ on VMQ and VPMQ samples was mainly observed. The results show that area of the absorption peaks were in the order of VMQ > VPMQ-1 > VPMQ-2 > VPMQ-3 > VPMQ-4. This is because more Si–CH=CH₂ was consumed with increasing additions of PDPS. Meanwhile, we have also pay attention to the characteristic peak at 2134 cm^{−1} for the Si–H group. Fortunately, the characteristic absorption peak of the Si–H bond was not found in all the samples, indicating that the Si–H group on the PDPS was consumed completely, and there was no free PDPS in the reaction system.

The structures of VMQ, PDPS and VPMQ were confirmed by ¹H NMR spectroscopy, as shown in Figure 3. The structures of the samples are shown in Figure 3a,b, revealing the ¹H NMR spectrum of

the polymers. Here, the characteristic peaks at 0~0.18 and 5.56~6.07 ppm are assigned to the silicon methyl and vinyl groups, respectively, for M units in the VMQ. The characteristic signals located about 2.63 ppm are attributed to the proton peaks of silicon-hydroxyl. For PDPS, the signal at about 0.12 ppm also corresponds to the protons on silicon-methyl, while the peak at about 4.51 ppm is assigned to the Si-H group. The signals at about 7.50, 7.25 and 7.05 ppm are related to the protons of the benzene of PDPS. In the ^1H NMR spectrum of VPMQ, we observed the chemical shifts of proton peaks of $-\text{CH}_3$ and $\text{Si}-\text{CH}=\text{CH}_2$ groups. The strong signal located at 0.65~0.8 ppm corresponds to the protons of the $\text{Si}-\text{CH}_2\text{CH}_2$ group. The signals located at 0.84~1.08 and 1.72~1.82 ppm for the protons of the $\text{C}-\text{CH}_3$ and $\text{C}-\text{H}$ group can also be seen. Moreover, the characteristic signals located at 7.50, 7.25 and 7.05 ppm belonging to the protons of phenyl region appear as well. This analysis indicated that VPMQ was synthesized successfully through Markownikow and Anti-Markownikow addition reactions, and the addition reaction was carried out a result of both a small amount of α and primarily β addition products [29].

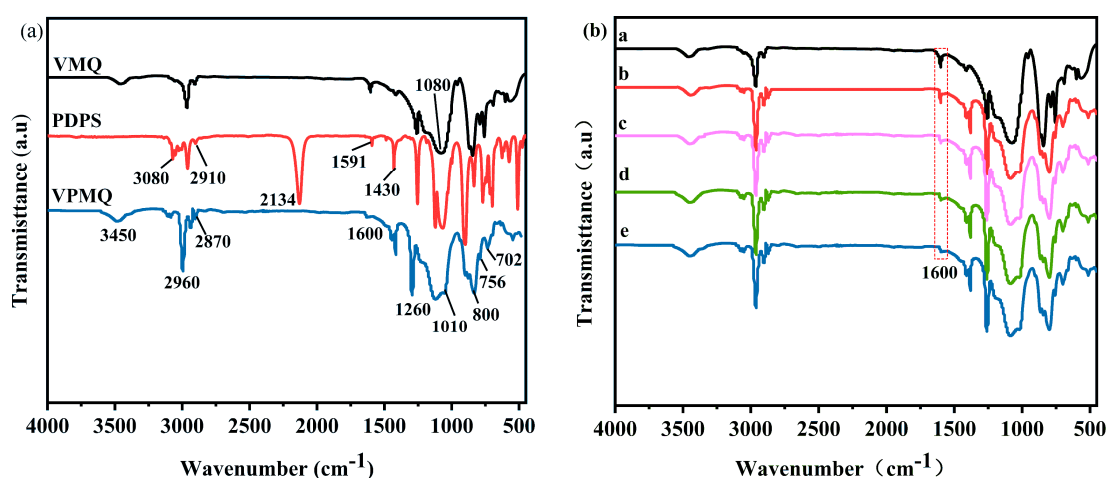


Figure 2. (a) Infrared spectra of VMQ, PDPS and VPMQ; (b) infrared spectra of VMQ and VPMQ series. (a–e) VMQ, VPMQ-1, VPMQ-2, VPMQ-3 and VPMQ-4, respectively.

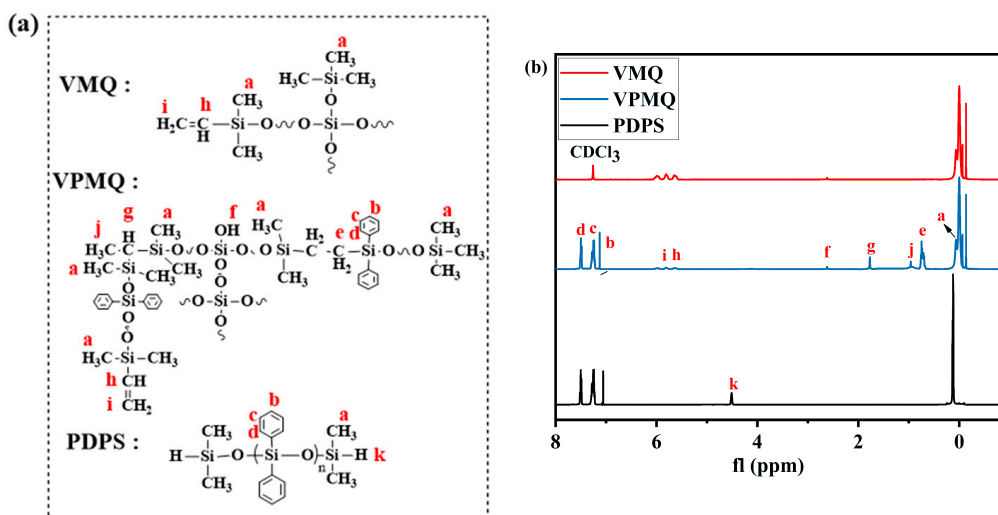


Figure 3. ^1H NMR spectrum of VMQ, VPMQ and PDPS: (a) Molecular formula of VMQ, VPMQ and PDPS; (b) ^1H NMR spectrum of VMQ, VPMQ-4 and PDPS.

^{29}Si NMR spectroscopy is a useful tool to characterize the skeleton structure of organosilicon polymers [30]. As shown in Figure 4a,b, the structures of PDPS, VMQ and VPMQ series were further

confirmed by ^{29}Si NMR spectra. In the spectra of PDPS, clusters of signal peaks at about -5.06 and -21.24 ppm are related to the $^{\text{H}}\text{M}$ ($\text{HR}_2\text{SiO}_{1/2}$) and D ($\text{Ph}_2\text{SiO}_{2/2}$) units. Similarly, there are Q ($\text{SiO}_{4/2}$), $^{\text{Vi}}\text{M}$ ($\text{R}_1\text{R}_2\text{SiO}_{1/2}$) and M ($\text{R}_3\text{SiO}_{1/2}$) units contained in the skeleton structure of the VMQ silicone resin, and it was found that their chemical shifts are located at -111.07 , -2.41 and 11.98 ppm, respectively [3]. In the spectra of VPMQ, the chemical shifts located at -21.24 and -2.41 ppm corresponding to D ($\text{Ph}_2\text{SiO}_{2/2}$) and $^{\text{Vi}}\text{M}$ ($\text{R}_1\text{R}_2\text{SiO}_{1/2}$) units were also noted, in addition to the characteristic signals at -111.07 and 11.98 ppm for Q and M units. This indicates that the VPMQ polymer contains a D ($\text{Ph}_2\text{SiO}_{2/2}$) unit introduced by linear PDPS, while still retaining a small amount of unreacted vinyl groups. Meanwhile, no chemical shifts were found at about -5.06 ppm for $^{\text{H}}\text{M}$ ($\text{HR}_2\text{SiO}_{1/2}$) units, while chemical shifts near $6.02\sim 7.98$ ppm corresponding to silicon-methine and silicon-methylene in M units are visible. This shows that VPMQ was prepared successfully through hydrosilylation, and that α and β addition products are contained in VPMQ polymers. Unfortunately, we failed to recognize which type of addition products were dominant from the ^{29}Si NMR spectra of VPMQ. Still, because the steric hindrance of the α addition would be much larger than that of the β addition, the reaction is commonly obtained a result of a trace amount of α addition products and primarily β addition products, as confirmed via ^1H NMR spectroscopy [31]. Moreover, the reaction state of VPMQ polymers with increasing molar ratios of Si-H/Si-CH=CH_2 was also investigated by observing the intensity of absorption bands located at -111.07 and -2.41 ppm from VPMQ-1 to VPMQ-4. As shown in Figure 4b, it was found that the area of the Q unit region at -111.07 ppm increased gradually from VPMQ-1 to VPMQ-4, but the area of $^{\text{Vi}}\text{M}$ units at -2.41 ppm decreased gradually. These observations indicate that with the increasing molar ratio of Si-H/Si-CH=CH_2 (from VPMQ-1 to VPMQ-4), more and more vinyl groups are consumed, and a novel MQ silicone resin with a larger molecular structure can be prepared.

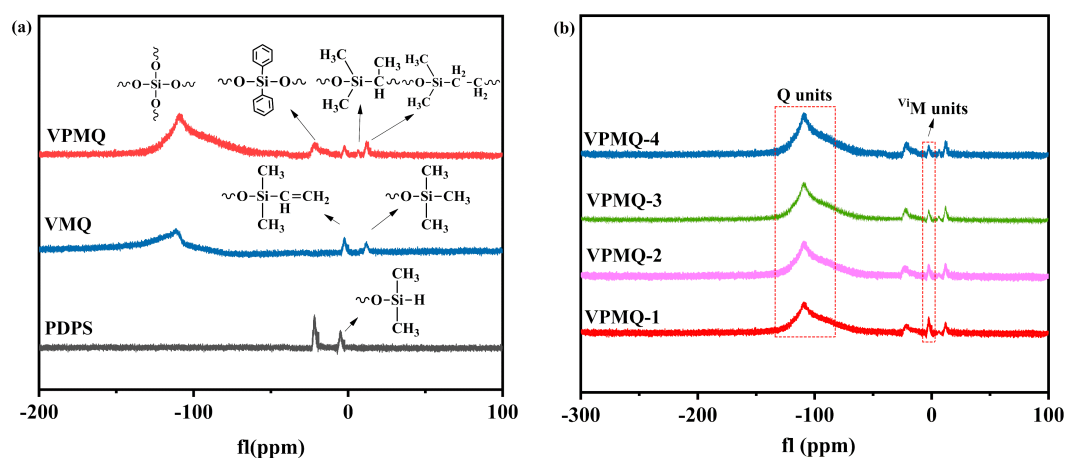


Figure 4. (a) ^{29}Si NMR spectra of VMQ, VPMQ and PDPS. (b) ^{29}Si NMR comparison of VPMQ samples.

The molecular weights of PDPS, VMQ and VPMQ samples were determined by GPC, as listed in Table 2. The weight average molecular weights (M_w) of PDPS, VMQ, VPMQ-1, VPMQ-2, VPMQ-3 and VPMQ-4 were 800, 4801, 31099, 77321, 97199 and 391817 $\text{dal}\cdot\text{mol}^{-1}$, respectively. The number average molecular weights (M_n) of PDPS, VMQ, VPMQ-1, VPMQ-2, VPMQ-3 and VPMQ-4 were 512, 2562, 17357, 29420, 37585 and 285494 $\text{dal}\cdot\text{mol}^{-1}$, with proper polydispersity indexes of 1.56, 1.87, 1.79, 2.68, 1.43 and 1.37, respectively. As can be seen, the molecular weights of VPMQ increased quickly with the increase of the molar ratio of Si-H/Si-CH=CH_2 , which can be attributed to the hydrosilylation reaction of VMQ and PDPS, in which PDPS was served as a bridge to achieving a high molecular weight. Note that VPMQ became gelatinous when the molar ratio value of Si-H/Si-CH=CH_2 reached 1 (shown in Table 2). This can be attributed to the occurrence of a cross-linking reaction when the number of Si-H groups is excessive. Therefore, it is necessary to control a proper molar ratio value of Si-H/Si-CH=CH_2 to obtain high molecular weight and dispersible VPMQ polymers.

Table 2. The gel permeation chromatography (GPC) data and refractive index of VPMQ samples.

| Entry | Mw (dal·mol ^{−1}) | Mn (dal·mol ^{−1}) | Mw/Mn | <i>n</i> _D ²⁵ |
|--------|--------------------------------|--------------------------------|-------|-------------------------------------|
| PDPS | 800 | 512 | 1.56 | 1.5440 |
| VMQ | 4801 | 2562 | 1.87 | 1.4840 |
| VPMQ-1 | 31,099 | 17,357 | 1.79 | 1.4850 |
| VPMQ-2 | 77,321 | 28,902 | 2.68 | 1.4889 |
| VPMQ-3 | 197,199 | 137,585 | 1.43 | 1.4890 |
| VPMQ-4 | 391,817 | 285,494 | 1.37 | 1.4994 |

3.2. Refractive Index Analysis

The refractive index of silicone resin is an interesting reference for the polymers used in applications with high optical requirements. The refractive index values of PDPS, VMQ and VPMQ series are also listed in Table 3. It was found that PDPS possessed the highest refractive index value (1.5440 for PDPS). Simultaneously, the refractive index of the VPMQ series was higher than that of VMQ, in the order of VPMQ-1 < VPMQ-2 < VPMQ-3 < VPMQ-4. This indicated that PDPS has good compatibility with VMQ. The refractive index values of the VPMQ series increased from 1.4850 to 1.4994 as the molar ratio value of Si–H/Si–CH=CH₂ increased from 0.2/1 to 0.8/1. This could be due to the introduction of the phenyl group, which has a refractive index as high as 25.46, which is barely below that of naphthyl in all groups yet discovered [32]. In terms of phenyl silicone resin polymers, their refractive index value is mainly determined by their phenyl contents, and remains almost unaffected by their structure [33]. Among all the VPMQ polymers, VPMQ-4 possessed the highest refractive index value (1.4994), as it contained the highest content of phenyl groups. This means that VPMQ-4 has greater application potential in the applications of optical encapsulation and bonding.

Table 3. The characteristic degradative data of VMQ and VPMQ samples.

| Entry | <i>T</i> _{max} (°C) | <i>T</i> ₅ (°C) | <i>T</i> ₁₀ (°C) | Residual Yield (%) |
|--------|------------------------------|----------------------------|-----------------------------|--------------------|
| PDPS | – | – | – | 0 |
| VMQ | 509.17 | 281.33 | 358.33 | 17.91 |
| VPMQ-1 | 496.17 | 341.67 | 416.13 | 21.29 |
| VPMQ-2 | 503.17 | 346.17 | 421.70 | 25.06 |
| VPMQ-3 | 496.17 | 363.33 | 424.74 | 29.71 |
| VPMQ-4 | 492.18 | 364.18 | 428.33 | 33.95 |

3.3. Thermal Properties

The physically status of PDPS and VMQ was a viscous liquid at room temperature. VPMQ samples varied from a high viscosity liquid to a semisolid with the increase of the molar ratio of Si–H/Si–CH=CH₂ from 0.2/1 to 0.8/1. The DSC curves in Figure 5 explain the thermal property in the range of −80 to 100 °C for all samples. A step transition but no melting peak was observed for PDPS and the VMQ polymer in the temperature range between −80 and 100 °C. The DSC curves indicate that PDPS and VMQ are amorphous polymers. However, obvious exothermic peaks near about −40 °C can be observed in all VPMQ samples. The outset exothermic temperatures appeared at −47.07 °C for VPMQ-1, −47.53 °C for VPMQ-2, −47.77 °C for VPMQ-3 and −48.29 °C for VPMQ-4. The exothermic peaks of the four VPMQ samples appeared at −43.69 °C for VPMQ-1, −43.25 °C for VPMQ-2, −40.73 °C for VPMQ-3 and −40.68 °C for VPMQ-4. The values of heat enthalpy for crystallization were 12.87 J/g for VPMQ-1, 11.56 J/g for VPMQ-2, 6.21 J/g for VPMQ-3 and 4.81 J/g for VPMQ-4. The outset exothermic temperatures were in the order of VPMQ-1 > VPMQ-2 > VPMQ-3 > VPMQ-4. In addition, the exothermal peak temperature of VPMQ-4 was higher than those of the other samples, but the heat enthalpy of VPMQ-4 was lowest among all the VPMQ samples. It is known that the crystallization temperature for crystalline polymers is sensitively influenced by

prehistory and cooling [34]. Thus, it was indicated that VPMQ-4 possesses a more obvious crystalline structure. In addition, the crystallinity of the polymers is also related to the regularity of their structure. Therefore, a novel regular macromolecule structure of VPMQ polymers was probably formed through the reaction of VMQ and PDPS, and the regularity was increased gradually as the molar ratio value of Si-H/Si-CH=CH₂ increased from 0.2/1 to 0.8/1.

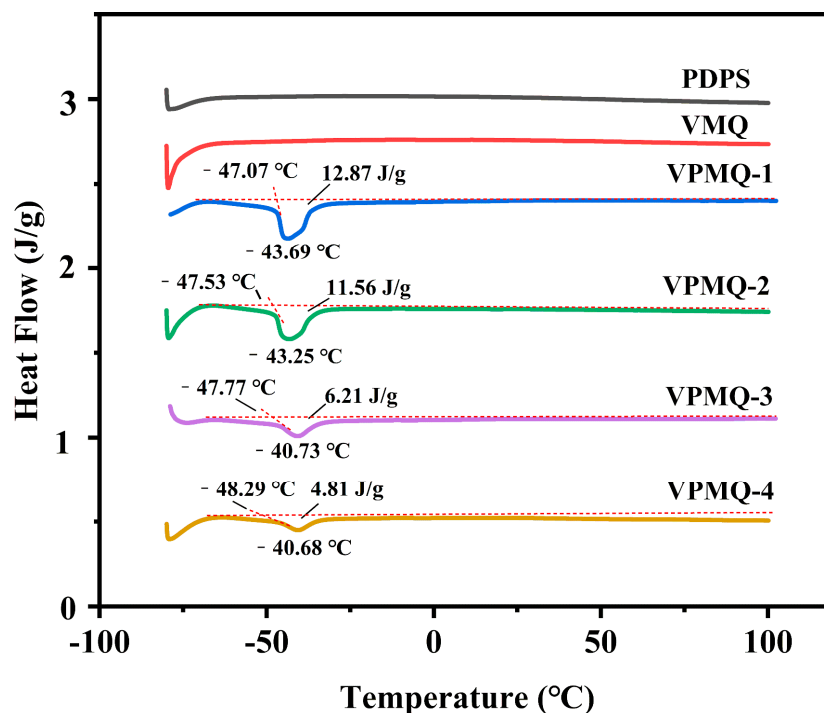


Figure 5. DSC thermograms of PDPS, VMQ and VPMQ samples with a heat rate of 10 °C/min in an N₂ atmosphere.

The thermal degradation behavior of PDPS, VMQ and VPMQ samples was investigated by TGA under a nitrogen atmosphere. Their TG and DTG curves are presented in Figure 6a,b. Values of 5% and 10% mass loss (T_5, T_{10}), the temperature of the maximum dissociation (T_{max}) and the residual yields at 800 °C are listed in Table 3. As can be seen, PDPS showed no degradation process, but evaporated completely when the temperature reached 220 °C. For VMQ and VPMQ samples, the first stage of thermal degradation at a range of 210–450 °C is attributed to the decomposition of organic groups, such as hydroxyl, hydrocarbyl and phenyl in the polymers [35]. In this degradation process, the temperatures of 5% and 10% mass loss of VPMQ samples were all higher than those of VMQ, the characteristic temperature of 5% mass loss was delayed from 281.33 to 364.18 °C, and the temperature corresponding to 10% weight loss increased from 358.33 to 428.33 °C. This was probably due to the introduction of phenyl and the formation of high molecular weight polymer structures. Meanwhile, the second thermal degradation stage may be related to the fracture and rearrangement of the backbone of VMQ and VPMQ polymers in the temperature range of 450–550 °C [36]. At this stage, VPMQ samples exhibited the maximum degradation rate, which was slightly smaller than that of VMQ, and began to slightly decrease with the increase of the molar ratio of Si-H/Si-CH=CH₂ (Table 3). This was attributed to the introduction of the difunctional segment of Ph₂SiO_{2/2} (D unit), whose degradation temperature is slightly lower than that of the four functional segments of SiO_{4/2} (Q units) [3]. Moreover, the residual yield at 800 °C of the VPMQ samples was obviously superior to that of the VMQ samples due to the novel macromolecular structure formed via the reaction of VMQ and linear PDPS.

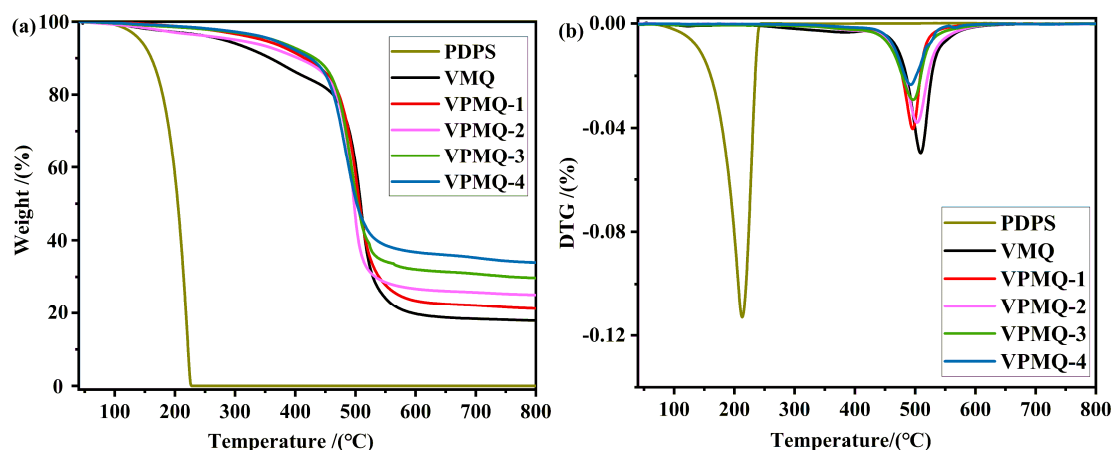


Figure 6. TG curves (a) and DTG (b) curves for VMQ and VPMQ series obtained under a nitrogen atmosphere.

4. Conclusions

Organic solvent-soluble high molecular weight MQ silicone polymers were prepared through the hydrosilylation reaction of VMQ and PDPS. Their weight average molecular weights were nearly $400,000 \text{ dal}\cdot\text{mol}^{-1}$ when the molar ratio of Si-H/Si-CH=CH_2 was 0.8/1, and no problem of gel production appeared. These novel VPMQ polymers exhibited high thermal stability, and a higher RI than that of base VMQ silicone resin due to the formation of a regular macromolecular structure and the introduction of phenyl groups, respectively. The VPMQ polymer is expected to be useful as a potential material for fillers of high heat-resistant, optical adhesives, high-performance liquid silicone rubber and heat-resistant coatings.

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References

- Huang, Z.; Wu, J.; Liu, X.; Ji, H.; He, R.; Pimhataivoot, P.; Chen, X. Versatile cascade esterification route to MQ Resins. *ACS Omega* **2018**, *3*, 4054–4062. [[CrossRef](#)] [[PubMed](#)]
- Ji, J.; Ge, X.; Pang, X.; Liu, R.; Wen, S.; Sun, J.; Liang, W.; Ge, J.; Chen, X. Synthesis and characterization of room temperature vulcanized silicone rubber using methoxyl-capped MQ silicone resin as self-reinforced cross-linker. *Polymers* **2019**, *11*, 1142. [[CrossRef](#)] [[PubMed](#)]
- Li, R.; Zhang, B.; Sun, Y.; Liu, B.; Wang, G. Synthesis of Vinylphenyl Oligomeric silsesquioxane based on MQ Silicone resin. *Asian J. Chem.* **2013**, *25*, 2541–2546. [[CrossRef](#)]
- Kuo, C.F.J.; Chen, J.B.; Shih, C.Y.; Huang, C.Y. Silicone resin synthesized by tetraethoxysilane and chlorotrimethylsilane through hydrolysis–condensation reaction. *J. Appl. Polym. Sci.* **2014**, *131*, 40317. [[CrossRef](#)]
- Kuo, A.C.M. *Silicone Release Coatings for the Pressure Sensitive Industry—Overview and Trends*; DC Corporation: Barry, UK, 2003; pp. 1–4.
- Chen, W.; Zeng, X.; Lai, X.; Li, H.; Pan, Z. Effect and mechanism of ureido-modified MQ silicone resin and platinum on tracking and erosion resistance of silicone rubber. *Polym. Test.* **2018**, *70*, 162–169. [[CrossRef](#)]

7. Lee, B.K.; Ryu, J.H.; Baek, I.B.; Kim, Y.; Jang, W.I.; Kim, S.H.; Yoon, Y.S.; Kim, S.H.; Hong, S.G.; Byun, S.; et al. Silicone-based adhesives with highly tunable adhesion force for Skin-contact applications. *Adv. Healthc. Mater.* **2017**, *6*, 1700621. [\[CrossRef\]](#)
8. Yilgör, E.; Yilgör, I. Silicone containing copolymers: synthesis, properties and applications. *Prog. Polym. Sci.* **2014**, *39*, 1165–1195. [\[CrossRef\]](#)
9. Wu, T.; Lai, X.; Liu, F.; Zeng, X. Efficiently enhancing the tracking and erosion resistance of silicone rubber by the synergism of fluorine-containing polyphenyl silsesquioxane and ureido-containing MQ silicone resin. *Appl. Surf. Sci.* **2018**, *459*, 483–491. [\[CrossRef\]](#)
10. Peng, D.; Mu, Q.H.; Zhang, S.; Li, S.; Wang, F. Synthesis and Properties of Phenyl Silicone Resin Reinforced Addition Type Liquid Phenyl Silicone Rubber. *Mater. Sci. Forum.* **2018**, *926*, 39–44. [\[CrossRef\]](#)
11. Jia, P.; Liu, H.; Liu, Q.; Cai, X. Thermal degradation mechanism and flame retardancy of MQ silicone/epoxy resin composites. *Polym. Degrad. Stabil.* **2016**, *134*, 144–150. [\[CrossRef\]](#)
12. Roberts, C.; Cosgrove, T.; Schmidt, R.G.; Gordon, G.V. Diffusion of poly (dimethyl-siloxane) mixtures with silicate nanopartic les. *Macromolecules* **2001**, *34*, 538–543. [\[CrossRef\]](#)
13. Kaneko, Y.; Coughlin, E.B.; Gunji, T.; Itoh, M.; Matsukawa, K.; Naka, K. Silse- squioxanes: Recent advancement and novel applications. *Int. J. Polym. Sci.* **2012**, *2012*, 453821.
14. Robeyns, C.; Picard, L.; Ganachaud, F. Synthesis, characterization and modification of silicone resins: An “Augmented Review”. *Prog. Org. Coat.* **2018**, *125*, 287–315. [\[CrossRef\]](#)
15. Elena, T.; Nataliya, V.; Aziz, M. Synthesis and Properties of MQ Copolymers: Current State of Knowledge. *Molecules* **2017**, *22*, 1768. [\[CrossRef\]](#)
16. Huang, W.; Huang, Y.; Yu, Y. Synthesis of MQ silicone resins through hydrol ytic condensation of ethyl polysilicate and hexamethyldisiloxane. *J. Appl. Polym. Sci.* **1998**, *70*, 1753–1757. [\[CrossRef\]](#)
17. Xu, X.; Wu, C.; Zhang, B.; Dong, H. Preparation, structure characterization, and thermal performance of phenyl-modified MQ silicone resins. *J. Appl. Polym. Sci.* **2013**, *128*, 4189–4200. [\[CrossRef\]](#)
18. Flagg, D.H.; McCarthy, T.J. Rediscovering silicones: MQ copolymers. *Macromolecules* **2016**, *49*, 8581–8592. [\[CrossRef\]](#)
19. Pan, K.; Zeng, X.; Li, H.; Liao, F.; Zhang, H.L.; Yin, C.Y. Synthesis of phenyl silicone resin with epoxy and acrylate group and its adhesion enhancement for addition-cure silicone encapsulant with high refractive index. *J. Adhes. Sci. Technol.* **2016**, *30*, 2699–2709. [\[CrossRef\]](#)
20. Xiang, H.; Ge, J.; Cheng, S. Synthesis and characterization of titania/MQ silicone resin hybrid nanocomposite via sol-gel process. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 635. [\[CrossRef\]](#)
21. Xie, C.; Zeng, X.; Fang, W.; Lai, X.; Li, H. Effect of alkyl-disubstituted ureido silanes with different alkyl chain structures on tracking resistance property of addition-cure liquid silicone rubber. *Polym. Degrad. Stabil.* **2017**, *142*, 263–272. [\[CrossRef\]](#)
22. Xie, H.; Hu, W.; Wu, Z.; Hu, G.; Zhu, G.; Liu, Q.; Jia, Z. Study on synthesizing MQ silicone with solid acid as catalyst and its properties. *China Adhes.* **2016**, *25*, 308–316. (In Chinese)
23. Wada, T.; Itoh, K. Heat-Curable Elastomeric Silicone Compositions. U.S. Patent 3,652,475, 28 March 1972.
24. Li, B.; Zhang, Z.; Ma, D.; Cai, Q.; Feng, S.; Zhang, J. Preparation and kinetic analysis of room-temperature vulcanized methylethylsilicone rubbers. *J. Appl. Polym. Sci.* **2015**, *132*, 42656. [\[CrossRef\]](#)
25. Choi, S.S.; Lee, A.S.; Lee, H.S.; Jeon, H.Y.; Baek, K.Y.; Choi, D.H.; Hwang, S.S. Synthesis and chara- cterization of UV-curable ladder-like polysilsesquioxane. *J. Polym. Sci. A Polym. Chem.* **2011**, *49*, 5012–5018. [\[CrossRef\]](#)
26. Chang, S.; Matsumoto, T.; Matsumoto, H.; Unno, M. Synthesis and characterization of heptacyclic ladder-siloxanes and ladder polysilsesquioxane. *Appl. Organomet. Chem.* **2010**, *24*, 241–246. [\[CrossRef\]](#)
27. Chen, J.; Fu, Z.; Huang, H.; Zeng, X.; Chen, Z. Preparation and properties of vinylphenyl-silicone resins and their application in LED packaging. *RSC Adv.* **2016**, *6*, 71924–71933. [\[CrossRef\]](#)
28. Witteman, L.; Evers, T.; Shu, Z. Hydrosilylation in Aryliminopyrrolide Substituted Silanes. *Chem. Eur. J.* **2016**, *22*, 6087–6099. [\[CrossRef\]](#)
29. Antosik, A.K.; Czech, Z. Pressure-Sensitive Adhesives (PSA) Based on Silicone. *Adv. Mater. Interfaces* **2016**, *7*, 249–274.
30. Ji, J.; Ge, X.; Liang, W.; Liang, R.; Pang, X.; Liu, R.; Wen, S.; Sun, J.; Chen, X.; Ge, J. A Simple Preparation Route for Bio-Phenol MQ Silicone Resin via the Hydrosilylation Method and its Autonomic Antibacterial Property. *Polymers* **2019**, *11*, 1389. [\[CrossRef\]](#)

31. Wei, Q.; Zan, X.; Qiu, X.; Öktem, G.; Sahre, K.; Kiri, A.; Voit, B. High Refractive Index Hyperbranched Polymers Prepared by Two Naphthalene-Bearing Monomers via Thiol-Yne Reaction. *Macromol. Chem. Phys.* **2016**, *217*, 1977–1984. [[CrossRef](#)]
32. Yang, S.; Kim, J.; Jin, J.; Kwak, S.; Bae, B. Cycloaliphatic epoxy oligosiloxane-derived hybrid materials for a high-refractive index LED encapsulant. *J. Appl. Polym. Sci.* **2011**, *122*, 2478–2485. [[CrossRef](#)]
33. Atkins, G.R.; Krolukowska, R.M.; Samoc, A. Optical properties of an ormosil system comprising methyl and phenyl substituted silica. *J. Non-Cryst. Solids* **2000**, *265*, 210–220. [[CrossRef](#)]
34. Takahashi, T.; Kashta, J.; Münstedt, H. Melt rheology and structure of silicone resins. *Rheol. Acta* **2001**, *40*, 490–498. [[CrossRef](#)]
35. Deshpande, G.; Rezac, M.E. Kinetic aspects of the thermal degradation of poly (dimethyl siloxane) and poly (dimethyl diphenyl siloxane). *Polym. Degrad. Stabil.* **2002**, *76*, 17–24. [[CrossRef](#)]
36. Pham, Q.T.; Chern, C.S. Thermal stability of organofunctional polysiloxanes. *Thermochim. Acta* **2013**, *565*, 114–123. [[CrossRef](#)]



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