

Network Crown Ether Resin with Pendent Sulfur Ether Group: Preparation, Thermodegradation, and Adsorption Behavior

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ABSTRACT: Network crown ether resin with the pendent sulfur ether group was prepared by ring-opening copolymerization of 3-thiopentyl glycidyl ether and diethylene glycol bisglycidyl ether with Na, NaOCH₂CH₂OCH₂CH₂OH, or BuLi as catalyst, respectively. The yield of network polymer and the conversion of functional monoepoxy monomer are varied from catalyst to catalyst, and the thermostability of the resin is related to the content of the sulfur ether group. The resins show high adsorption capacity toward Cu(II), Pb(II), especially, Hg(II) ions, but poor adsorption capacity toward Mg(II) ions.

Corresponding thermodynamic parameter of Hg(II) ion was deduced, and could be expressed approximately with the Freundlich equation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1445–1451, 2003

Key words: ring-opening polymerization; resins; networks; crown ether resin; thermogravimetric analysis; thermogravimetry–Fourier transform infrared; adsorption; divalent mercury ion

INTRODUCTION

The crown ether polymers and pseudocrown ether polymers were widely used as adsorbents or exchanges in separation science,^{1–4} analysis science,⁵ and the support of heterogeneous coordination catalyst in hydrosilylation reaction.^{6,7} These polymers exhibit good diffusivity of solutes, excellent chemical and physical stability, selectivity, and renewable and reusable conveniently. Warshawsky et al.⁸ prepared pseudocrown ether polymers from the reaction of chloromethylated polystyrene with the sodium salt of poly(ethylene glycol). We prepared pseudocrown ether polymers from cellulose derivative with poly(ethylene amine) via the crosslinking reaction of active macromolecular with noncrown ether monomers.^{9,10} These pseudocrown ether polymers can efficiently complex transition metal ions instead of alkali metal and alkali earth-metal ions, due to the bigger cavity of pseudocrown ether or nitrogenous ligand. However, it is more interesting in the network crown ether polymers prepared by polymerization reaction directly, from noncrown ether monomers. By copolymerization of bisepoxy monomer with monoepoxy monomers, network crown ether resins with pendent functional

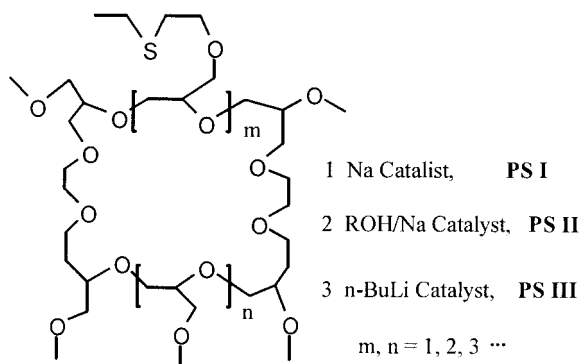
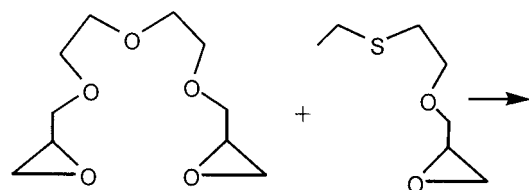
group, a new type of crown polymer, were reported.¹¹ The network structure units are composed of oxyethylene and oxypropylene units, and can be considered as a kind of crosslinked polyethers or crown ethers, and the yield of the network crown ether resins and the conversion of monoepoxy monomers are related to the kind of catalyst and reaction conditions. In this paper, we report on the preparation of network crown ether resin by the ring-opening copolymerization of diethylene glycol bisglycidyl ether with 3-thiopentyl glycidyl ether with various catalytic systems. The relationship between the yield of the network polymers, the conversion of 3-thiopentyl glycidyl ether and the catalyst used was discussed, and also the thermodegradation and adsorption behavior of the obtained resins. Thermogravimetry–Fourier transform infrared spectroscopy (TG-FTIR) was applied to study the thermal degradation of network crown ether resin. The reaction route and possible structure of network crown ether resins are shown in Scheme 1.

EXPERIMENTAL

Materials and chemicals

Diethylene glycol bisglycidyl ether was prepared according to the literature.¹² 1-Chloro-2,3-epoxypropane was supplied by Shanghai Chemical Reagents Co. (Shanghai, China) and distilled before use. 3-Thiopentyl alcohol was prepared by alkylation of β -mercaptoethyl alcohol with ethyl bromide; yield: 70%; boiling

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Scheme 1

point (bp) 84°C (2.0 kPa); literature (ref. 13), 90°C (3.33 kPa). Butyl lithium was prepared by the reaction of butyl chloride with metal lithium in cyclohexane. Other reagents were supplied by Shanghai Chemical Reagents Co. (Shanghai, China). All reagents are analytical-reagent grade and are used without further purification, unless otherwise stated.

Measurements

Elemental analysis was carried out by a 1106 elemental auto analysis apparatus (Carlo Erba, Italy). The FTIR spectra were recorded on a Nicolet 170SX FT-IR Spectrometer (Hitachi Co., Tokyo, Japan). The TG was carried out on a STA 409C thermal analyzer (Netzsch Co., German). The runs were performed at a heating rate of 15°C/min from 20 to 700°C in an atmosphere of dry nitrogen (100 mL/min). TG-FTIR (Bruker Spectrometer, Equinox 55) coupling apparatus was applied for qualitative analysis of gases evolved from a thermobalance during thermomicrogravimetric degradation. The concentrations of metal ions were determined by titration or by a 180–80 atomic absorption spectrometer (AAS, Hitachi Co., Tokyo, Japan).

Preparation of 3-thiopentyl glycidyl ether

3-Thiopentyl alcohol (10.6 g, 0.1 mol), dichloromethane (30 mL), PEG-400 (2.0 g), and potassium hydroxide (5.6 g, 0.1 mol) were added to a 100-mL round flask equipped with a magnetic stirrer. Then, epichlorohydrin (18.5 g, 0.2 mol) was dropped into the flask and stirred at 35°C for 12 h. After filtration, the filtrate was distilled under reduced pressure. 3-Thiopentyl glyci-

dyl ether (12.0 g) was obtained as a colorless liquid; yield: 74%; bp 78°C (0.08 kPa).

Preparation of network crown ether resins

The network crown ether resins with pendent sulfur ether group were prepared by the ring-opening copolymerization of diethylene glycol bisglycidyl ether and 3-thiopentyl glycidyl ether using metal sodium, sodium/diethylene glycol, or *n*-butyl lithium as catalyst, respectively. The mixture of diethylene glycol bisglycidyl ether (1.80 g, 8.23 mmol), 3-thiopentyl glycidyl ether (1.34 g, 8.23 mmol), and sodium metal (0.01 g, 0.44 mmol) was stirred at room temperature for 0.5 h, 120°C for 2.5 h under a nitrogen atmosphere. The crude product was extracted by acetone for 12 h and dried at 120°C under reduced pressure to a constant weight. Network crown ether resin (PS-I) was obtained as a light yellow powder, 2.986 g; yield: 95.1%.

The network crown ether resin PS-II was prepared similarly by using metal sodium (0.017 g, 0.74 mmol)/diethylene glycol (0.157 g, 1.48 mmol; Na/diethylene glycol, molar ratio 1:2) instead of metal sodium as catalyst, light yellow powder, 2.752 g; yield: 88.0%.

The network crown ether resin (PS-III) was prepared similarly by using *n*-butyl lithium/cyclohexane solution (1.0 mL, 1.0 mol/L; 1.0 mmol) instead of metal sodium as catalyst, light yellow powder, 2.335 g; yield: 74.6%.

Adsorption of resin for metal ions

Adsorption behavior of network resin toward metal ions was examined. The resin ($W = 0.02$ g) and metal ion solution ($V = 10$ mL) of a known concentration (C_0) 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_e) of the liquid phase was determined by titration with EDTA for Hg(II) and Pb(II), and by means of atomic adsorption spectrometry for Mg(II) and Cu(II). The adsorption capacity (Q) was calculated as follows:

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

RESULTS AND DISCUSSION

IR analysis of copolymers

The IR spectra of 3-thiopentyl glycidyl ether monomer (GE-S) and PS-I, PS-II, and PS-III are shown in Figure 1. The characteristic adsorption bands of the epoxy group of 3-thiopentyl glycidyl ether monomer appear at 1259 (overlapped with CH_2 bending vibration of $\text{CH}_2\text{—S}$), 916 and 860 cm^{-1} . Compared with the infra-

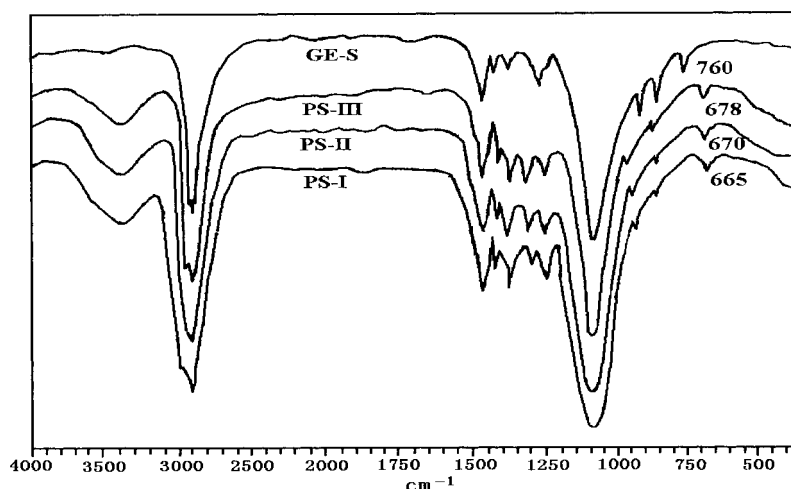


Figure 1 IR spectra of 3-thiopentyl glycidyl ether and network resins.

red spectra of monomer, the latter two vibration absorption bands disappear in the infrared spectra of network crown ether resins. The bands of CH_2 bending vibration of $\text{CH}_2\text{—S}$ of PS-I, PS-II, and PS-III appear at 1258, 1253 and 1251 cm^{-1} , respectively, and the relative intensity of the band increases with increasing sulfur content of copolymer. The wave number of C—S stretching vibration of three resins shifts from 760 cm^{-1} of monomer to 678, 670, and 665 cm^{-1} , respectively. Figure 1 also shows that the width of C—H and C—O stretching vibration bands of polymers widen, in the wave number range of 3000~2800 and 1200~1000, respectively. The stretching vibration of terminal O—H appears at about 3340 cm^{-1} .

The elemental analysis of copolymers

The data of elemental analysis, yield, catalyst, and the molar ratio of monomers to catalyst in the preparation of three copolymeric network crown ether resins are presented in Table I. The conversion of 3-thiopentyl glycidyl ether in the copolymerization reaction was calculated from the sulfur content of resin. The data of the Table I indicate that sulfur content of network crown ether resins increases with the increase of the yield of resins.

The molar ratio of diethylene glycol bisglycidyl ether to 3-thiopentyl glycidyl ether in the network crown ether resins is 1:0.925, 1:0.657, and 1:0.540 for PS-I, PS-II, and PS-III calculating from the content of sulfur given by Table I, respectively.

The effect of catalyst for copolymerization reaction

Table I also shows that the yield of three network crown ether resins and the conversion of 3-thiopentyl glycidyl ether varies from catalyst to catalyst. Using metal sodium catalyst, the yield of copolymer and the conversion of 3-thiopentyl glycidyl ether are the highest among three catalytic systems. This implies that the metal sodium catalyst is a preferable catalyst for the ring-opening copolymerization reaction of bisglycidyl ether with 3-thiopentyl glycidyl ether, i.e., it is of benefit to the formation of network structure in the ring-opening reaction of bisepoxy and monoepoxy monomer. The copolymer yield and the conversion of 3-thiopentyl glycidyl ether by using sodium/diethylene glycol or *n*-butyl lithium/cyclohexane as catalyst for PS-II and PS-III resins are lower than that of PS-I due to a part of non-network copolymer, i.e., linear polymer, was formed in the ring-opening reaction and extracted into acetone. Using the *n*-butyl lithium/cy-

TABLE I
The Analysis of Three Network Crown Ether Resins

Catalyst	$M_1/M_2/\text{Cat.}^a$ mole ratio	Yield (%)	Elemental analysis (%)			Conversion of M_2 (%)
			C	H	S	
Caled.	—	—	53.66	8.84	8.43	—
PS-I	Metal Na	95.1	53.70	8.52	7.80	88.0
PS-II	Na/ROH ^b	88.0	53.45	8.61	5.54	57.8
PS-III	<i>n</i> -butyl Li	74.6	54.01	8.44	4.55	40.3

^a $M_1/M_2/\text{Cat.}$ = diethylene glycol bisglycidyl ether/3-thiopentyl glycidyl ether/catalyst (metal sodium or lithium).

^b Na/ROH = metal sodium/diethylene glycol; molar ratio: 1 : 2.

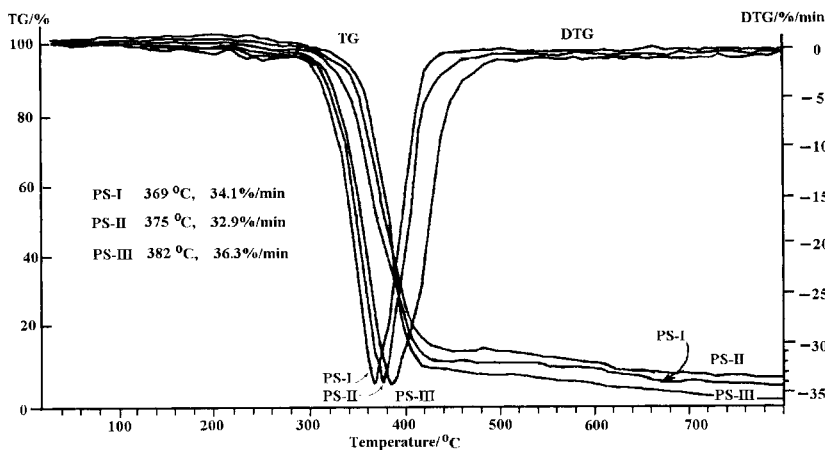


Figure 2 TG and DTG analysis of (a) PS-1, (b) PS-II, and (c) PS-III.

clohexane solution as catalyst, the yield of copolymer and the conversion of monoepoxy monomer are the lowest among three catalytic systems. This implies that the catalyst is not of benefit to the formation of network structure in the ring-opening copolymerization reaction.

Thermal analysis

The TG and differential thermogravimetry (DTG) curves of PS-I, PS-II, and PS-III are presented in Figure 2. TG curves of three resins show that there is no weight loss until 295°C. The DTG curves show that the temperature of 50% weight loss of PS-I, PS-II, and PS-III is 374, 380, and 386°C, respectively. The DTG curves also indicate that the weight loss rate is fastest at 369, 375, and 382°C, respectively. This implied that the thermal stability of three network crown ether

resins is slight increased with the decrease of sulfur percentage of copolymeric resin, i.e., the thermal stability of resin is related to the content of the pendent sulfur ether group.

TG-FTIR analysis

Fourier transform infrared spectroscopy (Equinox 55) was coupled to a thermomicrobalance of thermogravimetry. The coupling instrument (TG-FTIR) was applied to track the thermal decomposition process of the network crown ether resin PS-III, and study gasses evolved from a thermomicrobalance. The same flow of nitrogen was maintained throughout the experiment. Representative FTIR spectra of thermal degradation gasses were presented in Figure 3.

Figure 3 shows that only a little mixture of gases of water vapor, carboxyl compound, hydrocarbon, etc.,

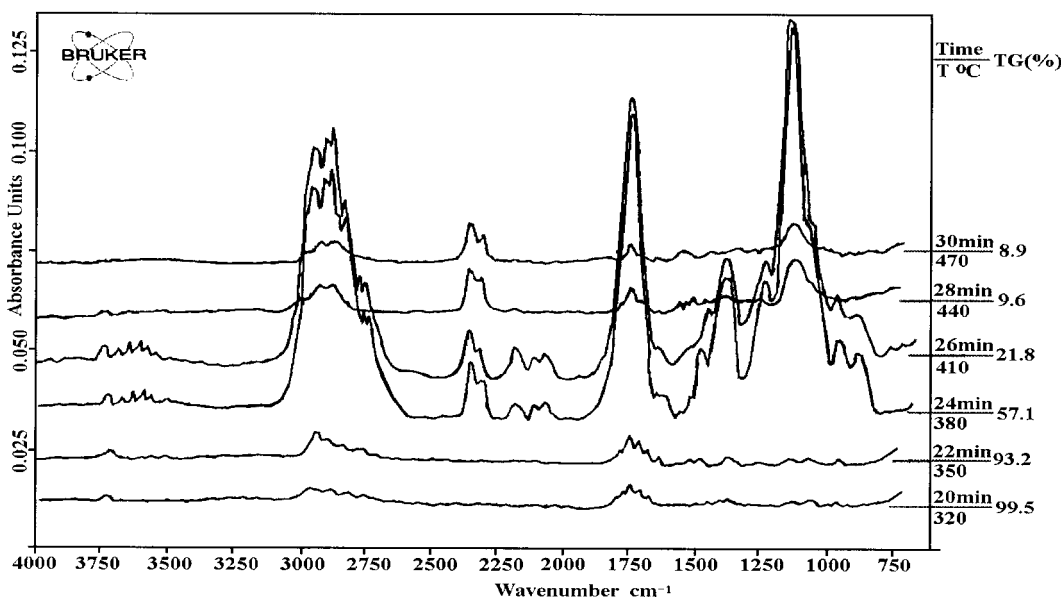


Figure 3 FTIR spectra of thermal degradation gasses of PS-III.

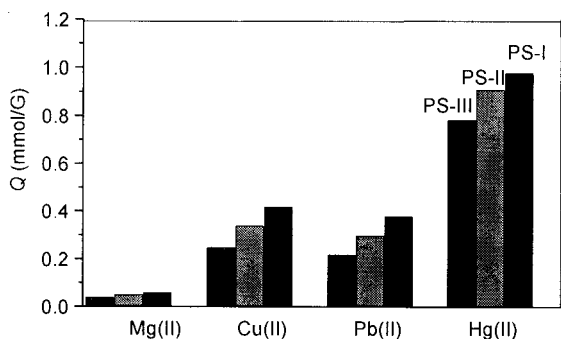


Figure 4 Adsorption capacity of the resins (30°C, 2 h, 3.4 mmol/L).

evolved at 320 and 350°C from the observation of the bands of the O—H, C—H, and C=O stretching vibration in a wavenumber range of about 3750 ~ 3600, 3100 ~ 2700, and 1800 ~ 1600, respectively, and the weight loss is 0.5 and 6.8%, respectively. This implies that the thermal degradation occurred in both the chain end and the internal chain of network structure.^{14,15} Figure 3 also indicates that the rapid decomposition of the network crown ether resin began abruptly at approximately 380°C, due to polymer depropagation, and strong vibration absorption bands appeared at ~1750 cm⁻¹ and in the range 3200 ~ 2700 and 1250 ~ 1000 cm⁻¹, respectively. The strong vibration absorption bands are caused by the C=O, C—H, and C—O stretching vibrations, respectively. The middle strong vibration absorption bands appear in the wavenumber range 2500 ~ 2000 cm⁻¹ and 1500 ~ 1250 cm⁻¹, caused by the stretching vibrations of carbon dioxide (2360 and 2340 cm⁻¹), carbon monoxide (2180 and 2100 cm⁻¹), and C—H bending vibration bands. The TG curve of PS-III resin indicates that the mass loss is 42.9 and 78.2%, at 380 and 410°C, respectively. In Figure 3, the vibration bands of containing sulfur group is not characteristic, because its intensity is weak, and overlapped with the vibration bands of CO₂ and C—H.

Figure 3 also presents infrared absorption spectra at 440 and 470°C, respectively. At the temperature the intensity of vibration absorption bands is weakened remarkably at ~1750 cm⁻¹ and in the wave number range of 3200 ~ 2700, 1250 ~ 1000 cm⁻¹. This means that the concentration of the carboxyl compound and hydrocarbon decrease remarkably in the mixture of gasses evolved. The stretching vibration bands of carbon monoxide (2180 and 2100 cm⁻¹) are almost disappeared. But the band of stretching vibrations of carbon dioxide (2360 and 2340 cm⁻¹) can be observed. At 440 and 470°C, TG curve of PS-III resin indicates that the weight loss is 90.4 and 91.9%, respectively.

Adsorption behavior of resins for metal ions

The adsorption capacity of PS-I, PS-II, and PS-III toward divalent magnesium, copper, lead, and mercury

ions were measured, respectively. The experimental results are plotted in Figure 4. Figure 4 indicates that the three network crown ether resins have a poor adsorption ability toward alkali-earth metal ions such as magnesium ion, and exhibit higher adsorption capacity toward divalent copper, lead, and mercury ions. This can be attributed to the contribution of the sulfur atom in pendent sulfur ether group and the bigger cavity of network crown ether. The sulfur atom in copolymer resins shows a better binding ability than that of oxygen atom toward copper, lead and mercury ions.

Figure 4 indicates that the adsorption capacity of three network crown ether resins toward same metal ion increases with the increase of sulfur content of resins. This implied that adsorption capacity of copolymer toward the metal ion is relative to coordination ability of sulfur atom. The adsorption capacity of resins toward the divalent mercury ion is the highest among all these metal ions.

Adsorption behavior of resins for divalent mercury ion

Effect of solution temperature

The adsorption capacity of the three network crown ether resins toward divalent mercury ion was measured in the temperature (T) range 293 ~ 323 K, and the curve of $1/T$ vs $\lg D$ is plotted in Figure 5. In Figure 5, D is the distribution ratio, $D = Q/C_e$, Q and C_e are adsorption capacity and the concentration of free metal ion at the equilibrium adsorption, respectively. The result indicates that the distribution ratio increased with an increase of the solution temperature. This implies that the adsorption process is an endothermal process and a chemical adsorption process. It also has a relation to the enhancement of the swelling ability of the network crown ether resin and the ionic diffusivity in an aqueous solution with an increase of the solution temperature.^{16,17} From Figure 5, it can be obtained that the linear slope is -0.537×10^3 , -0.354

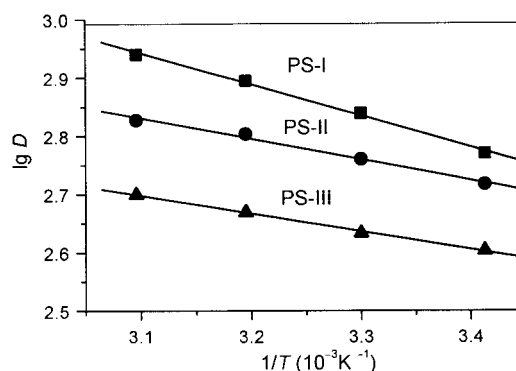


Figure 5 Effect of temperature for distribution ratio (C_0 3.4 mmol/L, 2 h).

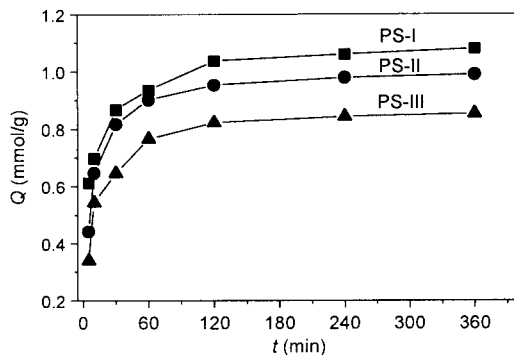


Figure 6 Adsorption rate of three resins for Hg(II) (40°C).

$\times 10^3$, and -0.307×10^3 for PS-I, PS-II, and PS-III, respectively. The correlation coefficient (r) is 0.997, 0.995, and 0.999, respectively. According to $\lg D = -\Delta H/2.303RT + C$, ΔH can be found as follows: $\Delta H = 10.28$ (kJ/mol) for PS-I, $\Delta H = 6.79$ (kJ/mol) for PS-II, and $\Delta H = 5.89$ (kJ/mol) for PS-III toward Hg(II).

Adsorption rate toward Hg(II) Ion

The concentration of divalent mercury ion in the solution was determined by using a constant concentration of Hg(II) ion ($C_0 = 3.4$ mmol/L) and resin ($C_R = 2$ g/L) at regular times. The obtained data are plotted in Figure 6. The three network crown ether resins have a high initial adsorption rate in the experimental condition, and the adsorption equilibrium almost was reached in about 1 h. Figure 6 also shows that the equilibrium adsorption capacity of PS-I is larger than that of PS-II and PS-III. It is relative to higher sulfur content of PS-I resin.

Adsorption isotherms

Using the constant concentration of the divalent mercury ion ($C_0 = 3.4$ mmol/L) and changing concentration (C_R) of three resins from 0.5 to 4.0 g/L, the concentration of the free mercury ion (C_e) in the solution was determined, and the adsorption capacity (Q_e) was calculated at the adsorption equilibrium. According to the Freundlich isotherms equation, $Q_e = K_F C_e^{1/n}$, and its rearrangement model to the linear form, $\lg Q_e = \lg K_F + 1/n \lg C_e$, $\lg C_e$ vs $\lg Q_e$ was plotted in Figure 7. Figure 7 indicates that the correlation coefficients (r) of linearity of $\lg C_e$ vs $\lg Q_e$ of PS-I, PS-II, and PS-III toward divalent mercury ion are 0.975, 0.979, and 0.989, respectively. It shows that the isotherm adsorption lines of three network crown ether resins toward divalent mercury ion fit close to the Freundlich model. The Freundlich parameters (K_F and n) can be obtained from Figure 7, for PS-I, PS-II, and PS-III, K_F : 1.04, 0.89, and 0.57; n : 3.03, 2.43, and 1.71, in sequence. From Freundlich parameters K_F and n value, the empirical

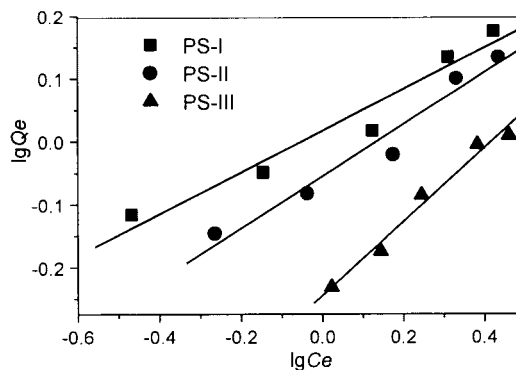


Figure 7 Linear Freundlich isotherm (40°C).

formulas can be found as follows for the adsorption of PS-I, PS-II, and PS-III toward divalent mercury ion: $Q_e = 1.04 C_e^{0.33}$, $Q_e = 0.89 C_e^{0.41}$, $Q_e = 0.57 C_e^{0.59}$, respectively. The Freundlich parameter n value is 3.03 and 2.43, for the adsorption of PS-I and PS-II toward divalent mercury ion. This implies that the coordinate adsorption of both resins for divalent mercury ion is easy.¹⁸

Coordination ratio of resins for Hg(II)

The equation of the coordination adsorption of network crown ether resin for divalent mercury ion is indicated as follows: $aL + \text{Hg(II)} = La \text{Hg(II)}$.

In the equation, a is the coordination ratio of resin with Hg(II). At the equilibrium of coordination adsorption, the equilibrium constant K_e equals $[La\text{Hg(II)}]/[L]^a[\text{Hg(II)}]$, $[La\text{Hg(II)}]/[\text{Hg(II)}] = D$. So the equation and its rearrangement model can be given as follows: $K_e = D/[L]^a$, $\lg D = \lg K_e + a \lg L$.

In the equation, D is the distribution ratio, and found from the ratio of the concentration of Hg(II) ion adsorbed (C_i) to free Hg(II) ion concentration (C_e) in the solution. L is sulfur mmol number calculated from the weight and sulfur content of resin.

Based on experiment data, $\lg D$ vs $\lg L$ was plotted in Figure 8. The coordination ratio a can be obtained

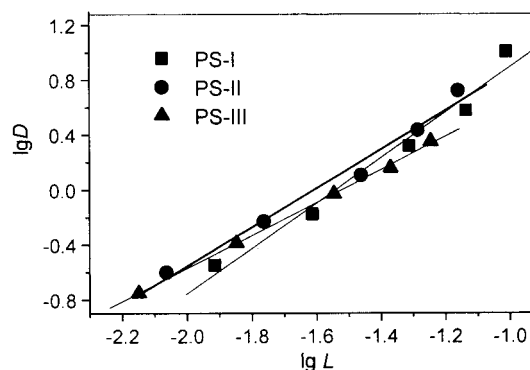


Figure 8 The relation $\lg D$ vs $\lg L$.

from the linear slope of Figure 8. Figure 8 indicates that a equals 1.65, 1.41, and 1.20 (correlation coefficient r : 0.988, 0.991, and 0.999) for PS-I, PS-II, and PS-III, respectively. The result shows that the coordination ratio of sulfur coordination group toward the divalent mercury ion is between 1 and 2 in three copolymeric network crown ether resins. The ratio value increases with the increase of sulfur content of resin. It implies that the adsorption of three resins toward Hg(II) ion is mainly the coordination adsorption of sulfur ligand group toward Hg(II)ion.¹⁹

CONCLUSION

Network crown ether resins with pendent sulfur ether groups were prepared by the ring-opening copolymerization of bisglycidyl ether with 3-thiopentyl glycidyl ether. The influence of the kind of catalyst used on the yield of network polymer and the conversion of monoepoxy monomer were discussed. The resins were characterized by elemental, IR, thermal analysis, and TG-FTIR. The thermal stability of three resins is high, and related to the content of the pendent sulfur ether group. The adsorption behavior of the resins toward Mg(II), Cu(II), Pb(II), and Hg(II) ions was determined. The highest adsorption capacity of resins among the ions tested is Hg(II) ion, and increases with the increase of sulfur content of resins. The thermodynamic parameter of the adsorption of three resins for Hg(II) was deduced, and their adsorption behavior could be approximately described with the Freundlich equation. The adsorption process is mainly coordination adsorption between sulfur ligand atom of pendent functional group and divalent mercury ion, and the coordination ratio is between 1 and 2.

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