

Polymeric Pseudocrown Ether Resins Containing Azacrown and Azathiocrown Ethers: Synthesis and Adsorption for Metal Ions

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ABSTRACT: Eight novel polymeric pseudocrown ether (PPCE) resins containing azacrown and azathiocrown ethers were prepared by chemical reactions of the precursor of 1-chloro-2,3-epoxypropane, 1-(2-chloroethoxy)-2,3-epoxypropane, 1-chloro-2,3-epithiopropene, and 1-(2-chloroethoxy)-2,3-epithiopropene with triethylamine or diethylamine in the presence of NaH. The maximum adsorption capacities of PPCE resins for noble metals are 4.67 mmol Au/g-resin, 2.2 mmol Pd/g-resin, 0.7 mmol Pt/g-resin, and 7.3 mmol Ag/g-resin. The structure of PPCE resins were characterized by IR spectra and element analysis. The adsorption of PPCE resins for noble metals is jointly conducted by PPCE polymer backbone and the azacrown or azathiocrown cavity. The XPS study shows that there are strong complexation interactions between PPCE and Au(III) or Pd(II). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 931–938, 1997

Key words: adsorption; noble metal ions; azacrown ether; azathiocrown ether; chelating resin

INTRODUCTION

It is well known that macrocyclic polyethers bind selectively alkali or alkaline ions.¹ Several macrocyclic polyethers attached to polymer supports have been prepared^{2,3} and successfully used as exchangers⁴ and adsorbents.^{5,6} Usually, the resins containing "soft basic" donor atoms such as S have excellent sorption performance for the "soft acid" metal ions such as Au(III), Pd(II), Pt(IV), and Ag(I). Several polymeric azacrown and thiocrown ethers for chelating Au(III), Pd(II), etc.,^{7–11} were synthesized. However, it is rather difficult to synthesize such macrocyclic polyethers. There-

fore, it is a goal in this field to employ a more convenient method to prepare macrocyclic polyethers resins, which rapidly and effectively sorb metal ions of the platinum group. This led us to synthesize two series of chelating resins containing azacrown and azathiocrown ethers. The reaction route and one of possible structures of the resins are shown in Scheme 1. This article reports the preparation of polymeric pseudocrown ether (PPCE) resins and their adsorption performances for platinum group metal ions and some transition-metal ions.

EXPERIMENTAL

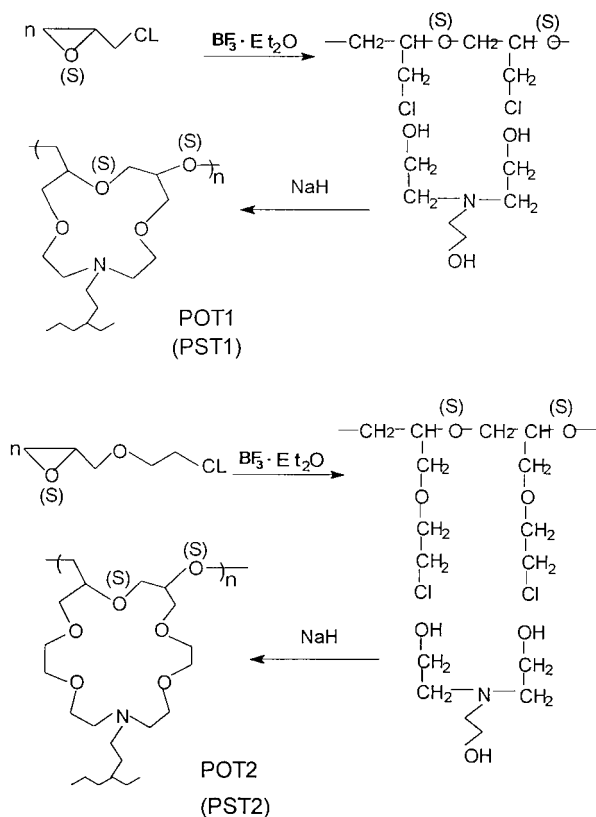
Materials

1-Chloro-2,3-epoxypropane was purified by distillation before use. 1-(2-Chloroethoxy)-2,3-ep-

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Scheme 1

oxypropane was prepared by the reaction of 1-chloro-2,3-epoxypropane with 2-chloroethanol in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$; yield: 45.6%; bp $59\text{--}60^\circ\text{C}$ (2 mmHg); $n_d^{25} = 1.4493$ (literature [Ref. 12] 1.4492). 1-Chloro-2,3-epithiopropene was prepared from reaction of 1-chloro-2,3-epoxypropane with thiourea in water solution at 0°C ; yield: 62.6%; bp $70\text{--}71^\circ\text{C}$ (68 mmHg); $n_d^{25} = 1.5225$ (literature [Ref. 13] 1.5222). 1-(2-Chloroethoxy)-2,3-epithiopropene was prepared by the reaction of 1-(2-chloroethoxy)-2,3-epoxypropane with thiourea at 0°C ; yield: 67%; bp $59\text{--}60^\circ\text{C}$ (0.8 mmHg); $n_d^{25} = 1.5095$ (literature [Ref. 14] 1.5093).

Diethylolamine and triethylolamine were dried by anhydrous CaCl_2 before use. Dioxane and *N,N*-dimethylformamide were refluxed and distilled over calcium hydride before use. Toluene was refluxed and distilled over sodium. Other reagents were commercially obtained and used without further purification.

Measurements

The IR spectra were recorded on a Nicolet 170SX FTIR spectrometer. The element analysis for

PPCE resins are conducted on an E.A. Mod-1106 element analysis spectrometer. The concentrations of metal ions were determined by titration or atomic emission on a Jarrel-Ash Atom Scan 2000 I.C.P. The XPS spectra were recorded on a Kratos XSAM 800X X-ray photoelectron spectrometer.

Preparation of the PPCE Resins

Table I shows the assignments of the PPCE resins.

Preparation of O1 Precursor

All the operations were performed under a nitrogen atmosphere. 1-Chloro-2,3-epoxypropane, 5.55 g (0.06 mol), and dioxane, 20 mL, were added to a 100 mL conical flask equipped with a magnetic stirrer and immersed in an ice-water bath. Then, 0.02 mL $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was added to the flask to initiate the polymerization at 0°C . Over a period of 2 h, the 1-chloro-2,3-epoxypropane precursor (O1), which is a linear poly(1-chloro-2,3-epoxypropane), was prepared.

Preparation of POT1 Resin

In another trinecked flask, equipped with a electric stirrer and refluxing condenser, immersed in a thermally controlled oil bath, 3.13 g (0.021 mol) diethylolamine and 20 mL dioxane were added, followed by the addition of the O1 precursor prepared as above. After that, 1.8 g NaH (Fluka CP grade, 80 wt %) was washed rapidly with dry ether and added slowly to the reaction mixture. The temperature was increased spontaneously to 100°C and maintained there for 24 h. Then, the reaction mixture was cooled to room temperature and 20 mL methanol was added slowly to the mixture to destroy excessive sodium hydride. Then, the polymer was filtrated and washed successively with distilled water and ethanol and extracted by acetone for 24 h. After that, the polymer was again washed with distilled water until washings contained no chlorine (Cl^-). The polymer was dried at 60°C under reduced pressure to constant weight. The other seven PPCE resins given in Table I were prepared in the same reaction conditions.

Adsorption of Metal Ions by PPCE Resins (Batch Method)

A 50 mL Erlenmeyer flask was charged with 25 mg PPCE resin and 25 mL metal-ion solution. The

Table I The Assignment of PPCE Resins

	1-Chloro-2,3-epoxypropane (O1)	1-(2-Chloroethoxy)-2,3-epoxypropane (O2)	1-Chloro-2,3-epithiopropene (S1)	1-(2-Chloroethoxy)-2,3-epithiopropene (S2)
Diethylolamine	POD1	POD2	PSD1	PSD2
Triethylolamine	POT1	POT2	PST1	PST2

mixture was shaken for 20 h and allowed to stand for 24 h at 25°C. The adsorption equilibrium was reached after 12 h. The ion concentration of the liquid phase was determined by the methods as follows: Ag(I) was titrated with Volhard titration; Cu(II), Zn(II), Hg(II), Mg(II), and Pb(II) were titrated with EDTA; the other ions were analyzed by an atomic emission spectrophotometer (I.C.P.). The adsorption capacity of PPCE resins for metal ions was calculated from the ion concentration of the original and resulting solution.

RESULTS AND DISCUSSION

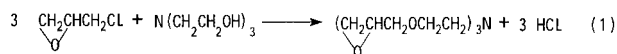
Reaction Conditions

We take the preparation of the POT1 resin for an example; the influences of reaction conditions on the yield of the synthetic reaction and the element contents of PPCE resins were investigated.

The Selection of the Solvent

Table II shows the synthesis results of POT1 and PST1 with different solvents. The expected carbon

content (C_E %) of POT1 is calculated from Formulas (1) and (2):



$$C_E \% = \frac{(9M_C + 6M_C) \times 100}{3M_{EP} + M_T - 3M_{HCL}} \quad (2)$$

where M_{EP} , M_T , M_{HCL} , and M_C are the molecular or atomic weight of 1-chloro-2,3-epoxypropane, triethylolamine, hydrogen chloride, and carbon. The measured carbon content (C_M %) of POT1 can be obtained by element analysis.

Furthermore, we can calculate the weight fraction (W_{EP}) of the precursor unit (1-chloro-2,3-epoxypropane) of POT1 by following formula:

$$C_M \% = W_{EP} \times C_{EP} \% + (1 - W_{EP}) \times C_T \%$$

where C_T % and C_{EP} % are the carbon content (in wt) of triethylolamine and 1-chloro-2,3-epoxypro-

Table II The Influence of Solvent on the Synthesis of POT1 and PST1 Resins^a

No.	Precursor (g)	Triethylolamine (g)	Solvent	Product and Element Analysis ^b							F_P ^d
				Wt (g)	Yield %	Cl % ^c	C %	H %	N %	S %	
POT1	5.55	3.12	Dioxane /DMF	3.86	55.6	0.26	56.70 (56.16)	8.50 (8.49)	4.80 (4.85)	—	0.746 (0.741)
POT1	5.55	3.12	Toluene	1.28	18.5	1.93	59.62	8.63	2.48	—	0.88
POT1	5.55	3.12	Dioxane	3.37	48.6	0.11	56.44	8.51	4.66	—	0.73
POT1	5.55	3.12	DMF	3.12	44.9	0	55.76	8.48	5.13	—	0.69
PST1	6.51	3.12	Dioxane /DMF	4.93	62.4	0.91	49.28 (49.30)	7.48 (7.46)	4.43 (4.26)	14.46 (14.60)	0.736 (0.741)
PST1	6.51	3.12	Toluene	1.77	22.4	2.09	48.95	7.18	2.36	19.84	0.86
PST1	6.51	3.12	Dioxane	4.01	50.7	1.07	49.04	7.40	3.84	15.78	0.75
PST1	6.51	3.12	DMF	3.68	46.6	0.23	49.23	7.60	5.28	11.77	0.62

^a Reaction conditions: O1 and S1 precursor (av mol wt 1200); —O1 : Cl (molar ratio) = 7/20, 100°C for 24 h, 10 mL of solvent per g of polymer, 1.8 g NaH (80% wt).

^b The value in the parentheses is the theoretical element content of PPCE resins with an idealized structure as shown in Scheme 1.

^c The chlorine content surviving in PPCE resins.

^d F_P represents the molar fraction of the precursor unit of PPCE resins and the value in the parentheses is the molar fraction of the precursor in the feeding.

pane, respectively. $C_M \%$ is the measured carbon content of POT1. Thus,

$$W_{EP} = \frac{C_M \% - C_T \%}{C_{EP} \% - C_T \%} \quad (3)$$

The molar fraction (F_{EP}) of the precursor unit of POT1 can be obtained by the following formula:

$$W_{EP} = \frac{F_{EP} \times (M_{EP} - M_{CL})}{F_{EP} \times (M_{EP} - M_{CL}) + (1 - F_{EP}) \times (M_T - M_H)}$$

where M_{EP} and M_T are the molar weights of 1-chloro-2,3-epoxypropane and triethylamine, respectively. M_{CL} and M_H are the atomic weights of chlorine and hydrogen, respectively. Thus,

$$F_{EP} = \frac{146W_{EP}}{57 + 89W_{EP}} \quad (4)$$

Comparing the feed ratio with the F_{EP} , we can infer some information about the structure of POT1. A larger F_{EP} probably means that the macromolecule network structure is prominent in the POT1; otherwise, the linear polymer would be dominant. The element contents of other PPCE resins are measured by similar method. Table II indicates that the mixed solvent of dioxane and *N,N*-dimethylformamide with a weight ratio of 1 : 1 is a preferable solvent. For toluene, the yield is very poor.

The Sodium Hydride Addition

Two different sodium hydride addition methods were tried: (a) the formation of the trisodium salt prior to the reaction with the polymeric precursor; and (b) the formation of trisodium salt simultaneously with the reaction with the polymeric precursor. Owing to that the first method is time-consuming and the yield of the PPCE is less than that of the second method, the second method was usually adopted.

The Molar Ratio of the —Ol : Cl

In crown-ether synthesis, the molar ratio of diol : halide decides both the nature and the yield of the product; it was therefore important to investigate the influence of such different ratios on the

synthesis of PPCE resins, as shown in Table III. The molar ratio of —Ol : Cl was varied from $\frac{1}{3}$ to $1\frac{1}{3}$. To remove the trace of water that may have survived in the mixture, the molar amount of NaH is slightly in excess of the molar amount of the polymeric precursor employed. The variations of “Ol : Cl” cause an obvious difference of the yield and the elements content of PPCE resins. The calculated value F_p is also summarized in Table III. Taking into account these factors, the molar ratio of —Ol : Cl was selected as $\frac{7}{20}$.

The Molecular Weight of the Polymeric Precursor

The variations of the molecular weight of the O1 and S1 precursors did not cause any significant change in the yield of the PPCE resins. Because all PPCE resins are crosslinking polymers, the molecular weight of the polymeric precursor has little influence on the yield of the reaction. However, if the average molecular weight (\bar{M}_n) of the polymeric precursor is less than 600, the reaction would fail and the obtained product would be a viscous liquid that cannot be further treated. Therefore, no attempt was made to control the molecular weight of all the polymeric precursors, because the \bar{M}_n of the polymeric precursors is 1600–3000 under the selected reaction conditions.

Synthesis of Various Polymeric Pseudocrown Ethers

The synthesis of various PPCE resins are summarized in Table IV. In all precursor preparations, the polymerization temperature must be controlled at 0°C; otherwise, the reaction would fail. In the condensation reactions of alkylolamines with the precursors in the presence of sodium hydride, it was necessary to raise the temperature to the refluxing temperature of dioxane for a higher yield of polymers. As far as the yield of reaction is concerned, diethylamine is a better crosslinking agent compared with triethylamine.

IR Analysis

In the synthesis of polymeric pseudocrown ethers, the selected reaction conditions were designed to minimize the risk of interchain crosslinking and mainly led to the pseudocrown ether structure.⁹ During the synthesis of PPCE resins, the trisodium salt formation and reaction with the polymeric precursors occurred simultaneously. The sodium salt of alkylamine is both the template

Table III Component Variations in the Synthesis of POT1 and PST1 Resins^a

No.	Precursor (g)	Triethylolamine (g)	O1/Cl	Product and Element Analysis ^b							F_P^d
				Wt (g)	Yield (%)	Cl (%) ^c	C (%)	H (%)	N (%)	S (%)	
POT1a	5.55	2.98	1.0/3	2.94	42.4	1.03	58.20	8.57	3.45	—	0.812 (0.75)
POT1b	5.55	3.13	1.05/3	3.86	55.6	0.26	56.70 (56.16)	8.50 (8.49)	4.80 (4.85)	—	0.746 (0.741)
POT1c	5.55	3.28	1.1/3	1.95	28.1	0.18	54.85	8.44	5.76	—	0.648 (0.732)
PST1a	6.51	2.98	1.0/3	3.92	49.6	1.22	49.44	7.21	2.50	22.36	0.805 (0.75)
PST1b	6.51	3.13	1.05/3	4.93	62.4	0.91	49.28 (49.31)	7.48 (7.46)	4.43 (4.26)	14.46 (14.60)	0.736 (0.741)
PST1c	6.51	3.28	1.1/3	2.95	37.3	0.33	48.9	7.66	5.67	10.71	0.521 (0.732)

^a Reaction conditions: O1 and S1 precursor (av mol wt 1600); the 1 : 1 (wt/wt) dioxane and *N,N*-dimethylformamide mixed solvent; 100°C for 24 h, 10 mL of dioxane per g of polymer, 1.8 g NaH (80% wt).

^b The value in the parentheses is the theoretical element content of PPCE resins with an idealized structure as shown in Scheme 1.

^c The chlorine content surviving in PPCE resin.

^d F_P represents the molar fraction of precursor unit of PPCE resins and the value in the parentheses is the molar fraction of the precursor in the feeding.

component for formation of the polymeric pseudocrown ether and the crosslinking agent. It is reasonably assumed that the PPCE's formation is somewhat complicated. Scheme 1 just presents the expected structure of PPCE resins.

We measured the IR spectra of all precursors,

alkylolamines, and PPCE resins to investigate the stretching vibration frequencies of ν_{C-N} , ν_{C-O} , and ν_{C-S} . Figure 1 shows the expanded IR spectra (between 400 and 2000 cm^{-1}) of eight PPCE resins. In the IR spectra of the precursors, ν_{C-O} and ν_{C-S} are around 1090 and 1420 cm^{-1} , respec-

Table IV The Synthesis of PPCE Resins^a

PPCE	Precursor ^b (g)	Alkylolamine ^c (g)	Product and Element Analysis							F_P^e (0.741)
			Wt (g)	Yield (%)	Cl (%) ^d	C (%)	H (%)	N (%)	S (%)	
POT1	O1/5.55	T/3.12	3.60	55.6	0.77	56.70	8.50	4.80		0.746
POT2	O2/8.19	T/3.12	4.82	52.8	0.42	55.90	8.52	3.16		0.734
POD1	O1/5.55	D/2.20	3.51	63.2	0	56.96	8.75	5.43		0.742
POD2	O2/8.19	D/2.20	4.98	60.8	0.23	56.31	8.68	3.53		0.751
PST1	S1/6.51	T/3.12	4.64	62.4	0	49.28	7.48	3.63	28.24	0.736
PST2	S2/9.15	T/3.12	6.27	62.2	0.14	50.68	8.01	2.86	19.82	0.744
PSD1	S1/6.51	D/2.20	4.82	71.4	0.12	48.58	7.02	4.26	30.06	0.747
PSD2	S2/9.15	D/2.20	6.07	66.3	0	50.23	7.69	3.12	21.11	0.733

^a Reaction conditions: 1 : 1 (wt/wt) dioxane and *N,N*-dimethylformamide mixed solvent; 100°C for 24 h, 10 mL of dioxane per g of polymer, 1.8 g NaH (80% wt);

^b O1, O2, S1, and S2 are assigned as in Table I.

^c T and D represent triethylolamine and diethylolamine, respectively.

^d The chlorine content surviving in PPCE resin.

^e F_P represents the molar fraction of precursor unit of PPCE resins and the value in the parentheses is the molar fraction of the precursor in the feeding.

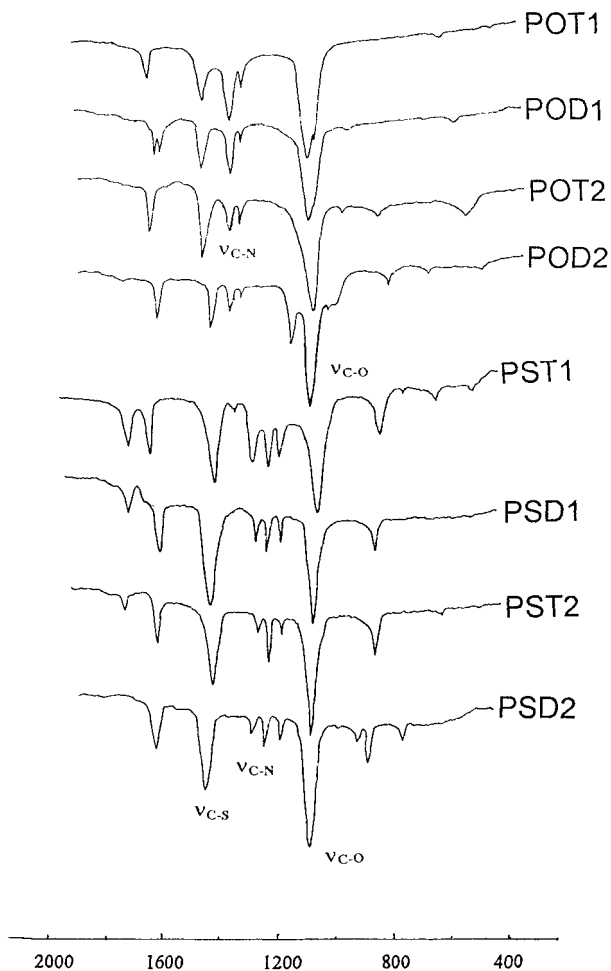


Figure 1 IR spectra of PPCE resins.

tively. In the IR spectra of alkylolamines, ν_{C-N} is around 1320 cm^{-1} . But in the IR spectra of PPCE resins, ν_{C-N} is around 1350 cm^{-1} and ν_{C-O} and ν_{C-S} are around 1110 and 1440 cm^{-1} , respectively. Compared with alkylolamine and the precursors, all the absorption frequencies of ν_{C-N} , ν_{C-O} , and ν_{C-S} move to $20\text{--}30\text{ cm}^{-1}$ higher bands. It seems that the PPCE's formation restricts the stretching vibrations of the molecular bond and increases the intermolecular stress and thus causes the absorption band of the stretching vibration frequencies of ν_{C-N} , ν_{C-O} , and ν_{C-S} to move to the higher frequency. The C—Cl bond absorption frequency, which is usually a strong and wide absorption band between 600 and 800 cm^{-1} , disappeared in the IR spectra of PPCE resins. Therefore, we cannot define exactly the macromolecule structure of PPCE resins; the main purpose in this work was to search for a convenient method to prepare some chelating resins

with high-adsorption performance for platinum group metal ions.

The Adsorption Performance of PPCE: The Adsorption Capacity

Table V shows the adsorption capacities of PPCE resins for platinum group metal ions, silver ions, and some transition-metal ions. The experimental results are summarized as follows:

- All PPCE resins have good adsorption abilities for platinum group metal ions in acid medium and have poor adsorption abilities for transition-metal ions.
- It was interesting finding that PPCE resins (POT2, POD2, PST2, PSD2) containing six coordinate atoms have a higher adsorption capacity than those resins containing four coordinate atoms (POT1, POD1, PST1, PSD1). This may have been caused by the size selection of the pseudocrown cavity. The first kind of PO resins, which have a greater pseudocrown cavity diameter, is a topological receptor for ion pairs of type H_yMCl_x (M : Au, Pd, Pt).
- In a neutral aqueous solution of $AgNO_3$, PO-type resins have over 2 mmol Ag/g-resin of adsorption. In a $1M\ HNO_3$ solution of $AgNO_3$, PO-type resins also have adsorbed over 1 mmol-Ag/g-resin . This part of the adsorption for Ag(I) can be attributed to the contribution of the azacrown ether cavity, because the tertiary amine group is converted into quaternary ammonium salt and adsorbs a little Ag(I) in an acid solution.¹⁵ So, this may be regarded as collateral evidence of the existence of the azacrown ether cavity.
- PS-type resins have much higher adsorption capacities than those of PO-type resins for Ag(I) in both mediums, because PS-type resins have a sulfur atom which binds more than does the oxygen atom with Ag(I). PO-type resins have higher adsorption than that of PS-type resins for Cu(II).

The Adsorption Rate for Ag(I).

Figure 2 shows the adsorption rate of PPCE resins for Ag(I) in neutral aqueous medium. PO-type resins have a higher adsorbing rate than that of PS-type resins, because the PO-type resins have a polymer backbone of polyoxyethylene which has

Table V The Adsorption Capacities of PPCE Resins^a (mmol Metal/g-Resin)

PPCE	Num. ^b	Au(III) 2M HCl	Pd(II) 2M HCl	Pt(IV) 2M HCl	Ag(I) 1M HNO ₃	Ag(I) pH 7	Hg(II) pH5·6	Pb(II) pH5·6	Cu(II) pH 5.6	Zn(II) pH5·6	Mg(II) pH5·6
POT1	3O, 1N	2.97	0.97	0.69	1.05	1.56	1.48	0	0.24	0.05	0
POT2	5O, 1N	4.22	1.54	0.77	1.21	2.24	0.12	0.56	0.98	0.05	0
POD1	3O, 1N	1.68	0.61	0.23	0.98	1.70	1.88	0	1.22	0.07	0
POD2	5O, 1N	3.88	1.25	0.33	1.26	2.89	0.20	0.46	1.46	0.12	0
PST1	2O, 1S, 1N	0.82	0.28	0.16	5.70	3.65	1.27	0.28	0.27	0.06	0
PST2	4O, 1S, 1N	3.86	1.89	0.69	6.69	5.60	1.32	0.32	0.62	0.17	0
PSD1	2O, 1S, 1N	0.96	0.62	0.12	5.24	4.43	1.68	0.24	0.16	0.06	0
PSD2	4O, 1S, 1N	4.67	2.20	0.72	7.29	5.84	1.38	0.12	0.57	0.12	0

^a [Au(III)], [Pt(IV)] = 0.005M, [Pd(II)] = 0.01M, [Ag(I)] = 0.05M, [Pb(II)—K(I)] = 0.05M, 25 mg PPCE resin, and 25 mL metal ions solution was used.

^b The total number of coordinate atoms of azacrown and azathiocrown ether cavities of the PPCE resin.

a better affinity with water than with poly(thioethylene).

X-ray Photoelectron Spectroscopy

The adsorption mechanism of PPCE resins for platinum group metal ions was investigated using

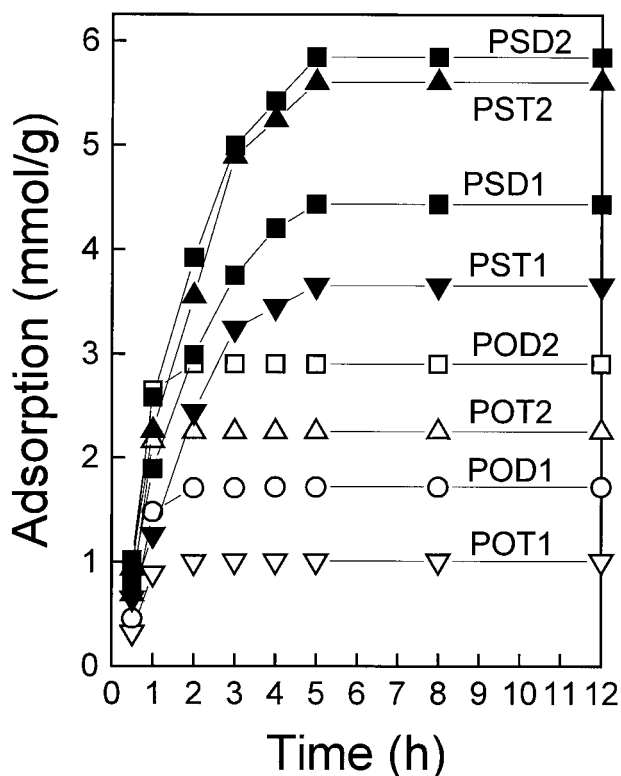


Figure 2 The adsorption rate of PPCE resins for Ag(I).

X-ray photoelectron spectroscopy. Table VI shows the different electrons' binding energies (BEs) of PPCE resins and the corresponding complexes. C1s BEs of PPCE–M complexes are almost same as those of PPCE resins; this indicates that C does not contribute to the adsorption for platinum group metal ions. N1s BEs of PPCE–M complexes are 2.4–3.3 eV higher than those of PPCE resins, O1s BEs of PPCE–M complexes are 0.3–0.8 eV higher than those of PPCE resins, and S2p BEs of PSD2–M complexes are 0.7–1.0 eV higher than those of PSD2 resins. All these results indicate that N, S, and O, in the order of N > S > O, contribute to the adsorption of platinum group metal ions. O1s BE shifts may be regarded as collateral evidence of the existence of azacrown and azathiocrown cavities in PPCE resins, because polyether does not adsorb Au(III) and O1s BEs will not be changed. Au4f and Pd3d BEs of PPCE–M complexes are 1.2–3.9 eV less than those of PPCE resins, indicating that there are strong complexation interactions between the platinum group metal ions and the PPCE resins. We may conclude that the adsorption of PPCE resins for platinum group metal ions is accomplished with complexions of metal ions and PPCE cavities. The adsorption of the PPCE resins for metal ions is a combined contribution for absorbing metal ions from the polymer backbone and the PPCE cavities.

In conclusion, PPCE resins prepared in this work have good adsorption performances for Au(III) and Ag(I). IR analysis and element analysis show that the preparation of PPCE is successful and convenient. XPS study shows that the adsorption of PPCE for Au(III) and Pd(II) is accom-

Table VI The Electron BEs (eV) of PPCE Resins and the PPCE-M Complexes

	C 1s	O 1s	N 1s	S 2p	Cl 2p	Pd 3d3/2	Pd 3d5/2	Au 4f5/2	Au 4f7/2
AuCl ₄ ⁻¹					199.1			90.4	87.0
PdCl ₄ ⁻²					200.7	345.2	339.8		
POD2	285.0	532.0	399.2						
PSD2	285.0	532.5	399.7	163.7					
POD2-Au	285.0	533.4	402.4		197.9			87.1	84.2
POD2-Pd	285.0	532.9	401.6		197.7	341.2	336.7		
PSD2-Au	285.0	533.3	402.9	164.6	198.6			89.3	85.6
PSD2-Pd	285.0	532.8	402.4	164.7	198.7	343.6	338.2		

plished by chemical complexation. The adsorption of the PPCE resins for metal ions is a combined contribution for absorbing metal ions from the polymer backbone and the PPCE cavities.

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REFERENCES

1. C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Int. Ed. Engl.*, **11**, 16 (1972).
2. S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).
3. G. W. Gokel and S. H. Korzeniowski, *Macrocyclic Polyether Synthesis*, Springer-Verlag, Berlin, 1982.
4. E. Blasius and K. P. Janzen, *Top. Curr. Chem.*, **98**, 163 (1981).
5. L. H. Wong and J. Smid, *J. Am. Chem. Soc.*, **99**, 5637 (1977).
6. J. Smid, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 364 (1980).
7. S. L. Regen, *Angew. Chem. Int. Ed. Engl.*, **18**, 421 (1979).
8. Y. Xu and S. Bai, *Polym. Commun. (Chin.)*, **4**, 226 (1983).
9. A. Warshawsky, R. Kalir, A. Deshe, and H. Berkovitz, *J. Am. Chem. Soc.*, **101**, 4249 (1979).
10. Y. Xu and S. Dong, *Acta Polym. Sin. (Chin.)*, **5**, 364 (1988).
11. S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).
12. J. R. Bacon and M. J. Collis, *Chem. Ind. (Lond.)*, **23**, 930 (1971).
13. I. Tabushi, Y. Tamaru, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, **47**, 1455 (1974).
14. V. A. Dzhafarov, *Dokl. Akad. Nauk. Az. SSR*, **11**, 49 (1977).
15. T. Saegusa, S. Kobayashi, K. Hayashi, and A. Yamada, *Polym. J.* **10**, 403 (1978).