

# Polysiloxane Resins Modified by Bisglycidyl Calix[4]arene: Preparation, Characterization, and Adsorption Behavior toward Metal Ions

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Received 7 November 2003; accepted 2 June 2004

DOI 10.1002/app.21318

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Two porous polysiloxane resins were prepared by the ring-opening polycondensation of epoxy groups of bisglycidyl calix[4]arene with amino groups of polysiloxane microparticles that were prepared by the sol-gel method of cohydrolysis and condensation from  $\gamma$ -aminopropyltriethoxysilane (RSC-I) or 4-aza-6-aminohexyltriethoxysilane (RSC-II) with tetraethylorthosilicate. The resins were characterized by elemental analysis, DR-Fourier transform infrared spectra, Raman scattering spectra, scanning electron micrographs, and thermogravimetric analysis. The porous polysiloxane resins exhibited high thermostability

and preconcentration potential for divalent Cu, Pb, and Hg ions, especially for the trivalent auric ion, relative to both the special cavity and the network structure of polysiloxane resins. The nitrogen atoms in resins also exert some auxiliary action. The enthalpy of the adsorption of two resins toward trivalent auric ion was evaluated to be 6.83 and 8.04 kJ/mol for RSC-I and RSC-II, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1310–1318, 2005

**Key words:** polysiloxanes; FTIR; thermogravimetric analysis (TGA); bisglycidyl calix[4]arene; adsorption

## INTRODUCTION

Polysiloxane resins exhibit nonswelling property and good diffusivity of solutes, excellent mechanical stability, and can be recovered and reused easily. For this reason, polysiloxane resins modified by organofunctional groups have been widely used as molecular imprinting materials<sup>1–3</sup> and adsorbents,<sup>4,5</sup> in analytical chemistry and separation science, as catalyst supports in catalysis and organic synthesis.<sup>6,7</sup> Polysiloxane resins can be prepared by a sol-gel technology based on cohydrolysis and polycondensation of functional organosilicone monomer with alkoxy silane, or sol-gel microparticles modified by organofunctional groups. Katz et al.<sup>8</sup> prepared the bulk and microporous polysiloxane resins by sol-gel, and found that the cavity with spatially organized functional groups covalently anchored to the pore walls. The polysiloxane resins could act as a shape-selective base catalyst. Markowitz and coworkers<sup>9</sup> reported that the surface of silica particles was modified by the template technique, and the silica particles of robust surface containing catalytic active sites exhibited very high catalytic activity in the hydrolysis reaction of substrate. Akiyama et al.<sup>10</sup> prepared polysiloxane modified by the copolymerizing of

acryloyl cyclodextrin with vinylated silica-gel in the presence of template molecule in water. They found that the polysiloxane is an eminent stationary phase for HPLC in water. Recently, Matsumoto et al.<sup>11</sup> reported the preparation of polyorganosiloxane spherical particles by a sol-gel method, whose average size was related to reaction condition and reaction time.

On the other hand, calixarenes, the third-generation host molecules after crown ethers and cyclodextrins, possess cavity-shaped cyclic molecules prepared by the ring-closing condensation of *p*-*tert*-butyl phenol and formaldehyde under alkaline conditions. Calixarenes and its derivatives exhibit outstanding complex ability toward ions and organic molecules.<sup>12,13</sup> In a previous work, the preparation and adsorption behavior of calix[4]arene-containing polysiloxane resins were described.<sup>4</sup> These polysiloxane resins were prepared by the cohydrolysis and the polycondensation of calix[4]arene-containing organosiloxane monomers and tetraethylsiloxane. The polysiloxane resins exhibit high thermostability and special adsorption behavior toward nitrogen under elevated temperature. The amount of calix[4]arene units loaded by this method obtaining the polysiloxane resins is high (0.75–0.85 mmol/g resin), but some calixarene units are trapped in the resins. So the ratio of the adsorption capacity of the resins toward metal ions versus calixarene units is low.<sup>4</sup> In this article we report two porous polysiloxane resins modified by the ring-opening

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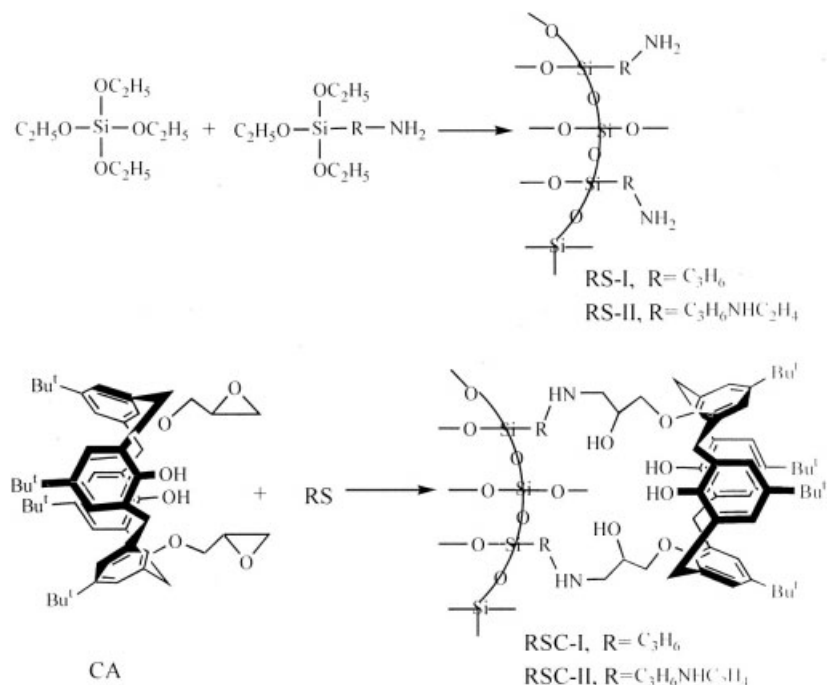


Figure 1 Synthetic route of polysiloxane resins modified by bisglycidyl calix[4]arene.

polycondensation of the epoxy groups of bisglycidyl calix[4]arene and the amino groups of polysiloxane microparticles that were prepared by the cohydrolysis and polycondensation of  $\gamma$ -aminopropyltriethoxysilane or 4-aza-6-aminoheptytriethoxysilane and tetraethylorthosilicate. They were characterized by elemental analysis, diffuse reflectance tool (DR)–Fourier transform infrared spectra, Raman scattering spectra, scanning electron micrographs, and thermogravimetric analysis. The porous polysiloxane resins exhibit high thermostability and preconcentration potentials for divalent Cu, Pb, and Hg ions, especially for trivalent Au ions. The reaction route and possible structure of polysiloxane resins are shown in Figure 1.

## EXPERIMENTAL

### Materials and chemicals

1-Chloro-2,3-epoxypropane was purified by treatment with a molecular sieve and distilled before use, supplied by Resin Factory of the Hunan Yueyang Chemical Industry Co. (China). 3-Aminopropyltriethoxysilane, 4-aza-6-aminoheptytriethoxysilane, and tetraethylorthosilicate were supplied by Chemical Plant of Wuhan University (China). *p*-*tert*-Butyl-calix[4]arene was synthesized by the reaction of *p*-*tert*-butylphenol with formaldehyde-aqueous solution in the presence of KOH under nitrogen atmosphere, yield: 55%, m.p. >300°C; [Lit.,<sup>12</sup> 50%]. The other reagents were supplied by Shanghai Chemical Reagents Co. (Shanghai,

China). All reagents were analytical-reagent grade and used without further purification.

### Measurements

Elemental analysis was carried out by a 1106 elemental autoanalysis apparatus (Carlo Erba Strumentazione, Milan, Italy). The infrared spectra were recorded on a 670 FTIR Fourier transform infrared spectrometer by a diffuse reflectance technique (Nicolet Analytical Instruments, Madison, WI). Raman scattering spectra were determined by a 670 FTIR–Raman united spectrometer by a Nd: YVO<sub>4</sub> laser source at a wavelength of 1064 nm (9398 cm<sup>-1</sup>) (Nicolet Analytical Instruments). A <sup>1</sup>H-NMR spectrum was obtained on an ARX-500 spectrometer (Bruker, Dormstadt, Germany). The mass spectrum was recorded on a ZAB 3FHF mass spectrometer by fast atom bombardment (FAB-MS, VG Analytical, Manchester, UK). Scanning electron micrographs (SEM) were performed with an X-650 scanning electron microscope (Hitachi, Osaka, Japan). Thermogravimetric analysis (TG) was carried out on an STA 409C thermal analyzer (Netzsch-Gerätebau GmbH, Bararia, Germany). The runs were performed at a heating rate of 20°C/min from 30 to 700°C in an atmosphere of dry nitrogen (80 mL/min). The concentrations of metal ions were determined by titration or by a 180-80 atomic absorption spectrometer (AAS, Hitachi, Japan).

### Preparation of polysiloxane microparticles

The 3-aminopropyltriethoxysilane (6.6 g, 30 mmol), tetraethylorthosilicate (6.3 g, 30 mmol), toluene (30 mL), and potassium hydroxide (1.2 mL, 1.0 mol/L) were added to a 100-mL three-neck round flask equipped with a magnetic stirrer. The mixture was stirred for 5 h at room temperature, and then refluxed at high temperature for 3 h under nitrogen atmosphere. After 2 mL distilled water was added to the flask, the reactant was stirred continuously at reflux temperature for 3 h. The increase of the reactant viscosity and the formation of gel were observed, and the sample turned into a light yellow solid after cooling. The solid was filtrated and washed successively with acetone, distilled water, acetone, toluene, and acetone. Subsequently, the product was dried at 110°C under reduced pressure. Aminopropylpolysiloxane microparticles (RS-I, Fig. 1) were obtained as a light yellow powder, 6.1 g; yield: 91.0%.

The 4-aza-6-aminoethylpolysiloxane microparticles (RS-II, Fig. 1) were prepared similarly by using 4-aza-6-aminoethyltriethoxysilane (7.9 g, 30 mmol) instead of the 3-aminopropyltriethoxysilane, a light yellow powder, 7.5 g; yield: 94.0%.

### Preparation of bisglycidyl calix[4]arene

The 1,3-bisglycidyl *p*-tert-butylcalix[4]arene [CA, Fig. 1] was prepared according to procedures reported in the literature<sup>14,15</sup> by the reaction of *p*-tert-butylcalix[4]arene with 1-chloro-2,3-epoxypropane in dry toluene and in the presence of anhydrous potassium carbonate as the base. The mixture was refluxed for 6 h. After filtration and evaporation of solvent under reduced pressure, the residue was washed with water and purified by column chromatograph (silica, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 1 : 2). The bisglycidyl *p*-tert-butylcalix[4]arene was obtained in 60% yield, m.p. 278–281°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δppm): 0.96, 0.97 (s, 9H each, ArCMe<sub>3</sub>), 1.28 (s, 18H, ArCMe<sub>3</sub>), 2.96 (m, 2H, 3-GlyH), 3.02, 3.06 (m, 1H each, 3-GlyH), 3.31 and 4.32 (AX, 4H, J = 12.7 Hz, ArCH<sub>2</sub>Ar), 3.33 and 4.30 (AX, 4H, J = 12.6 Hz, ArCH<sub>2</sub>Ar), 3.54 (m, 2H, 2-GlyH), 4.05 (m, 2H, 1-GlyH), 4.26 (m, 2H, 1-GlyH), 6.79 and 6.80 (AB, 4H, J = 2.6 Hz, ArH), 7.03 and 7.04 (AB, 4H, J = 2.6 Hz, ArH), 7.17 (s, 2H, ArOH). FAB-MS: *m/z* 760 (RI 70, M<sup>+</sup>). ANAL. calcd (%) for C<sub>50</sub>H<sub>64</sub>O<sub>6</sub>: C, 78.91; H, 8.48. Found (%): C, 78.51; H, 8.34.

### Preparation of polysiloxane resins modified by bisglycidyl calix[4]arene

The polysiloxane resin modified by bisfunctional molecule was prepared by the ring-opening polycondensation of the epoxy groups of bisglycidyl *p*-tert-

butylcalix[4]arene and the amino groups of polysiloxane microparticles. The bisglycidyl *p*-tert-butylcalix[4]arene (CA, 4.6 g, 6 mmol), aminopropylpolysiloxane microparticles (RS-1, 2.7 g, 14.9 mmol amino groups) and anhydrous acetonitrile (20 mL) were added to a 50-mL three-neck round flask equipped with a magnetic stirrer. The mixture was stirred for 48 h at 50°C under nitrogen atmosphere. The product was filtrated and washed successively with toluene, acetone, distilled water, and acetone. Subsequently, the product was extracted with toluene for 24 h under nitrogen atmosphere, washed by acetone, and dried at 110°C under reduced pressure. The polysiloxane resin modified by bisglycidyl calix[4]arene (RSC-1, Fig. 1) was obtained as a light yellow powder, 4.7 g; yield: 64.4%.

The polysiloxane resin modified by bisglycidyl calix[4]arene (RSC-II, Fig. 1) was prepared similarly by using the 4-aza-aminoethylpolysiloxane microparticles (RS-II, 3.2 g, 14.2 mmol amino groups) instead of the aminopropylpolysiloxane microparticles (RS-I), yielding a light yellow powder, 6.2 g; yield: 79.5%.

### Adsorption of resin toward metal ions

Adsorption behavior of polysiloxane resins toward metal ions was examined. The resin (*W* = 0.02 g) and metal ion solution (*V* = 10 mL) of a known concentration (*C*<sub>0</sub>) were placed in a 25-mL closed flask. A series of such flasks was shaken at a constant speed (100 times/min) and a specified constant temperature for 2 h. The metal ion concentration (*C*<sub>*e*</sub>) of liquid phase was determined by titration with EDTA for Cu(II), Pb(II), and Hg(II), and with AAS for Mg(II) and Au(III). The adsorption capacity (*Q*) was calculated as follows:

$$Q = (C_0 - C_e)V/W \text{ (mmol/g)} \quad (1)$$

## RESULTS AND DISCUSSION

### The elemental analysis of resins

The data of the elemental analysis of active xerogels (RS-I, RS-II) and polysiloxane resins (RSC-I, RSC-II) are presented in Table I. The data of Table I indicate that 1 g polysiloxane microparticle (RS-I and RS-II) loaded 5.51 and 8.85 mmol nitrogen, respectively. The data of Table I also show that 1 g polysiloxane resin (RSC-I and RSC-II) loaded 0.50 and 0.51 mmol calixarene units, respectively. The conversions of amino groups of polysiloxane microparticles RS-I and RS-II are 18.1 and 23.1%, respectively. The conversions of bisglycidyl *p*-tert-butylcalix[4]arene are 39.2 and 52.7% for RSC-I and RSC-II, respectively, which implies that most amino groups included in polysiloxane micro-

TABLE I  
Elemental Analysis of Resins

Resin	Yield (%)	Elemental analysis (%)			Loaded N / resin (mmol/g)	Loaded CA/resin (mmol/g)
		C	H	N		
RS-I	91.0	19.74	5.59	7.71	5.51	—
RS-II	94.0	26.46	7.20	12.39	8.85	—
RSC-I	64.4	40.38	6.45	3.97	2.84	0.50
RSC-II	79.5	42.35	7.39	5.59	3.99	0.51

particles did not participate in the reaction with bisglycidyl calix[4]arene.

#### DR-FTIR spectra analysis of CA, RS-I, RS-II, and RSC-II

The DR-FTIR spectra of CA, RS-I, RS-II, and RSC-II are shown in Figure 2. The assignments of main vibration absorption bands are presented in Table II.<sup>20–22</sup> The data of Table II show that the characteristic absorption bands of the epoxy group of CA appear at 1293 and 942  $\text{cm}^{-1}$ , and the bands disappear in the IR spectrum of RSC-II. The band of C—O stretching vibration (1197  $\text{cm}^{-1}$ ) of CA is strong. The bands of Si—O—Si stretching vibration (about 1100  $\text{cm}^{-1}$ ) of RS-I, RS-II, and RSC-II are strong and broad, whereas the intensity of bands of Si—C stretching vibration (about 800  $\text{cm}^{-1}$ ) is weak. The bands of stretching vibration of C—O and Si—O of RSC-II overlapped and shifted to a higher wavenumber (1126  $\text{cm}^{-1}$ ) than that of RS-I (1090  $\text{cm}^{-1}$ ) and RS-II (1078  $\text{cm}^{-1}$ ). In the IR spectrum of RSC-II, the absorption bands of C—H stretching vibrations and C=C stretching vibrations of CA aromatic ring (3039, 1591  $\text{cm}^{-1}$ ) are not charac-

teristic, which can be attributed to the overlapping with the bands of O—H stretching vibration (3290  $\text{cm}^{-1}$ ) and bending vibration (1654  $\text{cm}^{-1}$ ) of  $\text{NH}_2$  groups, respectively. Figure 2 also shows that bending vibration bands of  $\text{CH}_2$  and  $\text{CH}_3$  groups are presented at about 1460  $\text{cm}^{-1}$  for all samples determined. The intensity of  $\text{CH}_2$  bending vibration band of RS-II is higher than that of RS-I. This is related to the 4-aza-6-aminoethylpolysiloxane structure (RS-II, Figure 1).

#### Raman spectra analysis of CA, RS-I, RS-II, and RSC-II

The Raman scattering spectra of CA, RS-I, RS-II and RSC-II are shown in Figure 3. The assignments of main bands are presented in Table III.<sup>20–22</sup> The data of Table III show that the C—H stretching vibration band of aromatic ring of RSC-II shifts to a higher wavenumber (3093  $\text{cm}^{-1}$ ) compared with that of CA (3019  $\text{cm}^{-1}$ ), and the intensity of the band decreases. The characteristic bands of CA epoxy group (1251 and 925  $\text{cm}^{-1}$ ) disappear in the Raman spectrum of RSC-II, which implies that the reaction of the ring-opening condensation of bisepoxy functional groups of CA

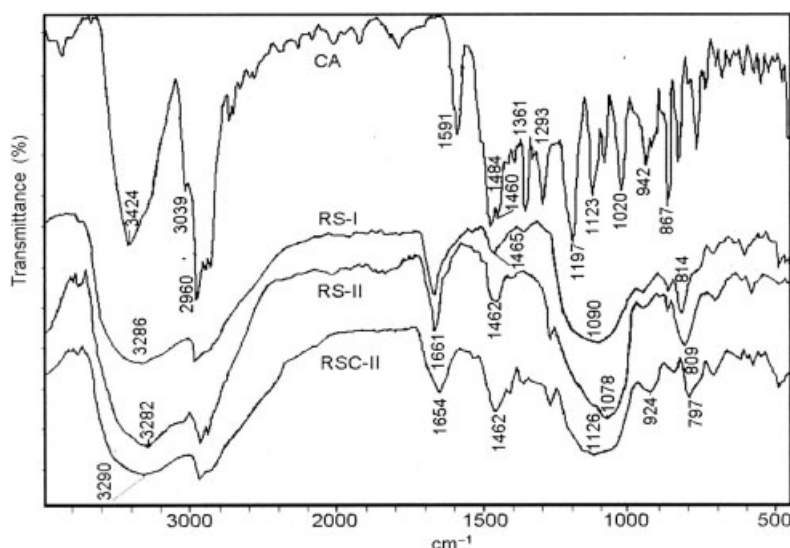


Figure 2 DR-FTIR spectra of CA, RS-I, RS-II, and RSC-II.

TABLE II  
Vibration Bands of CA, RS-I, RS-II, and RSC-II

Vibration ( $\text{cm}^{-1}$ )	$\nu_{\text{O-H}}$ + $\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$ (aromatic ring)	$\nu_{\text{C-H}}$	$\delta_{\text{NH}_2}$	$\nu_{\text{C=C}}$ (aromatic ring)	$\delta_{\text{C-H}}$	$\nu_{\text{as}}, \nu_{\text{s}}$ (epoxy group)	$\nu_{\text{Si-O-Si}}$ + $\nu_{\text{C-O}}$	$\nu_{\text{Si-C}}$
CA	3424 ( $\nu_{\text{O-H}}$ )	3039	2960	—	1591 1484	1460	1293 $\nu_{\text{as}}$ 942 $\nu_{\text{s}}$	1197 ( $\nu_{\text{C-O}}$ )	867 ( $\delta_{\text{C-H}}, \text{Ar}$ )
RS-I	3286	—	2955	1654	—	1465	—	1090	814
RS-II	3282	—	2942	1661	—	1462	—	1078	809
RSC-II	3290	—	2956	1654	—	1462	—	1126	797

with  $\text{NH}_2$  functional groups of RS-II has occurred. In Raman spectra of RS-I and RS-II, the bending vibration bands of  $\text{NH}_2$  ( $1657, 1655 \text{ cm}^{-1}$ ) are similar in intensity, but the intensity of the bending vibration band of  $\text{NH}_2$  of RSC-II ( $1658 \text{ cm}^{-1}$ ) is substantially decreased, implying that the amount of amino groups on the surface of RSC-II was clearly decreased because of the reaction of amino functional groups with bisepoxy functional groups. The increase of the relative intensity bending vibration bands ( $\sim 1450 \text{ cm}^{-1}$ ) of  $\text{CH}_2$  and  $\text{CH}_3$  groups is obvious compared with the corresponding IR absorption bands (Fig. 2). The band of C—H bending vibration of  $\text{CH}_2\text{—Si}$  ( $\sim 1415 \text{ cm}^{-1}$ ) does not exist in the Raman spectrum of CA. The bands of Si—O and C—O stretching vibration are medium, but the bands of the corresponding IR spectrum are very strong. The bands of Si—O—Si symmetric stretching vibration of RS-I and RS-II locate at about  $485 \text{ cm}^{-1}$ , which shifts to  $476 \text{ cm}^{-1}$  for RSC-II. The strong bands presented in the range from  $3000$  to  $2800 \text{ cm}^{-1}$  can be attributed to saturated C—H stretching vibration bands. The  $\nu_{\text{C=C}}$  of aromatic ring in RSC-II shifts to lower wavenumber ( $1591 \text{ cm}^{-1}$ ) than that of CA ( $1597 \text{ cm}^{-1}$ ).

## SEM

SEM micrographs of the surface morphology of the polysiloxane resin modified by bisglycidyl *p-tert-butyl* calix[4]arene are presented in Figure 4. Figure 4 shows that the polysiloxane resin consists of particles of irregular shape, and about  $100$  to  $300 \mu\text{m}$  in size. The polysiloxane resins have abundant porous structure, and the size of pores on the surface of polysiloxane resins is about  $4$  to  $10 \mu\text{m}$ .

## Thermogravimetric analysis of CA, RSC-I, and RSC-II

Thermogravimetry (TG) and the differential thermogravimetry (DTG) curves of CA, RSC-I, and RSC-II are presented in Figure 5(a), (b), and (c), respectively. Figure 5 shows that there is no weight loss until  $380, 394,$  and  $390^\circ\text{C}$  for CA, RSC-I, and RSC-II, respectively. The starting temperature of weight loss for CA is lower than that of either RSC-I or RSC-II. DTG curves show that the temperature of the fastest weightless rate occurs at  $433, 485,$  and  $480^\circ\text{C}$  for CA, RSC-I, and RSC-II, respectively, which implies that the

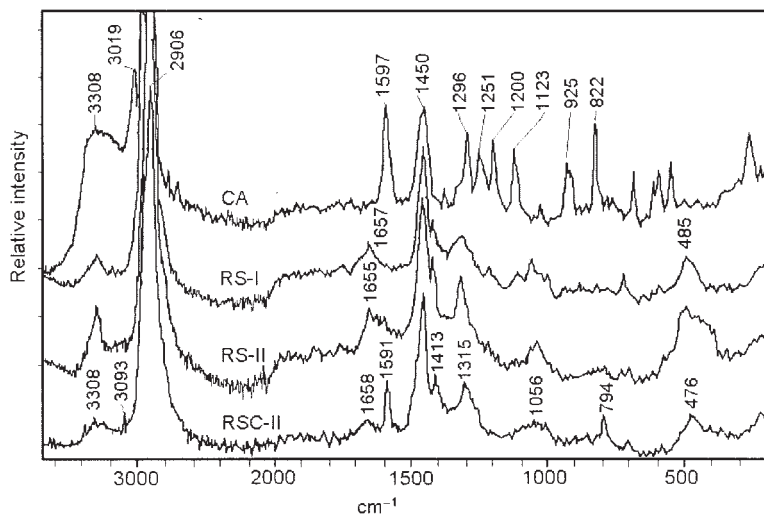


Figure 3 Raman scattering spectra of CA, RS-I, RS-II, and RSC-II.

TABLE III  
Raman Shift of CA, RS-I, RS-II, and RSC-II

Vibration ( $\text{cm}^{-1}$ )	$\nu_{\text{O-H}}$ + $\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$ (aromatic ring)	$\nu_{\text{C-H}}$	$\delta_{\text{NH}_2}$	$\nu_{\text{C-C}}$ (aromatic ring)	$\delta_{\text{C-H}}$	$\nu_{\text{as}}, \nu_{\text{s}}$ (epoxy group)	$\nu_{\text{Si-O-Si}}$ $\nu_{\text{as}}$	$\nu_{\text{Si-O-Si}}$ $\nu_{\text{s}}$
CA	3308	3019	2960	—	1597	1450	1251/ $\nu_{\text{as}}$	1123	867
RS-I	( $\nu_{\text{O-H}}$ ) 3295	—	2955	1657	—	1465	925/ $\nu_{\text{s}}$	( $\nu_{\text{C-O}}$ ) 1062	( $\delta_{\text{C-H}}, \text{Ar}$ ) 485
RS-II	3300	—	2942	1655	—	1462	—	1050	486
RSC-II	3308	3093	2956	1658	1591	1462	—	1056	476

thermal stabilities of RSC-I and RSC-II are higher than that of CA. The DTG curves also indicate that the weight losses of RSC-I and RSC-II are step by step from 380 to 650°C, and the rates of the fastest weight loss for RSC-I and RSC-II are much lower than that of CA. At 650°C the weight losses of CA, RSC-I, and RSC-II are 62, 28, and 25%, respectively, which also indicates that the thermal stability of both polysiloxane resins modified by bisglycidyl calix[4]arene is close to, but a little higher than, that of CA. TG curves also show that the weight is increased with increasing temperature until 321.7, 216.0, and 231.4°C for CA, RSC-I, and RSC-II, respectively. The weight increases by 7.5% at 321.7°C, 10.0% at 216.0°C, and 11.6% at 231.4°C over the initial weight under nitrogen atmosphere (80 mL/min) for CA, RSC-I, and RSC-II, respectively. The value of increase in weight is lower than that reported in the literature.<sup>4</sup> It is clear that the adsorption ability of the polysiloxane resins toward nitrogen is related to both the network structure and the amount of calix[4]arene units loaded in the resins under an elevated temperature.

#### Adsorption behavior of resins toward metal ions

The adsorption capacities ( $Q$ ) of RSC-I and RSC-II toward divalent magnesium, copper, lead, and mer-

cury ions, and trivalent auric ion were measured, respectively. The experimental results shown in Figure 6 indicate that RSC-I and RSC-II have poor adsorption ability toward alkaline earth metal magnesium ion, and exhibit higher adsorption capacity toward divalent copper, lead, mercury ions, and trivalent auric ion. The adsorption capacity for trivalent auric ion is the highest among all these metal ions. Figure 6 also indicates that the adsorption capacity of RSC-II for all these metal ions is higher than that of RSC-I. Besides the contribution of both the network structure of resin and the special cavity of calix[4]arene, the adsorption ability of resin toward metal ion is related to the amount of nitrogen atoms in the resins.

It is reported<sup>4</sup> that 1 g of resins prepared by the reaction of calixarene-containing organosiloxane monomer and tetraethoxysilane loaded 0.75–0.85 mmol calixarene units. The amount of calixarene units loaded is higher than that of RSC-I and RSC-II (~0.5 mmol/g resin), but the adsorption capacity of the organosiloxane resins toward metal ions, such as Cu(II), Pb(II), Hg(II), and Au(III), is much lower than that of RSC-I and RSC-II resins. This can be attributed to the contribution of the network structure on the surface of RSC-I and RSC-II resins. At the equilibrium adsorption, the adsorption capacities of RSC-I and RSC-II toward Au(III) are 0.35 and 0.48 mmol/g, respectively.

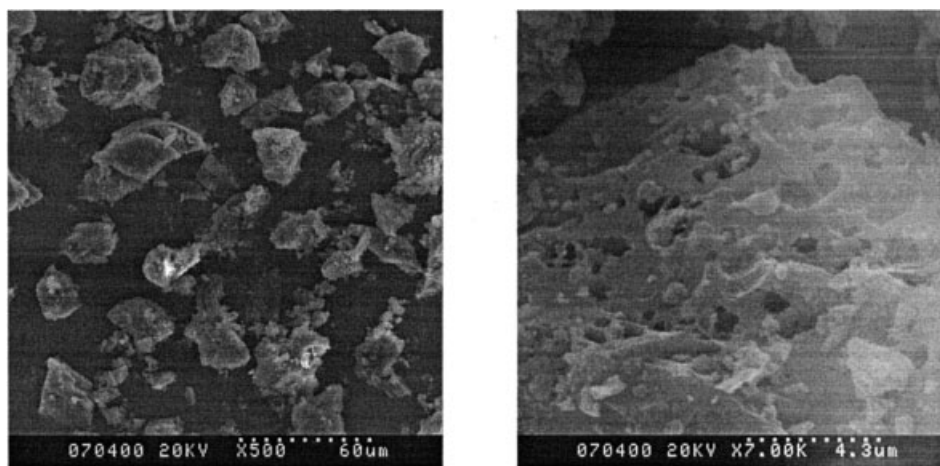


Figure 4 SEM micrographs of polysiloxane resin (RSC-II).

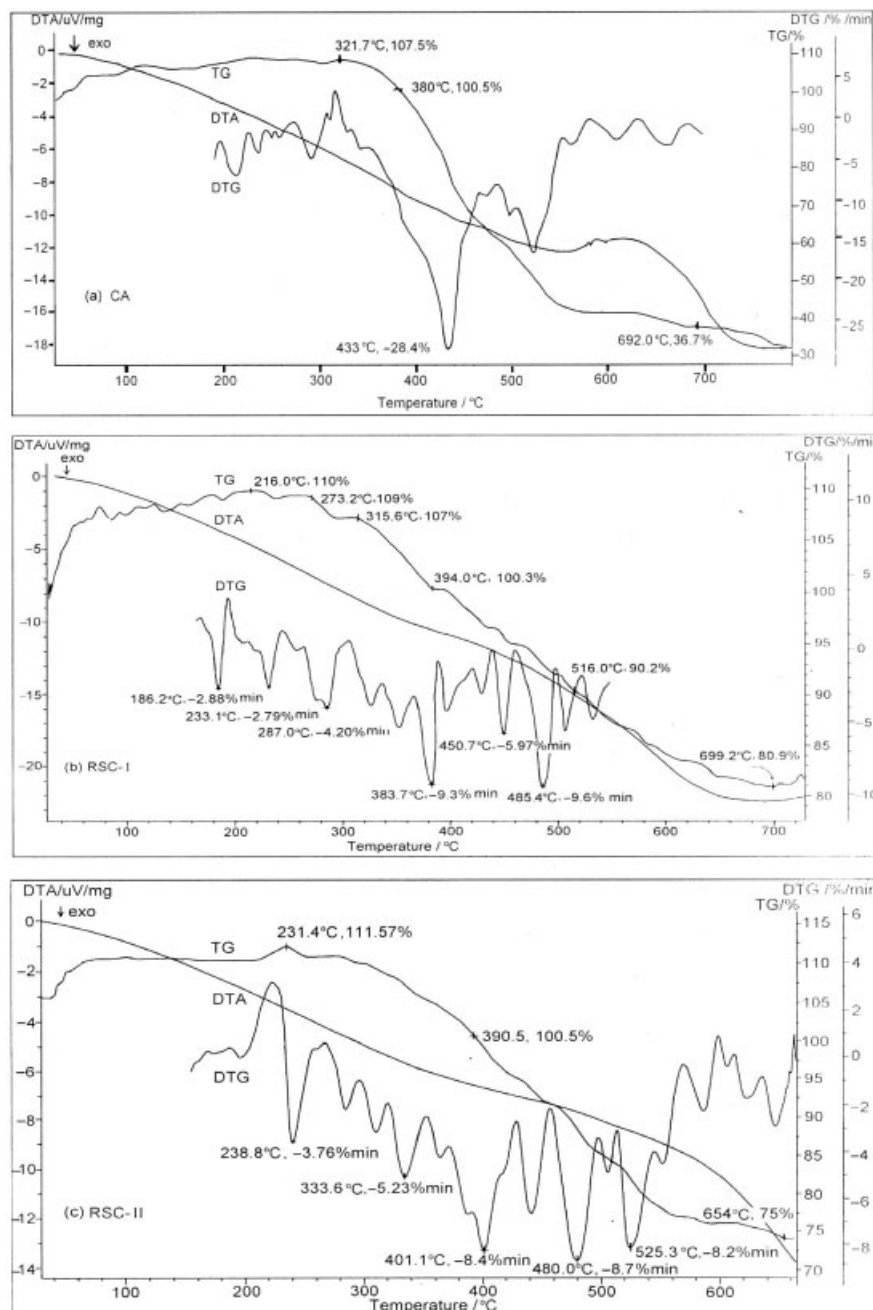


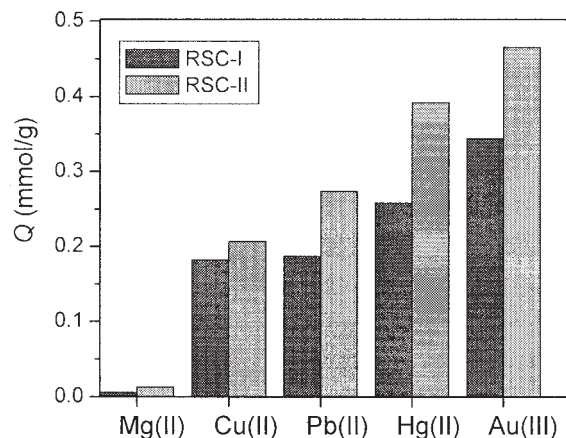
Figure 5 TG and DTG analyses of (a) CA, (b) RSC-I, and (c) RSC-II.

### Adsorption behavior of resins for trivalent auric ion

The concentration of trivalent auric ion in the solution was determined by using a constant concentration of Au(III) ion ( $C_0 = 0.2$  mmol/L) and resin ( $C_R = 2.0$  g/L). The experimental data plotted in Figure 7 indicate that the two resins have a high initial adsorption rate under the experimental condition, and the adsorption equilibrium was almost reached in about 1 h. Figure 7 also shows that the equilibrium adsorption capacity of RSC-II is higher than that of RSC-I, which is related to the

higher nitrogen content of RSC-II resin. It also implied that adsorption ability of resins toward trivalent auric ion is not only related to the network structure modified by bisglycidyl calix[4]arene and the special cavity, but the nitrogen atoms in the resins also exert some auxiliary action.

The adsorption capacities of RSC-I and RSC-II toward trivalent auric ion were measured in the temperature ( $T$ ) range 298–338 K, and the curve of  $1/T$  versus  $\log D$  is plotted in Figure 8, where  $D$  is the distribution ratio.  $D = Q/C_e$ , where  $Q$  and  $C_e$  are the adsorption

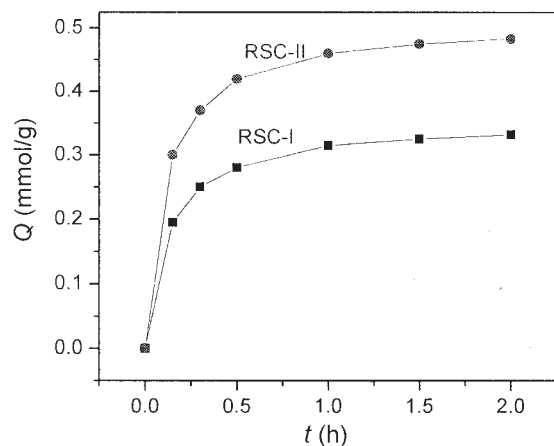


**Figure 6** Adsorption capacity of the resins ( $C_0$ : 2.0 mmol/L, 35°C, 2 h).

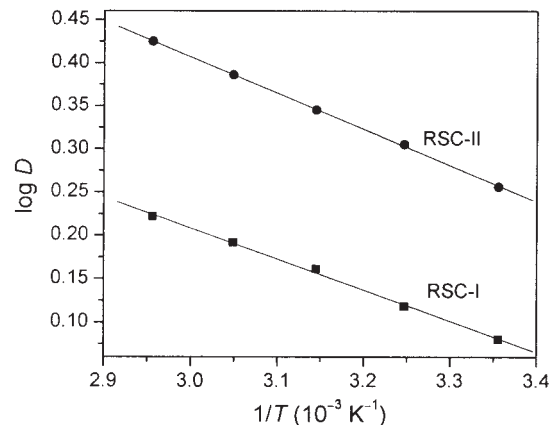
capacity and the concentration of free metal ion at the equilibrium adsorption, respectively. The result indicates that the distribution ratio increased with increasing solution temperature. This implies that the adsorption process is an endothermal process and a chemical adsorption process. The increase of distribution ratio also can be caused by the enhancement of the swelling ability of the resin's network structure and the ionic diffusivity in an aqueous solution with increasing solution temperature.<sup>18,19</sup> From Figure 8, it can be obtained that the linear slopes are  $-0.357 \times 10^3$  and  $-0.420 \times 10^3$  for RSC-I and RSC-II, respectively; the correlation coefficients are 0.9987 and 0.9998, respectively. According to  $\log D = -\Delta H/2.303RT + C$ ,  $\Delta H$  can be found as follows: 6.83 and 8.04 kJ/mol RSC-I and RSC-II, respectively.

## CONCLUSIONS

Polysiloxane resins modified by bisglycidyl calix[4]arene units were prepared by two steps. The



**Figure 7** Adsorption rate of two resins for Au(III) (35°C).



**Figure 8** Effect of temperature on distribution ratio ( $C_0$ : 0.2 mmol/L, 2 h).

first step is the preparation of the active xerogel microparticles by the reaction of cohydrolysis and condensation from  $\gamma$ -aminopropyl triethoxysilane or 4-aza-6-aminoethyl triethoxysilane and tetraethylorthosilicate. The second step is the reaction of the ring-opening polycondensation of bisglycidyl calix[4]arene and amino groups of polysiloxane microparticles. The polysiloxane resins were characterized by elemental analysis, DR-Fourier transform infrared spectra, Raman scattering spectra, scanning electron micrographs, and thermogravimetric analysis. The resins are particles of irregular shapes and have abundant porous structure on the surface. They exhibit high thermostability and potential preconcentration for divalent Cu, Pb, and Hg ions, especially for trivalent auric ion. Not only are these results related to both the special cavity and the network structure of resins, but the nitrogen atoms in resins also exert some auxiliary action. The enthalpy  $\Delta H$  of the adsorption of the resins toward trivalent auric ion was evaluated to be 6.83 and 8.04 kJ/mol for RSC-I and RSC-II, respectively.

The authors thank H. Wang of the Coal Combustion Lab., Center China University of Science and Technology, for assistance in thermal analysis experiments.

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