Preparation and Adsorption Properties of the Chelating Fibers Containing Amino Groups

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SYNOPSIS

Four kinds of amino-group-containing chelating fibers were prepared by reacting diethylenetriamine, diethanolamine, diethylamine, and aminopyridine, respectively, with a grafted fiber PVA-g-GMA containing epoxy groups. The γ -ray preirradiation initiated graft copolymerization of GMA onto PVA fiber, the functionalization of the grafted fiber PVA-g-GMA with amino compounds, and the adsorption properties of the obtained chelating fibers were systematically investigated. It is concluded that with increasing monomer concentration, reaction time, and temperature, the grafting percentage increases significantly. In the functionalization of the grafted fiber, reaction time, temperature, solvent, and amount of amine used greatly influence the reaction. 1,4-Dioxane is a reasonable solvent for the reaction. The chelating fibers present great adsorption amounts and high adsorption rates for Cu²⁺ ion and Au³⁺ ion. Among the chelating fibers, the fiber with diethylenetriamine group is the most reasonable chelating fiber for the adsorption of Cu^{2+} and Au^{3+} . The chelating fibers present good selectivities for Cu^{2+} in the solution with Cu^{2+} , Mn^{2+} , Ni^{2+} , Co²⁺, and Zn²⁺, while presenting quite high selectivities for Au³⁺ ion in the solution with Cu²⁺, Au³⁺, Zn²⁺, and Cr³⁺ ions. The chelating fiber with diethanolamine or diethylamine can reduce the adsorbed Au³⁺ into metallic gold. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Reactive polymeric materials for wastewater treatment and metal recovery has received much attention. Because ion-exchange chelating fiber can be conveniently used in various cases and possesses large specific area leading to the great adsorption capacity and the high adsorption rate of the material, increasing interest has been focused on ion-exchange chelating fiber recently.¹⁻⁹ In our previous work, several kinds of chelating fibers were prepared, and some of the chelating fibers were successfully used in the recovery of precious metal from wastewater and in the extraction as well as separation of rareearth metallic ion from aqueous chloride solution.⁸⁻¹³ Recently we developed four kinds of amine-groupcontaining chelating fiber. In this study, the preparation and the adsorption behaviors of those fibers were investigated.

EXPERIMENTAL

Materials and Reagents

Polyvinyl alcohol (PVA) fiber and nonwoven fabrics are supplied by Beijin Institute of Special Fiber. Diethylenetriamine, diethanolamine, diethylamine, aminopyridine, and 1,4-dioxane are chemically pure reagents. AuCl₃, CuCl₂, ZnCl₂, MnCl₂, FeCl₃, and methanol were analytically pure reagents. Glycidyl mathacrylate had been distilled before used.

Preparation of Epoxy-Group-Containing Reactive Fiber

Glycidyl methacrylate (GMA), deionized water, methanol, and PVA fiber, having been preirradiated by γ -ray in the presence of air, were put into a 100mL Wolff bottle equipped with an electromagnetic stirrer and a heating bath. Nitrogen then was blown into the flask and the bath was heated to a preset temperature. After the graft copolymerization was carried out under designed condition, the grafted

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fiber PVA-g-GMA was washed with methanol and then with deionized water. The homopolymer PGMA was removed by extracting the grafted fiber with methanol in a Soxhlet's extractor.

The grafting percentage was calculated as follows:

$$G = \frac{W_2 - W_1}{W_1} \, 100 \tag{1}$$

where G is grafting percentage (%), W_1 and W_2 are the weights of the PVA fiber before and after graft copolymerization, respectively (g).

Preparation of Chelating Fibers

The grafted fiber PVA-g-GMA contains the epoxy group, 1,4-dioxane, which acted as medium, and an amine compound such as diethylenetriamine(I), diethanolamine(II), diethylamine(III), and aminopyridine (IV), which were put into a 100-mL Wolff bottle equipped with an electromagnetic stirrer, a reflux condenser, and a heating bath. After the reaction, the obtained chelating fibers were washed with deionized water. The scheme of the reaction is shown as follows:

where $HN(R_1)R_2$ are diethylenetriamine (I), diethanolamine (II), diethylamine (III), and aminopyridine (IV), respectively.

Infarad Spectrometry

The dried sample was pressed into a pellet with KBr and then analyzed with a Nicolet 170 SX FT-IR spectrometer.

Elemental Analysis

The dried sample was analyzed with a Perkin-Elmer 240C elemental analyzer, and the functional group content of the chelating fiber was calculated according to the content of nitrogen in the fiber.

Adsorption Amount and Distribution Factor

The adsorption was carried out at constant temperature in a vibrator equipped with a bath. The ratio of the volume of solution to the weight of chelating fiber was 50 mL : 10 mg. The concentration of ion was detected by an ICAP-9000 inductive coupling plasma spectrometer. The adsorption amount was calculated as follows:

$$A = \frac{V(C_1 - C_2)}{W}$$
(3)

where A is adsorption amount (mg/g), W is the weight of the chelating fiber (g), V is the volume of solution (L); and C_1 and C_2 are the concentrations of ion before and after adsorption respectively (mg/L).

The distribution factor was calculated as follows:

$$D = A/C_2 \tag{4}$$

where D is distribution factor (L/g).

Wide-Angle X-ray Diffraction

The wide-angle X-ray diffraction (WAXD) measurement was carried out in a Rigaku D/max-3A X-ray diffractrometer using Ni-filtered CuK_{α} radiation.

RESULTS AND DISCUSSION

Graft Copolymerization

The effects of reaction conditions, such as preirradiation dose rate, monomer concentration, time, temperature, and solvent, on the graft copolymerization were investigated.

It is well known that grafting percentage of the irradiation-initiated graft copolymerization greatly depends on the radiation dose and dose rate. According to the results shown in Table I, when the preradiation dose is 2.5×10^7 rad, the radiation dose rate slightly influences the grafting percentage. Therefore, as far as the operation efficiency is concerned, preirradiation at relatively high dose rate (radiation time is relatively short) is reasonable.

Figure 1 indicates the effect of monomer concentration. With increasing monomer concentration, the grafting percentage obviously rises. Figure 2 shows the effects of reaction temperature and time on the grafting percentage. With the increases of reaction time and temperature, the grafting per-

Dose Rate				
(rad/min)	3100	3500	6300	6867
Grafting percentage				
(%)	2842	2857	2947	2933

 Table I
 Effect of Irradiation Dose Rate

 on the Grafting Percentage^a

^a Reaction temperature 50°C; reaction time 5 h; monomer concentration 30%; irradiation dose 2.5×10^7 rad.

centage increases. In the case where the reaction temperature is 60° C, the chain transfer and chain termination become significant during the growth of grafted side chain, so the increase of the grafting percentage with prolonging reaction time is not remarkable after 1 h of reaction.

Usually, water is a suitable solvent for the hydrophilic PVA fiber. However, the monomer GMA is insoluble in water. Accordingly, a mixture of methanol and deionized water was used as solvent in this graft copolymerization. Table II shows the effect of methanol content on the grafting percentage. Obviously, the graft copolymerization in the solvent mixture presents higher grafting percentage than in pure methanol or pure water.

Curves 1 and 2 in Figure 3 are the IR spectra of PVA fiber and the obtained grafted fiber, respectively. In curve 2 the absorption peak at 1725 cm⁻¹ is due to the vibration of -CO bond in the carboxyl group of PGMA side chain, and the peaks at 910, 841, and 765 cm⁻¹ are due to the vibrations of the epoxy group in PGMA side chain. Therefore the obtained fiber is confirmed to be a grafted fiber PVAg-GMA that contains epoxy groups in the branch chains.



Figure 1 Relation between monomer concentration and grafting percentage (temperature 50°C; time 5 h; preirradiation dose 2.5×10^7 rad).



Figure 2 Relation between reaction temperature, time, and the grafting percentage (monomer concentration 30 v %; dose 2.5×10^7 rad; dose rate 6500 rad/min; temperature (1) 60°C, (2) 50°C, (3) 40°C, and (4) 30°C.

Functionalization of the Grafted Fiber

According to Eq. (2), the functionalization of the grafted fiber is a ring-opening reaction, and there is no other low molecule released. Therefore it is reasonable to describe the conversion of epoxy groups by the increasing percentage of the fiber weight (defined as the increase of the fiber weight divided by the weight of the fiber before reaction, and referred to as IPW in the following discussion). Figure 4 shows the relationship between IPW and the content of functional group in the obtained chelating fiber calculated according to the nitrogen content of the fiber. Obviously, the more the functional group, the greater the IPW.

Figure 5 shows the effects of reaction temperature and time on the IPW in the reaction of diethanolamine with PVA-g-GMA. With increasing time and temperature, the IPW increases. However, when the reaction is carried out at 80° C, the IPW decreases and then rises with prolonging reaction time. Figure 6 indicates the effect of the amount of amine used on the IPW. With increasing amine, the IPW in-

Table IIRelationship between GraftingPercentage and Methanol Content in AqueousMethanol Solvent*

Content of methanol			-			
(v %)	100	83	79	71	66	0
Grafting percentage						
(%)	0	3030	2839	2980	2988	2782

^a Reaction temperature 50°C; reaction time 5 h; monomer concentration 30%; dose 2.5×10^7 rad; dose rate 6500 rad/min.



Figure 3 IR spectra of PVA fiber: (1) PVA-g-GMA grafted fiber, (2) functionalized fiber (3), (4), (5), and (6).

creases. Table III shows the effect solvent on the reaction. Among the solvent used in this reaction, 1,4-dioxane is the most reasonable solvent for the reaction.

Curve 3, 4, 5, and 6 in Figure 3 are the IR spectra of the fibers prepared from the reaction of PVA-g-GMA with diethylenetriamine, diethanolamine, di-



Figure 5 Effects of reaction temperature and time on the IPW of the reaction between diethanolamine and PVA-g-GMA fiber: (1) 80°C, (2) 60°C, and (3) 50°C.

ethylamine, and aminopyridine, respectively. In curves 3, 4, and 5, the peaks at 906, 842, and 750 cm⁻¹ corresponding to the epoxy group all disappear, and the new peaks at 1380–1260 cm⁻¹ corresponding to the stretch vibrations of C — N bond and at 1600 cm⁻¹ corresponding to the bend vibration of — NH₂ appear; in curve 6, the peaks at 906, 842, and 750 cm⁻¹ weaken, and two new peaks at 1582 and 1646 cm⁻¹, respectively, corresponding to the stretch vi-



Figure 4 Relationship between the content of functional group and IPW.



Figure 6 Effect of the amount of the used amine on the IPW, (temperature 60°C; time 7 h). (1) type (I) fiber; (2) type (II) fiber; (3) type (III) fiber; and (4) type (IV) fiber.

Solvent	1,4-Dioxane	Anhydrous Alcohol	Acetone	Benzene
IPW (%)	42.5	40.9	40.7	41.7

Table IIIEffect of Solvent on theFunctionalization of PVA-g-GMA*

 $^{\rm a}$ Temperature 50°C; time 3 h; amount of used diethylamine 10 g/g fiber.

bration of bond C = C and C = N in the pyridine ring appear. From the above, the obtained fiber contains the desired amine group. In the following discussion, the chelating fibers containing diethylenetriamine, diethanolamine, diethylamine, and aminopyridine are, respectively, referred to as type (I), (II), (III), and (IV) fiber. The measured elemental contents and the functional group contents of the chelating fiber calculated according to the nitrogen content are shown in Table IV.

Adsorption Properties of the Chelating Fibers

Adsorption Amount for Metallic Ions

Table V shows the adsorption amounts of metallic ions on the prepared chelating fibers. The prepared chelating fibers all present high adsorption amounts for Cu^{2+} , Zn^{2+} , Au^{3+} , Mn^{2+} , and Fe^3 . Therefore those chelating fibers can be applied in the treatment of metallic ion-containing wastewater and in the recovery of metal such as copper, zinc, and gold. In addition, among those four fibers, the fiber with diethylenetriamine group (type I fiber) presents greatest adsorption amount for Cu²⁺, and the fiber with diethanolamine group (type II) or diethylamine group (type III) presents relatively high adsorption amount for Au^{3+} . As far as the adsorption capacity of a functional group is concerned, the functional group diethylenetriamine has greater adsorption capacity than the others. Accordingly the diethyl-

Table IVMeasured Element Contents and theCalculated Functional Group Contents

	Сог	Element Content (wt %)					
Chelating Fiber	С	Н	N	Group (mmol/g)			
Type (I)	48.98	7.84	8.99	2.14			
Type (II)	49.99	8.14	4.70	3.35			
Type (III)	58.43	9.15	5.45	3.89			
Type (IV)	53.82	6.88	5.15	1.84			

Table VAdsorption Amounts of the ChelatingFibers Containing Amino Group^a

		Adsorption Amount (mmol/g)						
Ion	pH	Type (I)	Type (II)	Type (III)	Type (IV)			
Mg^{2+}	$5 \sim 6$	0.10	0.18	0.20	0.18			
Ca ²⁺	5	1.00	2.00	0.32	0.34			
Cd^{2+}	5	1.30	0.69	0.38	0.69			
Pb^{2+}	5	0.52	0.53	0.17	0.54			
Fe ³⁺	2	1.80	1.33	1.38	0.22			
Mn^{2+}	5	1.71	0.37	1.01	0.71			
Zn^{2+}	5	2.43	1.85	2.67	1.04			
Ni ²⁺	5	1.23	0.84	0.68	0.52			
Co^{2+}	5	1.45	0.57	1.07	0.69			
Cu^{2+}	3	3.48	2.34	2.54	1.12			
UO_2^{2+}	5	0.82	0.40	0.37	0.20			
Au ³⁺	5	2.39	3.31	3.78	0.83			
Ag^+	5	1.08	0.71	0.70	0.62			

^a Adsorption temperature 30°C; time 8 h.

enetriamine group is the most suitable functional group for the adsorption of Au^{3+} and Cu^{2+} .

Adsorption Behaviors of Cu²⁺ on the Chelating Fibers

Figure 7 indicates the relationships between adsorption time and adsorption amount of the chelating fibers. The fibers all present high adsorption rate for Cu^{2+} , and after about 1 h the adsorptions tend to be in equilibrium. According to the adsorption equation, $-\ln(1-F) = Kt + C$ (where t is adsorption time, K is an adsorption rate constant, E_t is the adsorption amount at time t, E_e is an equilibrium adsorption amount, C is a constant and $F = E_t/$



Figure 7 Relationship between adsorption time and Cu^{2+} adsorption amount (initial concentration of Cu^{2+} is 0.05M; temperature 30°C; pH 4.7). (1), (2), (3), and (4) are type (I), (II), (III), and (IV) fibers, respectively.



Figure 8 Plots of t vs. $-\ln(1-F)$. (1), (2), (3), and (4) are type (II), (III), (I), and (IV) fibers, respectively.

 E_e),¹⁴ the experimental results of Figure 7 can be converted into the plots of $-\ln(1-F)$ vs. t as shown in Figure 8, and the adsorption rate constants of the fibers calculated from the slops of the plots are 1.48 $\times 10^{-4}$ s⁻¹ for type (I) fiber, 2.36×10^{-4} s⁻¹ for type (II) fiber, 1.60×10^{-4} s⁻¹ for type (III) fiber, and 1.22×10^{-4} s⁻¹ for type (IV) fiber, respectively. Figure 9 shows the effect of temperature on the adsorption amounts of type (I) and type (III) fibers. With rising temperature, the adsorption amount increases, then decreases due to the desorption at high temperature.

Adsorption Behaviors of Au³⁺ onto the Chelating Fibers



Figure 10 shows the relationship between adsorption time and adsorption amount. Adsorption amount of Au^{3+} ion onto type (II) fiber rises rapidly with time,

Figure 9 Effect of temperature on the adsorption amounts of Cu^{2+} ion onto the chelating fibers (initial concentration of Cu^{2+} is 0.05M; pH 3.0; time 4 h). (1) type (I) fiber; (2) type (III) fiber.



Figure 10 Relationship between adsorption time and Au^{3+} adsorption amount of the type II fiber (temperature 30°C; initial concentration of Au^{3+} ion is 500 mg/L; pH 2.8).

and equilibrium adsorption amount will be reached after 1.5 h. Table VI shows the effects of temperature and pH on the adsorption amount. With increasing adsorption temperature or the pH value of Au^{3+} aqueous solution modulated by a NaAc-HAc buffer, the adsorption amount increases significantly.

During the adsorption process, the white chelating fiber became brown at first, and then large amounts of golden precipitates on the surface of the chelating fiber appeared. Having been washed with deionized water and dried at room temperature, the fiber was tested by means of WAXD and scanning electron microscopy (SEM). According to the WAXD diagram of the fiber with adsorbed Au³⁺, as



Figure 11 WAXD diagrams of the chelating fibers after adsorption process. (1) type (I) fiber with adsorbed Au^{3+} ion of 626.7 mg/g; (2) type (II) fiber with adsorbed Au^{3+} ion of 943.2 mg/g.

Temperature (°C)		30			40		5	0
pH	3.8	4.8	5.5	3.8	4.8	5.5	3.8	4.8
Adsorption amount (mg/g)	931	1465	1783	1088	1569	1914	1350	1671

Table VI Effects of Temperature and pH on the Adsorption Amount of the Type (II) Chelating Fiber^a

^a Concentration of Au³⁺ 420 mg/L; time 6 h.

is shown in Figure 11, the values of the interplanar spacings relating to the diffraction peaks of the precipitate are, respectively, quite similar to those relating to the planes (111), (200), (220), and (311) in the crystallite of metallic gold.¹⁵ Therefore it is concluded that the precipitates on the surface of the fiber are metallic gold. Consequently the adsorbed Au^{3+} is reduced to metallic Au by the functional group in the fiber. Mechanism on the reduction will be reported in following studies.

Selectivities of the Chelating Fibers

The Cu²⁺ selective adsorption performances of the chelating fibers in a chloride aqueous solution with Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , and Cu^{2+} are shown in Table VII. The chelating fibers all present good selectivities for Cu^{2+} in the above solution. In addition, the type (I) fiber possesses the greatest distribution factor for Cu²⁺ among the chelating fibers. The selective adsorption performance for Au^{3+} of type (II) and type (III) chelating fibers were tested in an aqueous chloride solution with Au^{3+} , Cu^{2+} , Cr^{3+} , and Zn²⁺. The results are shown in Table VIII. Although the chelating fibers present high selectivities for Cu²⁺ as shown in Table VII, the chelating fibers present high selectivities to the Au³⁺ ion and do not adsorb the Cu^{2+} ion in the solution with Cu^{2+} , Au^{3+} , Zn^{2+} , and Cr^{3+} ions. Because the chelating fibers present such a good selectivity for Au³⁺ and is able to reduce the adsorbed Au^{3+} ion into metallic gold, these fibers are obviously helpful for the recovery of gold from Au^{3+} ion-containing solution.

CONCLUSIONS

It is possible to prepare chelating fibers with amino functional groups by reacting amine with grafted fiber PVA-g-GMA containing epoxy groups. In the graft copolymerization of GMA onto PVA fiber, preirradiation dose rate has little effect on the grafting percentage. With increasing monomer concentration, reaction time, and temperature, the grafting percentage increases significantly. In the functionalization of the grafted fiber, reaction time, temperature, solvent, and the amount of amine used greatly influence the reaction. 1,4-Dioxane is a reasonable solvent for the reaction, and increasing amine amount, reaction time, and temperature below 80°C are advantageous to the reaction.

The chelating fibers present great adsorption amounts and high adsorption rates for Cu^{2+} ion and Au^{3+} ion. Among the chelating fibers, the fiber with diethylenetriamine group is the most reasonable chelating fiber for the adsorption of Cu^{2+} and Au^{3+} .

The chelating fibers present good selectivities for Cu^{2+} in the solution with Cu^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} , while presenting quite high selectivities

Table VII Selective Adsorption Behavior of the Chelating Fibers in the Solution Containing Zn²⁺, Co²⁺, Ni²⁺, Mn²⁺, and Cu^{2+ a}

	a		Adsorpti (m:	ion Amount mol/g)		Distribution Factor (L/g)			
Ion	(mM)	Type (I)	Type (II)	Type (III)	Type (IV)	Type (I)	Type (II)	Type (III)	Type (IV)
\mathbf{Zn}^{2+}	4.74	0.24	0.29	0.40	0.37	0.057	0.068	0.095	0.088
Co^{2+}	5.09	0.19	0.27	0.32	0.35	0.041	0.058	0.068	0.076
Ni ²⁺	5.28	0.23	0.22	0.26	0.29	0.048	0.045	0.053	0.060
${ m Mm^{2+}}$ ${ m Cu^{2+}}$	5.28 4.80	$\begin{array}{c} 0.12 \\ 2.01 \end{array}$	0.29 1.71	$\begin{array}{c} 0.34 \\ 2.32 \end{array}$	0.38 0.98	$0.024 \\ 5.950$	$0.060 \\ 0.807$	$0.071 \\ 1.340$	$0.080 \\ 0.290$

^a Adsorption temperature 30°C; time 8 h.

Ion	Au^{3+}	Cu ²⁺	Cr ³⁺	Zn ²⁺
Concentration (ppm) Adsorption amount (mg/g)	2075	4250	14.5	875
Type (II) fiber	716.8	0	0	44.8
Type (III) fiber	852.3	0	0	94.7

Table VIII Selective Adsorption of Chelating Fibers for the Ions in the Aqueous Solution with Au^{3+} , Cu^{2+} , Zn^{2+} , and Cr^{3+a}

^a Temperature 30° C; time 6 h; pH = 2.8.

for the Au^{3+} ion in solution with Cu^{2+} , Au^{3+} , Zn^{2+} , and Cr^{3+} ions.

The chelating fiber with diethanolamine or diethylamine can reduce the adsorbed Au^{3+} into metallic gold.

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