

Synthesis and Characterization of a Silicone Resin with Silphenylene Units in Si-O-Si Backbones

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ABSTRACT: A silicone resin with silphenylene units in Si-O-Si backbones was synthesized by hydrolysis-polycondensation of 1,4-bis(hydroxydimethylsilyl)benzene (BHB) with chlorosilanes. The structure and property of this novel silicone resin were characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TG), scanning electron microscope (SEM), and electrochemical impedance spectrum (EIS). This silicone resin could be applied as the film forming material of coating when it is prepared under the condition of R/Si, Ph/R, and the content of silphenylene units being 1.3, 0.5, and 10 mol %, respectively. GPC, IR, and NMR results show that the silphenylene units have been

incorporated into the polymer of silicone resin. The TG analysis indicates that this novel silicone resin has good heat resistance with the onset degradation temperature of 500.3°C and residual weight of 85.6% at 900°C. SEM results demonstrate that the silicone resin with silphenylene units can form full and uniform films, and its surface morphology of clear paints were not damaged by heat below 350°C. EIS analysis reveals that clear paints of the silicone resin with silphenylene units have good resistance to corrosion. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 971–977, 2009

Key words: synthesis; high-temperature materials; silicone resin; silphenylene; polycondensation

INTRODUCTION

With the rapid increase of world's consumption of fossil fuels, nuclear energy has been receiving more and more attention. The nuclear electric power, as a clear energy with little adverse environmental effects, demonstrates good potential. It is very important to ensure that the nuclear plants running safely and effectively to prolong its lifetime.¹ Pressure vessel of nuclear reactor, which is the core part of nuclear power station, always works in extremely wretched conditions, including high irradiation, temperature and humidity, especially when loss of coolant accident happens. Under these conditions, the coatings that are applied to protect the pressure vessel of nuclear reactor from corrosion should have no film failure including blistering, cracking, chalking, and loss of adhesion, otherwise jamming of devices such as pipelines, nozzles, and pumps or other serious accidents will take place. It is a pity that resistance of heat and irradiation, and adhesion power of present coatings cannot satisfy practical needs.

Therefore, it makes great senses to develop coatings with excellent resistance of heat, irradiation, and corrosion, which can be cured in room temperature.²

Apparently, how to develop resins with high quality is the bottleneck, because they are film forming materials of heat and irradiation resistant coatings. At the present time, polyaryletherketone resins, polyimide resins, and silicone resins are three usual heat and radiation resistant resins. Although polyaryletherketone resins are so difficult to be solved to form good films that just several kinds of solvent can qualify, and polyimide resins can be cured only under high temperature and are not suitable to be used under circumstance of high temperature and humidity for their easy hydrolysis.

Silicone resins are known to be a kind of cross-linked semi-inorganic polymer with the Si-O-Si as backbones and some organic groups as side chains. They have been widely used in fields of electronic technology, aeronautics, military weapons, and architecture because of their extraordinary properties such as excellent electric insulativity, good resistance to heat, solvent, aging, weathering, and radiation.^{3–6} Nevertheless, because most usual silicone resins have backbones chains comprised entirely of siloxane units, they are susceptible to degrade to low-molecular weight cyclic siloxanes by “unzipping” and “random main chain scission” reactions,^{6–10} when exposed to temperatures above 250°C and

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high-energy irradiation for an extended period of time. As the circumstance deteriorates, such as the elevation of temperature and radiation, usual silicone resin cannot satisfy the practical needs, therefore resins with good mechanical property and corrosion resistance under high temperature and irradiation are increasingly demanded. For linear, high-molecular polysiloxanes, it has been reported that their thermal stability,¹¹⁻¹⁵ radiation resistance,^{9,16-18} and mechanical property^{19,20} can be significantly improved by incorporating aryl units into side chains, especially into Si-O-Si backbones, to replace siloxane units with some arylene groups. And these higher properties were ascribed to the presence of the rigid *p*-arylene groups, which would hinder the formation of volatile cyclic oligomers by intramolecular exchange of Si-O bonds.^{12,13,21} It is suggested that silicone resins containing some arylene units in the backbones will exhibit higher thermal stability, radiation resistance, and mechanical property than usual silicone resin with methyl and phenyl groups in side chains. Unfortunately, very few related studies have been reported. In this work, on the basis of usual silicone resins having Ar-Si unit in side chains, silicone resins with silphenylene units in backbones were synthesized by incorporating some Si-Ar-Si units into Si-O-Si main chains of these silicone resins, and then were characterized.

EXPERIMENTAL

Materials

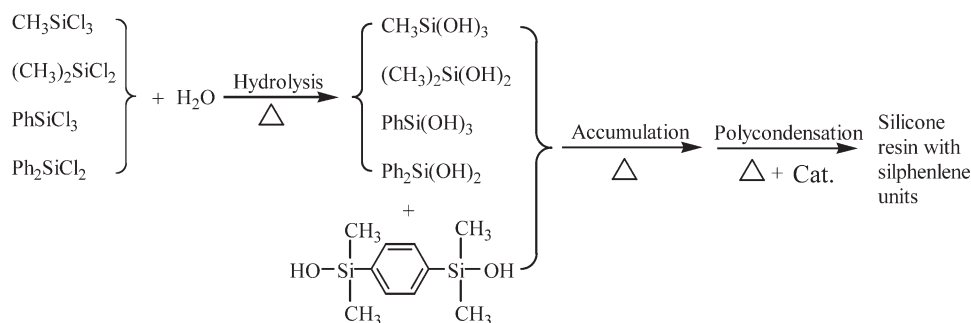
Methyltrichlorosilane, dimethyldichlorosilane, phenyltrichlorosilane, and diphenyldichlorosilane were obtained from Tianjin ShenTai Chemical Reagent

Co., Ltd., Tianjin institute of GangFu Chemistry and Hefei YaBang Chemical Co., Ltd. All the monomers were purified before use by fractional distillation under atmosphere or vacuum.

BHB whose purity is 97% was purchased from ABCR GmbH & Co. KG in Germany. The white crystals melted at 135°C. KH-CL was purchased from Institute of Chemistry Chinese Academy of Science. All other solvents were purchased from Beijing Chemical Works and used without further purification.

Synthesis of silicone resin with silphenylene units in backbones

Water, acetone, and xylene were poured into a three-necked round bottom flask equipped with a thermometer, a mechanical stirrer and a dropping funnel, and then heated to 40°C in water bath. Under a dry atmosphere, diphenyldichlorosilane, dimethyldichlorosilane, phenyltrichlorosilane, and methyltrichlorosilane were slowly added to xylene at room temperature. BHB was dissolved in THF and then mixed with the chlorosilanes. The aforementioned mixture of chlorosilanes was added slowly into the flask through the dropping funnel over a period of 1 h under vigorous stirring. After the addition of chlorosilanes, the hydrolyzate was stirred for another 5 h and then phase separated. The top organic phase was washed with water several times and separated. The silicone resin containing silphenylene groups in backbones was then obtained after accumulation and polycondensation of the organic phase. The synthetic scheme of silicone resin with silphenylene units in backbones is shown as follows:



Preparation of clear paints

The novel silicone resin was dissolved in xylene at 60 wt % and then KH-CL was added as curing reagent with the amount of 5 wt %. The clear paint of this novel silicone resin was applied on standard steel panels according to standard GB 1727-1992.

Mechanical property tests

After being heated at 280°C for 5 h, the adhesion power, hardness, flexibility, and shock resistance of the silicone resin clear paint were measured on with QFD, QBY, QTX, and QCJ according to standard GB/T 1720-1993, GB/T 1730-1993, GB/T 1731-1993, and GB/T 1732-1993, respectively.

TABLE I
Influence of R/Si, Ph/R, and Content of Silphenylene Units on Properties of Silicone Resin

Recipe			Mechanical property				Reaction time (h)	Experimental phenomena	Yields (%)
R/Si	Ph/R	BHB (%)	Shock resistance (kg cm)	Adhesion (Grade)	Hardness	Flexibility (mm)			
1.5	0.5	10	50	1	0.36	1	4.0	Ununiform film	96.0
1.4	0.5	10	50	1	0.41	1	2.9	Ununiform film	92.4
1.3	0.5	10	50	1	0.62	1	1.5	Uniform film	91.2
1.2	0.5	10	30	1	0.71	2	1.0	Uniform film	90.5
1.3	0.2	10	50	1	0.34	1	0.3	Many gels	62.3
1.3	0.3	10	50	1	0.39	1	0.3	A few gels	75.8
1.3	0.4	10	50	1	0.45	1	0.5	Ununiform film	91.6
1.3	0.6	10	50	1	0.79	1	4.5	Uniform film	95.3
1.3	0.5	5	20	2	0.74	3	3.0	Uniform film	93.7
1.3	0.5	15	50	1	0.55	1	1.0	Ununiform film	92.1
1.3	0.5	20	50	1	0.33	1	0.3	Ununiform film	92.8

Gel permeation chromatography

Gel permeation chromatography (GPC) was performed in duplicate on a WATERS-515 at 30°C eluted with THF.

FTIR spectroscopy

Fourier transform infrared (FTIR) spectra were measured on a Bruker Vector22 infrared spectrophotometer. Specimens were prepared as KBr pellet and were scanned at wavenumber range of 4000–400 cm^{-1} at 25°C.

$^1\text{H-NMR}$ spectroscopy

The $^1\text{H-NMR}$ spectra were obtained through a Bruker AV600 at ambient temperature. The silicone resin was dissolved in deuterated chloroform (CDCl_3).

$^{29}\text{Si-NMR}$ spectroscopy

The $^{29}\text{Si-NMR}$ spectra were recorded on a Bruker AV600 at ambient temperature. The silicone resin was also dissolved in deuterated chloroform (CDCl_3).

Thermogravimetry

The thermogravimetry (TG) analysis was carried out on NETZSCH TG 209 at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

Scanning electron microscope

The surface morphology of the silicone resin clear paints was studied by exploring a Hitach S-4700 scanning microscope.

Electrochemical impedance spectrum

The electrochemical impedance spectra (EIS) were recorded at open circuit potential using a Zahner IM6e a.c. impedance system and a three electrode configuration. A high surface area platinum mesh, saturated calomel electrode and the coated panel were used as counter, reference and working electrodes, respectively. The impedance measurements in all cases were carried out over a frequency range of 100 kHz to 0.1 Hz using a 10 mV peak-to-peak sinusoidal voltage.

RESULTS AND DISCUSSION

Proportion of materials

It is well known that the quality of silicon resins is determined by R/Si (the average number of organic groups linked to Si atom) and Ph/R (the content of phenyl in substituent organic groups). For silicone resin with silphenylene groups in backbones, the content of silphenylene units also plays an important role on the property. The effects of aforementioned three factors on properties of this novel silicone resin are shown in Table I. With the increase of R/Si, the shock resistance and reaction time increase, whereas hardness and film formability decrease. When Ph/R goes up, no obvious change has been observed for the shock resistance, adhesion power and flexibility, whereas the hardness and reaction time become higher. If more BHB is added, the shock resistance, adhesion power, and flexibility all improve, and the hardness, reaction time, and film formability reduce. As shown in Table I, yields of silicone resin with silphenylene units are all above 90% except when the Ph/R is lower than 0.3, and the loss is because part of hydrolyzate of silanes was solved by water when the organic phase was washed with water and some cyclic siloxane oligomers was distilled out when the organic phase was accumulated and polycondensed.

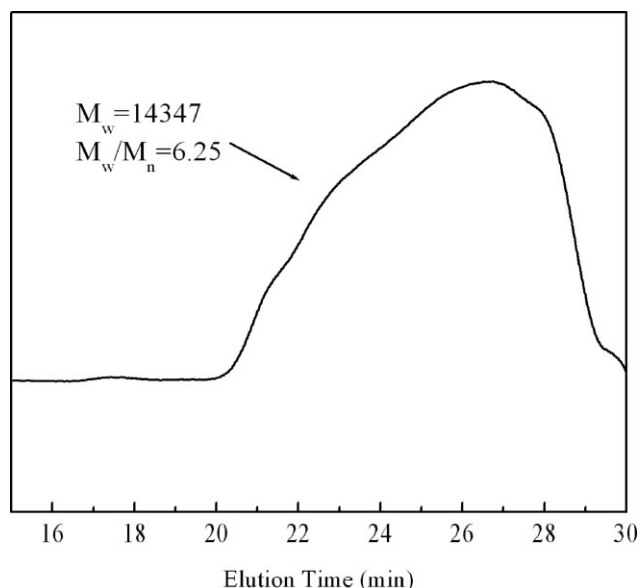


Figure 1 GPC profile of silicone resin with silphenylene groups in backbones.

Furthermore, apparent gels appear when the Ph/R is lower than 0.3 because the high content of silanes with three functional groups in the prescription makes their hydrolyzate self-polymerize rapidly to gels with high degree of crosslinking, and this is the reason why yields of silicone resin decrease to lower than 80%.

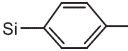
In a word, by investigating effects of aforementioned three factors on the performance of silicone resin with silphenylene units in backbones, it has been found that we can obtain silicon resin in high quality when R/Si, Ph/R, and BHB mol % are 1.3, 0.5, and 10%, respectively. The eventual products prepared under this condition can be applied to panels to form full and uniform films with good mechanical properties.

GPC analysis

Figure 1 shows the GPC profile of silicone resin containing silphenylene groups in backbones eluted with THF as an example. It is observed that the weight-average molecular weight of synthesized silicone resin is 14,347, indicating the formation of a uniform polymer and the absence of low-molecular weight species such as monomers and cyclic oligomers. It can also be seen that the molecular weight distribution (M_w/M_n) of synthesized silicone resin is 6.25, which is very appropriate for the film forming material of coating.

FTIR spectroscopy

The infrared spectra of (A) silicone resin containing silphenylene groups in backbones and (B) methyl-

phenylsilicone resin were shown in the Figure 2. In curve (B) of Figure 2, the peaks at wave number of 1261 cm^{-1} can be ascribed to Si-CH₃ groups. The absorption at 1593 cm^{-1} is due to the stretching vibration of phenyl groups in the Si-C₆H₅ structure, and the 1064 cm^{-1} absorption peak is caused by the Si-O stretching vibration in the Si-O-Si structure. The wide absorption peak appearing at $3200\text{--}3600\text{ cm}^{-1}$ belongs to Si-OH groups. Compared with curve (B), two special absorption peaks at 820 and 1134 cm^{-1} which are the typical characteristic absorption of si--si groups appear in curve (A), proving that silphenylene structure has been incorporated.^{22,23} In addition, the intensity of the peak for Si-OH groups is much higher.

¹H-NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a usually used technique for the qualitative and quantitative analysis of polymer, and it can also be effectively applied to polysiloxanes. The ¹H-NMR and ¹³C-NMR assignments and chemical shifts of characteristic absorption peaks of silarylene-siloxane polymers have been reported by Dvornic and Lai.^{14,24,25} Figure 3 shows ¹H-NMR spectra of (A) silicone resin with silphenylene units and (B) methylphenylsilicone resin. In curve (B) of Figure 3, the wide and strong absorption peaks at 0.10 and 7.25 ppm can be ascribed to CH₃ groups and C-H bonds in phenyl groups, respectively. Comparing curve (B) to (A), the peaks of CH₃ groups and C-H bonds in phenyl groups do not change obviously, but there are several new peaks appearing. The new absorption peaks at 0.32 and 7.54 ppm are the particular

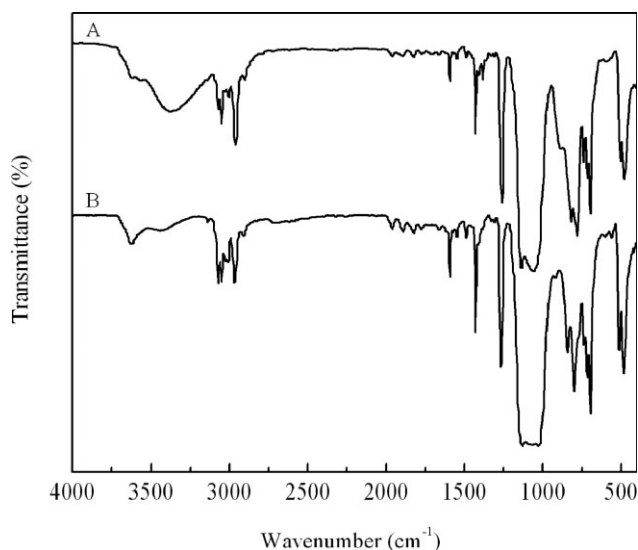


Figure 2 FTIR spectra of the silicone resin: (A) silicone resin with silphenylene units in backbones and (B) methylphenylsilicone resin.

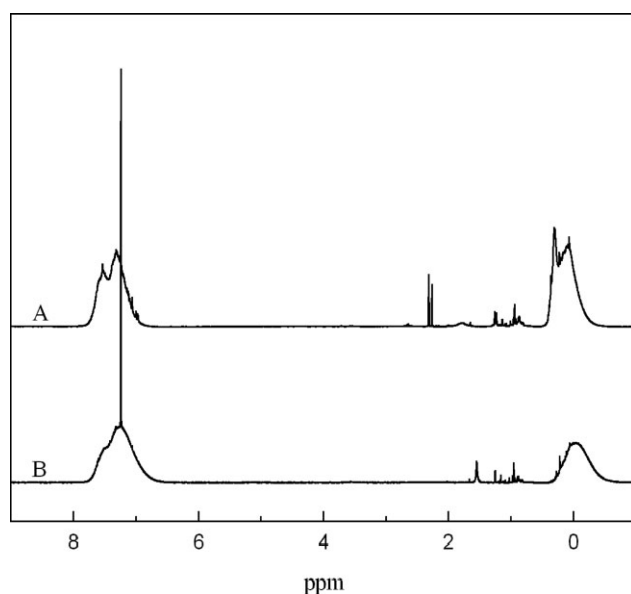


Figure 3 $^1\text{H-NMR}$ spectra of the silicone resin: (A) silicone resin with silphenylene units in backbones and (B) methylphenylsilicone resin.

absorption of silicone resin with silphenylene units, and are related to CH_3 groups in $-\text{OSi}(\text{CH}_3)_2\text{Ar}-$ structure and C-H bonds in $-\text{C}_6\text{H}_4-$ phenylene structure, respectively.²⁶

$^{29}\text{Si-NMR}$ spectroscopy

$^{29}\text{Si-NMR}$ is a well known powerful tool to characterize polysiloxanes. It is frequently used to determine the sequences structure of copolymer containing siloxanes²⁷⁻²⁹ and do kinetic analysis of

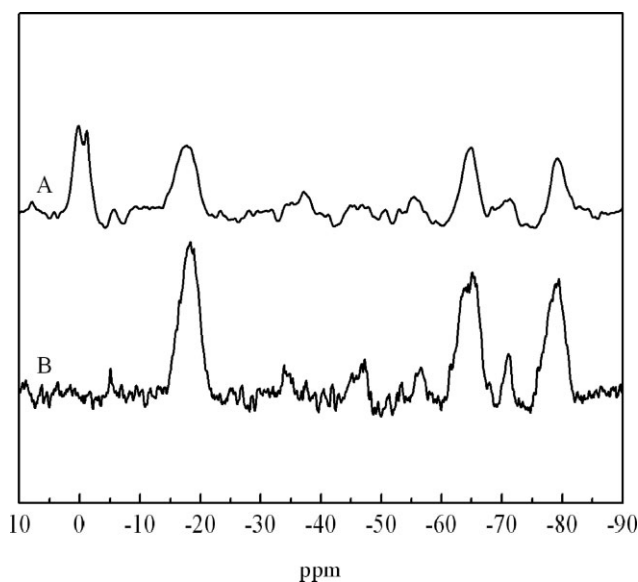


Figure 4 $^{29}\text{Si-NMR}$ spectra of the silicone resin: (A) silicone resin with silphenylene units in backbones and (B) methylphenylsilicone resin.

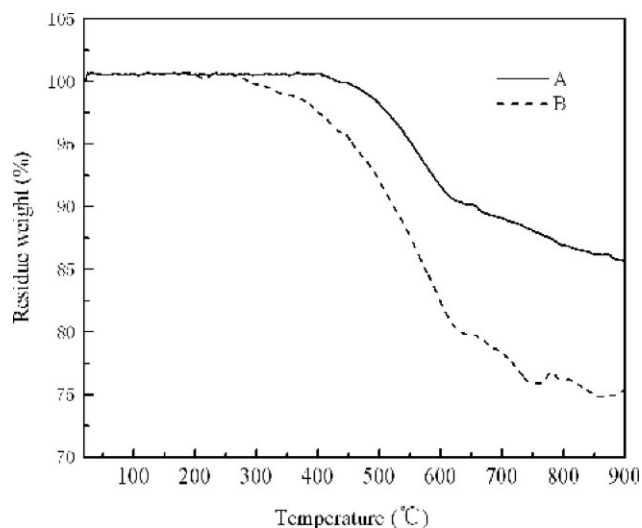


Figure 5 TG curves in nitrogen of silicone resin: (A) silicone resin with silphenylene units in backbones and (B) methylphenylsilicone resin.

silicon condensation polymers.²⁹ Figure 4 illustrates representative $^{29}\text{Si-NMR}$ spectra of (A) silicone resin with silphenylene units in backbones and (B) methylphenylsilicone resin. The silicon spectra of (B) methylphenylsilicone resin shows major absorption at -18.0 , -47.0 , -65.0 , and -79.0 ppm due to $(\text{Me})_2\text{SiO}$, $(\text{Ph})_2\text{SiO}$, $(\text{Me})\text{SiO}_{3/2}$, and $(\text{Ph})\text{SiO}_{3/2}$ groups, respectively.³⁰ The additional minor peaks at -34.0 , -55.0 , and -70.0 ppm, which are related to $\text{HO}(\text{Ph})_2\text{SiO}_{1/2}$, $(\text{HO})(\text{Me})\text{SiO}$, and $\text{HO}(\text{Ph})\text{SiO}$, are very weak because the polycondensation was completed so adequately that very few Si-OH groups had left. Compared with methylphenylsilicone resin, the $^{29}\text{Si-NMR}$ spectra of silicone resin containing silphenylene groups in backbones has another new major absorption peaks at -1.1 ppm which is attributed to $\text{Si}-\text{C}_6\text{H}_4-\text{Si}$ structure.

TG analysis

The thermogravimetric analysis of silicone resin with silphenylene units in backbones was performed from 20 to 900°C at a rate of 10°C min^{-1} under nitrogen atmosphere, and its results are shown in Figure 5 and Table II. In Figure 5, TG curve of

TABLE II
TG Analysis in Nitrogen for Silicone Resin

Silicone resin	Onset of degradation (°C)	Temperature for 5% weight loss (°C)	End of degradation (°C)	Residual weight (%)
A	500.3	553.8	609.3	85.6
B	455.2	457.5	587.6	75.2

A, Silicone resin with silphenylene units in backbones; B, methylphenylsilicone resin.

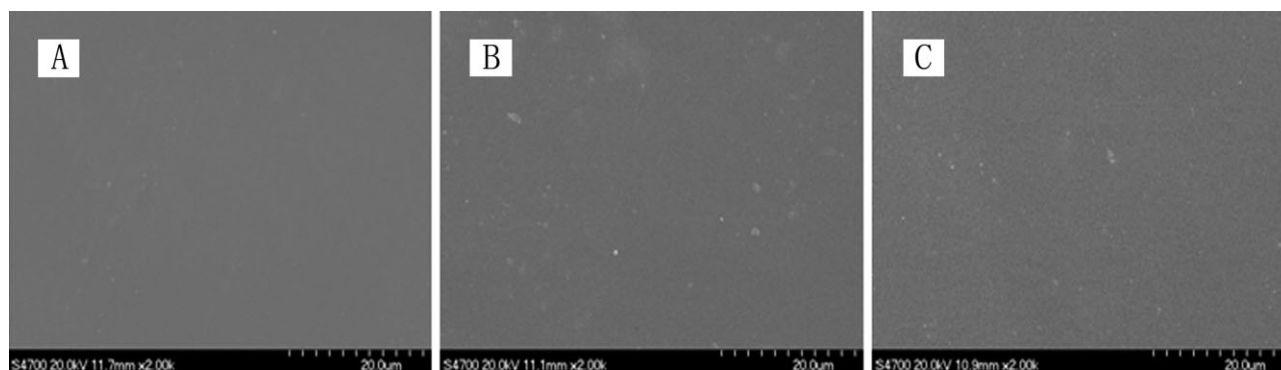


Figure 6 Scanning electron microscope of the clear paints of silicone resin with silphenylene units: (A) cured at room temperature, (B) heated at 280°C for 5 h, and (C) heated at 350°C for 5 h.

silicone resin with silphenylene units illustrates that it starts to lose its weight when the temperature reaches 330°C, and its mass loss is <3.0% at the temperature of 500°C. Compared with usual methylphenylsilicone resin, the onset and end of degradation and temperature for 5.0% weight loss of this novel silicone resin all increase by a lot, and its residual weight increases by almost 15.0% which is indicated in Table II.

It is well known that silicone resin degrades to volatile low-molecular weight cyclic siloxanes by a two-step process in nitrogen, and these two steps are “unzipping” reactions induced by silanol terminal groups and “random main chain scission” reactions, respectively. The rigid *p*-arylene groups which exist in silicone resin with silphenylene units, would hinder the formation of volatile cyclic oligomers by intramolecular exchange of Si—O bonds.^{12,13,21} This is the reason why silicone resin with silphenylene units is more thermally stable than usual methylphenylsilicone resin. At the temperature of 900°C, almost all silicone resin degrades to SiO₂. As less sil-

icon element of silicone resin with silphenylene units degrades into volatile cyclic oligomers than that of usual methylphenylsilicone resin, more SiO₂ of silicone resin with silphenylene units at the temperature of 900°C is left. In a word, this novel silicone resin with silphenylene units in backbones exhibits good thermal stability.

Scanning electron microscope

Figure 6 shows the surface morphology of clear paints of silicone resin with silphenylene units before and after being heated at different temperature. In picture (A) of Figure 6, the synthesized silicone resin can form full and uniform films with no objection when it is applied to panels. Comparing picture (B) and (C) with (A), there are no obvious change about films of silicone resin clear paints, which indicates that heat below 350°C could not damage the surface morphology of this novel silicone resin clear paint.

Electrochemical impedance spectrum

EIS is an effective technique for evaluating organic coatings.³¹ It is usually used to study the corrosion resistance and corrosion destruction mechanism of organic coatings by investigating their a. c. impedance over a wide range of frequency.³² Figure 7 shows the Bode plots of clear paints of silicone resin with silphenylene units after being heated at 280°C for 5 h. In Figure 7, $\lg Z$ and $\lg f$ is in linearity relation, and the phase angle is nearly -90° in a wide range of frequency, which demonstrates that silicone resin clear paint is an isolating layer with high-electrical resistance and low-electrical capacitance.³³

CONCLUSION

A novel silicone resin with silphenylene units in backbones has been synthesized by hydrolysis-polycondensation of BHB with chlorosilanes. The

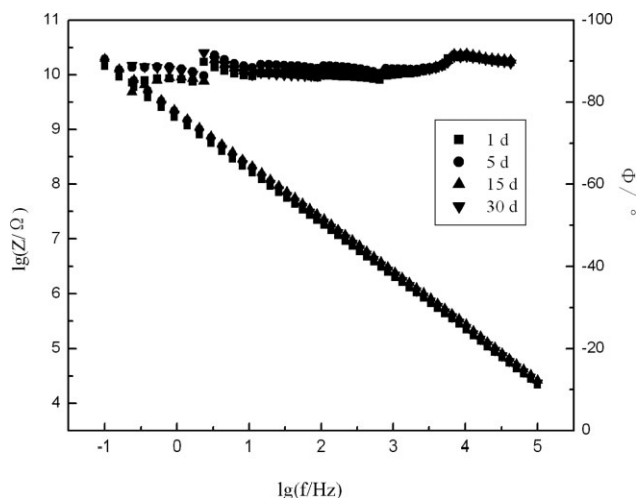


Figure 7 Bode plots for clear paints of silicone resin with silphenylene units after being heated at 280°C for 5 h.

structure and property of this novel silicone resin were characterized. The results show that the silphenylene units have been incorporated into the polymer of silicone resin. This silicone resin exhibits excellent heat resistance with the onset degradation temperature of 500.3°C, the 5% weight loss temperature of 554.8°C, the end degradation temperature of 609.3°C, and residual weight of 85.6% at 900°C. Also, it has good resistance of corrosion proved by EIS analysis. This procedure of synthesizing silicone resin with silphenylene units in backbones would be useful to prepare a film forming material of anti-corrosion coating with good resistance of heat and irradiation, and adhesion power.

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