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W. Li^a; Z. Shen^a; Y. Zhang^a

^a Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, P. R. of China

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SYNTHESIS OF FUNCTIONAL RESINS FROM POLY(CHLOROMETHYL THIIRANE) AND THEIR SORPTION PROPERTIES FOR NOBLE METAL

Weishi Li, Zhiquan Shen,* and Yifeng Zhang
Department of Polymer Science and Engineering
Zhejiang University
Hangzhou 310027, P. R. of China

Key Words: Poly(chloromethyl thiirane), Functional Resin, Noble Metal Sorption

ABSTRACT

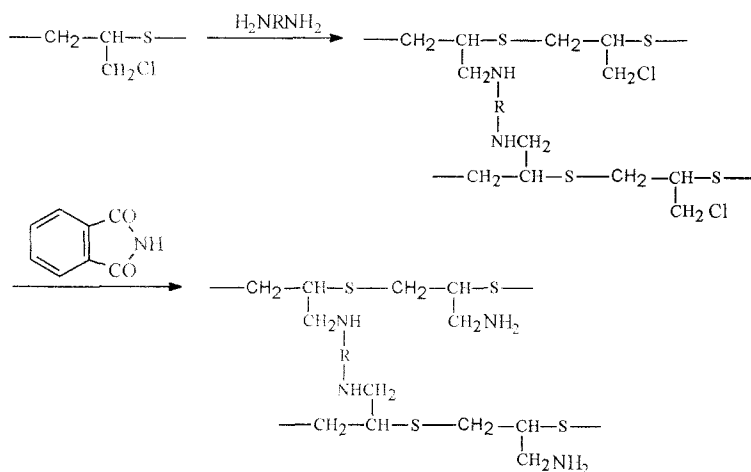
Three new kinds of functional resins bearing polythioether backbone and primary amino group (CA), or dithiocarbamate (CDTC) or Schiff base (CSB) in side chain, were synthesized from poly(chloromethyl thiirane). The sorption capacities of CA resins for noble metals were 5-8 mmol Au(III)/g resin and 7-9 mmol Ag⁺/g resin. CDTC resins could absorb 9-11 mmol Ag⁺ per gram resin, but little Au(III). CSB had similar properties as CDTC. These resins all exhibited low capacities, no more than 2 mmol/g resin, for Hg²⁺, Pb²⁺, Ni²⁺, Fe³⁺, Zn²⁺, and Cu²⁺. Thus, Au(III) and Ag⁺ can be separated successfully from the above common ions. The resins were easily regenerated and reused without an obvious decrease in the sorption capacity for Ag⁺.

INTRODUCTION

Functional resins are useful in the preconcentration, separation, recovery, purification, and hydrometallurgy of noble metal. Most functional resins were prepared from chloromethylated poly(styrene), poly(acrylate), etc., whose backbones are all made of C-C structures and contribute nothing to sorption [1]. Recently,

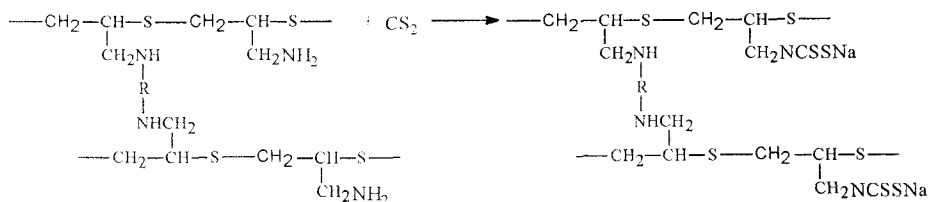
poly(chloromethyl thiirane) (PCMT) containing polythioether backbone and active chloromethyl groups in side chain has been introduced into synthesis functional resins which exhibited better sorption properties for noble metals [2-4].

In the present work, a new kind of functional resins bearing primary amino group in side chain, named CA resins, was prepared from PCMT after the Scheme 1:

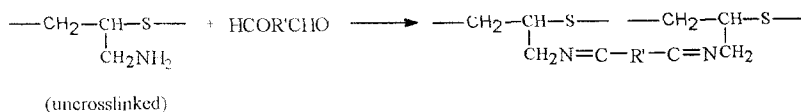


SCHEME 1

where R is CH_2CH_2 (CA1), $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$ (CA2) and $\text{CH}_2\text{CH}_2(\text{NHCH}_2\text{CH}_2)_2$ (CA3). CA resins reacted with carbon disulfide giving CDTC resins and with dialdehyde compounds resulting in CSB resins, as shown in Schemes 2 and 3, respectively.



SCHEME 2



SCHEME 3

where R is CH_2CH_2 (CDTC1), $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$ (CDTC2) and $\text{CH}_2\text{CH}_2(\text{NHCH}_2\text{CH}_2)_2$ (CDTC3) and R' is none (CSB1), $\text{CH}_2\text{CH}_2\text{CH}_2$ (CSB2) and *o*- C_6H_4 (CSB3). These resins all exhibited excellent sorption properties for noble metals, especially CA resins for Au(III) and CDTC resins for Ag^+ , but low capacities for Hg^{2+} , Pb^{2+} , Ni^{2+} , Fe^{3+} , Zn^{2+} , and Cu^{2+} . This may be useful in the noble metal separation industry.

EXPERIMENTAL

Materials

Poly(chloromethyl thiirane) with molecular weight of 30,000-50,000 and polydispersity of 2-4 was obtained with rare earth superacid $\text{SO}_4^{2-}/\text{TiO}_2/\text{Nd}^{3+}$ catalyst developed in our laboratory [5]. The agents engaged in the resins' synthesis procedures were all chemically pure. 1,4-Dioxane, dimethylformamide (DMF) and ethanol, used as solvent, were dehydrated and purified prior to use.

Synthesis of CA1 Resin

0.092 mol ethylenediamine, as crosslinking agent, was added dropwise into 30 mL 1,4-dioxane solution containing 10 g PCMT, then reacted at room temperature for 2 hours and at 80°C for another 16 hours. The ethylenediamine precross-linked PCMT1 was obtained from filtration.

Precrosslinked PCMT1 5 g were swelled in 50 mL DMF, then added phthalimide 6.5g, K_2CO_3 6.1 g and KI 6.1 g. After reacting at 80°C for 5 hours, a brown intermediate resin was obtained by filtration and treated with hydrazine in refluxing ethanol and gave 2.6 g yellow CA1 resin.

Synthesis of CDTC1 Resin

After 2 g, CA1 resin were swelled in 20 mL anhydrous ethanol, 4.74 g CS_2 (molar ratio $\text{CS}_2/\text{NH}_2=4$) was added and stirred at room temperature for 30 hours, then mixed with a 20 mL ethanol solution dissolving 0.96 g sodium and reacted for 1 hour at $65\text{-}70^\circ\text{C}$. The brown resultant CDTC1 resin was obtained from filtration with a yield of 75%.

Synthesis of CSB Resins

CSB resins were prepared from uncrosslinked CA resin. The CA resin dissolved in DMF and dropped with a DMF solution containing dialdehyde compounds listed in Table 4 with a molar ratio of 0.5 to amino group contained in

TABLE 1. Precrosslinking of PCMT^a

Name	Crosslinking agent	Yield(%)	Residual Cl content(%)	
			Found	Calculated ^b
PCMT1	Ethylenediamine	89	26.0	26.3
PCMT2	Diethylenetriamine	82	23.2	25.4
PCMT3	Triethylenetetraamine	96	19.1	24.5

^a Reaction conditions: molar ratio of $\text{NH}_2/\text{Cl}=1/5$, $\text{Et}_3\text{N}/\text{NH}_2=1.2$, at 80°C for 16h, 1,4-dioxane as solvent

^b From the amount of primary amino group contained in crosslinking agent.

the CA resin. After reacting at $80\text{-}100^\circ\text{C}$ for above 12 hours and filtrating, a puce CSB resin was yielded.

Measurements

C, H and N contents of these resins were determined by a Perkin-Elmer 240 elemental analyzer. The contents of Cl and S were obtained after the method described in literature [6]. IR spectra were measured by a Nicolet FT-IR spectrometer. The concentrations of Au(III) and other ions in mixture solution were measured by a HITACHI 180-50 atomic absorption spectrometer. Ag^+ concentration was determined after Volhard's method. The common ions' concentration were obtained by titration, that of Hg^{2+} with NaSCN , and those of Pb^{2+} , Ni^{2+} , Fe^{3+} , Zn^{2+} , and Cu^{2+} with EDTA.

RESULTS AND DISCUSSION

Synthesis of Resins

Based on the optimum conditions reacted between PCMT and diamine compounds [2], the precrosslinked PCMT were obtained. The residual Cl contents were determined, as shown in Table 1, that were smaller than that calculated. The more secondary amino groups contained in crosslinking agent, the greater difference between the two Cl contents. It illustrated that not only primary amino group, but also secondary amino group reacted.

The synthesis conditions of CA resins were studied focusing on the Gabriel reaction of precrosslinked PCMT with phthalimide. Adding KI or increasing reaction temperature could promote the reaction (Table 2). But above 120°C , an

TABLE 2. Effects of KI and Temperature on Gabriel Reaction in CA1 Resins Synthesis^a

Temperature(°C)	60	80 ^b	80	100
Residual Cl content(%)	6.8	2.8	1.1	0.6
Functional conversion(%)	61	83	93	99.6

^a Precrosslinked PCMT1, phthalimide/Cl=1.2, K₂CO₃/phthalimide=1, KI/Cl=1, 5h.

^b Not adding KI

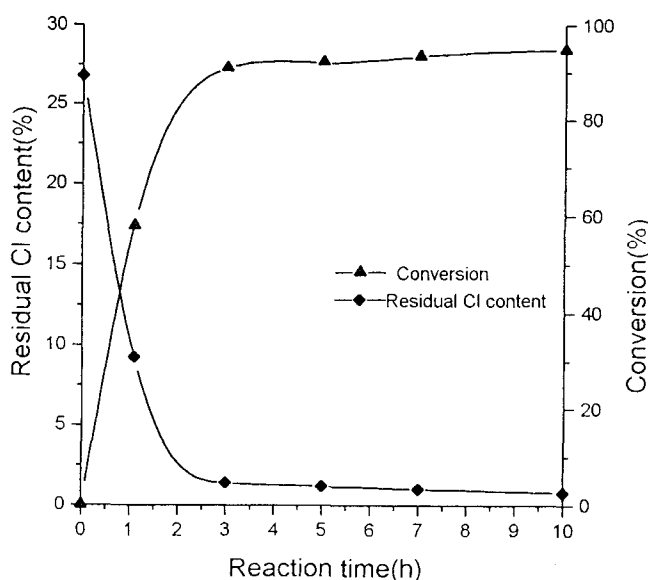


Figure 1. Influence of reaction time on functional conversion and residual Cl content in synthesis of CA resins. Molar ratio phthalimide/Cl=1.2, K₂CO₃/phthalimide=1, KI/Cl=1, 80°C.

unfavorable odor gave off. The residual Cl content decreased vary rapidly when the reaction began (Figure 1). After 3 hours, the residual Cl content reduced to 1.4% and the functional conversion reached 90%.

Tables 3-5 list the synthesis results of CA, CDTC and CSB resins, respectively. Compared with CA resins, CDTC resins have higher S content but lower N content. The S, N contents of CSB resins were found to be lower than that of CA resins. The higher molecular weight of dialdehyde compound, the greater the

TABLE 3. Synthesis of CA Resins^a

Name	Precursor	Yield (%)	Residual Cl content (%)	N content (%)	S content (%)	Functional conversion(%)	Functional capacity (mmol/g resin)
CA1	PCMT1	60	2.3	5.90	28.0	85	7.80
CA2	PCMT2	58	1.9	6.64	27.2	86	5.33
CA3	PCMT3	58	2.0	6.88	26.9	84	5.39

^a Synthesis condition: phthalimide/Cl=1.2, K₂CO₃/phthalimide=1, KI/Cl=1, 80°C, 5h

TABLE 4. Synthesis of CDTC Resins^a1/1.5, Ethanol as Solvent

Name	Precursor	Yield (%)	N content (%)	S content (%)
CDTC1	CA1	75	4.69	37.0
CDTC2	CA2	68	4.82	34.0
CDTC3	CA3	72	5.11	29.4

^a Synthesis conditions: CS₂/NH₂=4, Na/CS₂=1/1.5, ethanol as solvent

TABLE 5. Synthesis of CSB Resins^a

Name	Dialdehyde compound ^b	Yield (%)	N content (%)	S content (%)
CSB1	Glyoxal(58)	65	5.00	29.4
CSB2	Glutaric dialdehyde(100)	58	4.18	22.6
CSB3	Phthalic dicarboxaldehyde(134)	51	3.54	17.0

^a Prepared from uncrosslinked CA resin, DMF as solvent.

^b Including in the space is the molecular weight of dialdehyde compound.

decrease. The functional group capacities of CA resins were calculated from the Cl contents of precrosslinked PCMT and CA resins. Those of CDTC and CSB resins were difficult to obtain due to the complex of CA resins' structures and reactions' mechanism. The successful conversion of functional groups of these resins were confirmed by IR spectra.

Sorption Properties of Resins

From Table 6, CA resins were found to have sorption capacity for Au(III) of 5-7 mmol/g resin, which was rather higher than that of CDTC and CSB resins.

TABLE 6. Sorption Capacities for Metal Ions (mmol/g Resin)^a

Resin	Au(III)	Ag ⁺ ^b	Ag ⁺ ^c	Hg ²⁺	Pb ²⁺	Ni ²⁺	Fe ³⁺	Zn ²⁺	Cu ²⁺
CA1	5.19	7.55	6.94	1.67	0.469	0.220	0.992	0.274	1.150
CA2	5.52	7.69	7.42	1.65	0.040	0.190	0.340	0.046	0.170
CA3	6.76	8.79	8.45	1.98	0.115	0.192	0.948	0.124	1.013
CDTC1	1.24	10.64	9.63	1.46	0.719	0.050	0.498	0.295	0.660
CDTC2	0.43	9.94	9.57	1.57	0.249	0.018	0.375	0	0.213
CDTC3	0.70	9.88	9.50	1.42	0.976	0.032	0.377	0.134	0.725
CSB1	0.02	6.21	5.20	0.29	0.070	0.025	0.098	0.021	0.093
CSB2	2.15	6.43	5.41	1.58	0.094	0.141	0.333	0.084	0
CSB3	0.14	4.23	2.36	0.11	0.017	0.080	0.176	0.016	0.200

^a Sorption conditions for Au(III): 12.5mg resin, 25mL 1.0mg/L Au(III) solution, in 2NHCl; for Ag⁺: 100mg resin, 25mL 0.1mol/L Ag⁺ solution, ^b in 1NHNO₃, ^c in pH=7; for Hg²⁺: 60mg resin, 25mL 0.025mol/L Hg²⁺ solution, in 1NHNO₃; for other ions: 60mg resin, 25mL 0.025mol/L ion solution, pH=5.6; at room temperature for 24h.

TABLE 7. Sorption Experiments in Mixture Solution

Resin	Sorption percentage in mixture A (%) ^a					Sorption capacity in mixture B (mmol/g resin) ^b			
	Au(III)	Ni ²⁺	Cu ²⁺	Zn ²⁺	Fe ³⁺	Ag ⁺	Mg ²⁺	Zn ²⁺	Pb ²⁺
CA2	100	0	0	0	0.1	3.07	0	0.16	0.32
CDTC1	99.8	0	0.49	4.5	7.6	7.13	0	0.926	0

^a 12.5mg resin; 25mL mixture ion solution A containing 0.1mg/mL Au(III) and 1.0mg/mL Ni²⁺, Cu²⁺, Zn²⁺ and Fe³⁺, in 2N HCl, at room temperature for 24h.

^b 60mg resin; 25mL mixture solution B containing 0.025mol/L Ag⁺, Mg²⁺, Zn²⁺, and Pb²⁺ respectively; pH=7, at room temperature for 24h.

For Ag⁺, CDTC resins showed the best ability among the three kinds of resins. Their sorption capacities for Ag⁺ were 7-9 mmol/g CA resin, 9-11 mmol/g CDTC resin and 4-6 mmol/g CSB resin. Compared with sorption in neutral environment, resins exhibited better sorption capacity in 1N HNO₃. Absorbing a large amount of Ag⁺ but rather little of Au(III), a special property that CDTC and CSB presented, may make the two resins used in the separation of Ag⁺ from Au(III). The different sorption capacities for Au(III) and Ag⁺ can be correctly explained by the function groups and the nature of the resins. The dithiocarbamate functional group with nega-

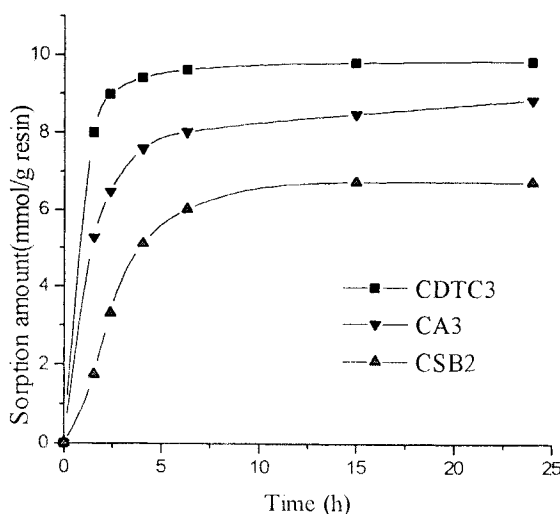


Figure 2. Sorption process for Ag^+ . 100mg resin, 0.1mol/L Ag^+ , solution total volume: 25 mL, in 1N HNO_3 , at room temperature.

tive charge contained in CDTC resins promoted the cation Ag^+ sorption but repelled the anion AuCl_4^- .

However, these resins all showed low abilities in sorption for Hg^{2+} , Pb^{2+} , Ni^{2+} , Fe^{3+} , Zn^{2+} , and Cu^{2+} as shown in Table 6. The highest result was 1.98 mmol Hg^{2+} per gram CA3 resin. The great difference between sorption for noble metals and for non noble metals make it possible to use these resins in recovery noble metals from non noble metal ions. The two experimental results of sorption in mixture ion solution, as shown in Table 7, confirmed this. CA2 and CDTC1 resins both absorbed Au(III) quantitatively in mixture solution A containing Ni^{2+} , Cu^{2+} , Zn^{2+} and Fe^{3+} with concentration of ten times as that of Au(III). Although CA2 and CDTC1 resins decreased their sorption capacities for Ag^+ slightly, compared with Table 6, they almost absorbed none of Mg^{2+} , Zn^{2+} and Pb^{2+} in mixture solution B.

Figure 2 shows the dependence of the absorbed amount of Ag^+ of resins on the contacting time. The time required to reach half of the equilibrium sorption capacity ($T_{1/2}$) of resins was 0.77 hours for CDTC3, 1.2 hours for CA3 and 2.42 hours for CSB2, respectively. The data of Figure 2 can be transferred into Figure 3 where $F=Q_t/Q$, and Q_t and Q are the sorption amounts at sorption time t and equilibrium, respectively. According to Brykina method [7], the sorption rate constant K can be calculated from the following equation:

$$-\ln(1-F) = Kt$$

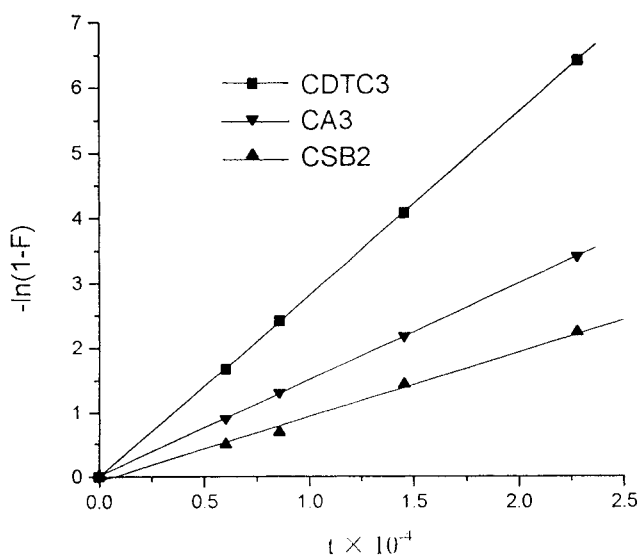


Figure 3. The dependence of $-\ln(1-F)$ on sorption time.

TABLE 8. Sorption Capacity for Ag^+ of Regenerated Resin (mmol/g Resin)^a

Resin	Regeneration time			
	0	1	2	3
CA2	7.69	7.50	7.10	6.50
CDTC1	10.64	10.50	10.48	10.20
CSB1	6.21	6.26	6.18	6.01

^a 100mg resin, solution total volume: 25mL, concentration of Ag^+ : 0.1mol/L, in 1N HNO_3 , at room temperature for 24h.

and the results are as follows: $2.81 \times 10^{-4}\text{s}^{-1}$ (CDTC3), $1.49 \times 10^{-4}\text{s}^{-1}$ (CA3), and $1.00 \times 10^{-4}\text{s}^{-1}$ (CSB2). The values of $T_{1/2}$ and rate constant K illustrate that CDTC3 resin can absorb Ag^+ more quickly than CA3 and CSB2 resins.

Ag^+ absorbed on resins could be eluted by 15% aqueous ammonia. Then the resin was washed thoroughly with water and could be reused (Table 8). After three times regeneration, CA2, CDTC1, and CSB1 remained 85%, 96% and 96% of original sorption capacity for Ag^+ in 1N HNO_3 respectively, which illustrate that these resins have excellent reusability.

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