# New Chelating Polymers for Heavy Metal Ion Sorption

GALINA G. TALANOVA, LONGGUI ZHONG, RICHARD A. BARTSCH

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061

Received 23 November 1998; accepted 22 February 1999

**ABSTRACT:** Twenty-six new chelating polymers containing pyridyl (Py) or bipyridyl (Bipy) units as ligating centers were synthesized by free-radical reactions of 2-vinylpyridine, 4-vinylpyridine, or 4-methyl-4'-vinyl-2,2'-bipyridine with different dimethacrylate crosslinkers and evaluated for heavy metal ion sorption from aqueous solutions. Both the Py- and Bipy-containing polymers are highly selective for Cu(II) over Co(II) and Ni(II) and for Hg(II) over Cd(II). The polymeric materials with Bipy binding sites generally exhibit more efficient metal ion sorption than do the corresponding Pycontaining copolymers. The metal ion sorption capacity of the copolymer also depends on the structure of the dimethacrylate crosslinker. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 849–856, 1999

Key words: chelating polymers; pyridyl and bipyridyl groups; heavy metal ions; sorption

#### **INTRODUCTION**

Polymeric materials containing chelating groups which sorb heavy metal ions are applied in the solution of a variety of ecological and industrial waste problems.<sup>1–3</sup> Therefore, such polymers continue to attract the attention of many researchers.<sup>3</sup> In particular, inclusion of heterocyclic amine units into polymeric matrices as the chelating centers results in promising materials for the separation of heavy metal ions from aqueous solutions.<sup>3–16</sup> However, only a few of those polymeric sorbents contain bipyridyl (Bipy) or pyridyl (Py) groups,<sup>6,13</sup> even though such heterocyclic amines are known to form stable complexes with transition metal ions in solutions<sup>17</sup> and thereby might be expected to behave as efficient chelators for metal ion sorption as well.

We now report the synthesis of a series of new Py- and Bipy-containing copolymers and the examination of their sorption abilities toward the hazardous heavy and transition metal ions of Cd(II), Co(II), Cu(II), Hg(II), and Ni(II).

#### **EXPERIMENTAL**

#### Materials

Reagent-grade starting materials and solvents were purchased from commercial suppliers. The dimethacrylate crosslinkers were obtained from Monomer-Polymer & Dajac Laboratories Inc. (Feasterville, PA). The free-radical initiator 2,2'azobisisobutyronitrile (AIBN) from Aldrich (Milwaukee, WI) was purified by recrystallization from absolute ethanol below 40°C in subdued light, dried *in vacuo* at room temperature over  $P_2O_5$ , and stored in vacuo in the dark below -10°C. The 4-methyl-4'vinylbipyridine was synthesized by a literature procedure.<sup>18</sup> Anhydrous methanol was prepared from the reagent-grade solvent by refluxing for 2-3 h over magnesium turnings in the presence of iodine followed by distillation.

Correspondence to: R. A. Bartsch.

Contract grant sponsors: Texas Higher Education Coordinating Board–Advanced Research Program; Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy.

Journal of Applied Polymer Science, Vol. 74, 849-856 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/040849-08



Figure 1 Structures of the chelating monomers.

## Equipment

IR spectra were measured with a Perkin–Elmer Model 1600 FTIR spectrophotometer. TGA analysis was performed with a Shimadzu TGA-50 thermogravimetric analyzer with a temperature increase rate of 10°C/min. A Perkin–Elmer Model 5000 atomic absorption spectrophotometer was used for the determination of the metal ion concentrations in aqueous solutions before and after sorption. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ). The circulating water bath for temperature control during polymer syntheses utilized a Lauda Model B1 thermocouple-controlled heating unit and a Lauda Model C pump connected to a 2-L glass container.

# General Procedure for the Preparation of the 2-Vinylpyridine (2-VPy), 4-Vinylpyridine (4-VPy), and 4-Methyl-4'-vinyl-2,2'-bipyridine (MVBipy) Copolymers

The chelating monomer (Fig. 1) (5.10 mmol) was added to 5.0 mL of a methanol-benzene solution (1 : 1 by volume) in a  $34 \times 24$ -cm reaction tube and the mixture was stirred with a magnetic stir-

rer bar until the monomer dissolved. The dimethacrylate crosslinker (Fig. 2) (5.10 mmol for copolymers 1, 5, and 9; 10.20 mmol for copolymers **2**, **6**, **10**, and **15–27**; 15.30 mmol for copolymers **3**, **7**, and **11**; 20.40 mmol for copolymers **4**, **8**, and **12**) was added with a pipette and the mixture was stirred until a homogeneous solution was observed. AIBN (0.050 g) was added and stirring was continued to obtain a solution which was degassed by a freeze-pump-thaw method. Thus, the solution was frozen with an acetone-dry ice bath and the reaction tube was evacuated with a vacuum pump. The contents of the evacuated tube were allowed to thaw at room temperature to form a solution. This procedure was repeated three times and then the reaction tube was partially immersed in a 60°C water bath. After reaction for 18 h at 60°C, the solvent was decanted and the solid was washed three times with 50 mL of methanol-benzene (1:1 by volume). The product was dried in vacuo at 100°C for 24 h and ground with a Wigg-L-Bug<sup>TM</sup> apparatus into a fine powder that passed through a 100-mesh sieve. Yields and elemental analysis data for the copolymers are listed in the Tables I and II. IR spectra (KBr) for the copolymers showed absorptions in the ranges 1749–1726 (C=O), 1596– 1585 and 1502 (aromatic ring), and 1167-1138  $(C - 0) \text{ cm}^{-1}.$ 

# Synthesis of Poly(ethylene glycol dimethacrylate) (13)

Ethylene glycol dimethacrylate (EGDMA) (2.47 g, 12.47 mmol) was added with a pipette to 5.0 mL of the methanol-benzene solution (1 : 1 by volume) in



Figure 2 Structures and abbreviations for the crosslinkers.

Chelating Monomer	Copolymer	Crosslinker/Chelating Monomer Molar Ratio			Elemental Analysis			
		Feed Ratio	Found <sup>a</sup>	Yield (%)		% C	% H	% N
2-VPy	1	1.0:1.0	1.0:1.0	98	Calcd	67.33	6.93	4.62
-					Found	67.46	6.73	4.86
"	2	2.0:1.0	2.0:1.0	98	Calcd	64.67	6.99	2.80
					Found	64.39	7.02	2.82
II	3	4.0:1.0	4.0:1.0	98	Calcd	62.88	7.02	1.56
					Found	62.87	7.05	1.69
"	4	8.0:1.0	8.0:1.0	100	Calcd	61.81	7.04	0.83
					Found	61.63	7.03	0.70
4-VPy	5	1.0:1.0	1.0:1.0	92	Calcd	67.33	6.93	4.62
					Found	67.50	7.04	4.34
"	6	2.0:1.0	2.0:1.0	96	Calcd	64.67	6.99	2.80
					Found	64.56	6.72	2.86
"	7	4.0:1.0	4.0:1.0	96	Calcd	62.88	7.02	1.56
					Found	63.10	7.13	1.58
"	8	8.0:1.0	8.0:1.0	95	Calcd	61.81	7.04	0.83
					Found	61.97	7.13	0.65
MVBipy	9	1.0:1.0	1.0:1.0	96	$Calcd^{b}$	69.27	6.74	6.92
					Found	69.11	6.71	6.92
	10	2.0:1.0	2.0:1.0	97	Calcd <sup>c</sup>	65.44	7.05	4.49
					Found	65.56	6.69	4.46
	11	4.0:1.0	4.0:1.0	96	Calcd	64.37	6.88	2.83
					Found	64.37	6.97	2.74
"	12	8.0:1.0	8.0:1.0	100	Calcd	62.25	7.06	1.55
					Found	61 97	7.06	1 66

Table I Synthesis of 2-VPy, 4-VPy, and MVBipy Copolymers with EGDMA

<sup>a</sup> As determined from the elemental analysis results.

<sup>b</sup> Calculated with 0.3 CH<sub>3</sub>OH per repeat unit.

<sup>c</sup> Calculated with 0.65 CH<sub>3</sub>OH per repeat unit.

a 34 × 24-cm reaction tube. The mixture was stirred to obtain a solution and AIBN (0.050 g) was added. The mixture was stirred to obtain a solution that was degassed by the freeze–pump–thaw method described above. Polymerization was conducted at 60°C for 18 h and then the solvent was decanted. The solid was washed with a methanol–benzene solution (1 : 1 by volume), dried *in vacuo*, and ground into a powder (<100 mesh) as described above. Homopolymer **13** was obtained as a white solid (2.42 g, 98%). IR (KBr): 1730 (C=O) and 1159 (C-O) cm<sup>-1</sup>.

#### Single Heavy Metal Ion Species Sorption

A mixture of 5.0 mL of an aqueous 10.0 mM solution of Cu(II), Cd(II), or Hg(II) nitrate (pH 4.6, acetate buffer) and 0.050 g of the polymer was shaken for 24 h in a 30-mL, pear-shaped flask at room temperature with a Burrell wrist-action shaker. The solid was filtered and the filtrate was

analyzed for Cu(II) or Cd(II) content by atomic absorption. The concentration of Hg(II) was determined photometrically after extraction into chloroform with dithizone ( $\lambda_{max} = 496$  nm).

# Competitive Cu(II), Co(II), and Ni(II) Sorption

Sorption was performed from an aqueous solution which was 10.0 mM in each of the three metal nitrates by the procedure given above. Metal ion concentrations after sorption were determined by atomic absorption.

## **RESULTS AND DISCUSSION**

#### **Polymer Synthesis and Characterization**

New copolymers **1–12** were prepared by a freeradical reaction of a chelating monomer (Fig. 1) and EGDMA as a crosslinker. For the formation

<b>~</b> ]		Polymer	Yield (%)	Elemental Analysis			
Chelating Monomer	Crosslinker				% C	% H	% N
4-VPy	BPDMA	14	99	Calcd	75.56	6.47	1.64
				Found	75.51	6.71	1.85
"	DEGDMA	15	100	Calcd	66.79	7.72	2.51
				Found	66.76	7.78	2.72
"	TEGDMA	16	99	Calcd	68.52	8.32	2.28
				Found	68.67	8.34	2.40
"	CHDMA	17	97	Calcd	70.38	8.27	2.11
				Found	70.09	8.39	2.25
II	GDMA	18	100	Calcd	62.03	6.95	2.50
				Found	62.23	7.16	2.90
"	TMDMA	19	99	Calcd	63.16	7.31	2.38
				Found	63.57	7.37	2.48
	HMDMA	20	100	Calcd	62.04	7.53	2.07
				Found	62.39	7.70	2.13
MVBipy	BPDMA	21	100	Calcd	76.62	6.49	3.03
				Found	76.32	6.74	3.01
"	DEGDMA	22	100	Calcd	68.52	7.41	4.32
				Found	68.39	7.59	4.37
	TEGDMA	23	100	Calcd	69.89	7.95	3.98
				Found	69.49	8.06	3.86
	CHDMA	<b>24</b>	100	Calcd	71.43	7.94	3.70
				Found	71.23	7.97	3.76
"	GDMA	25	97	$Calcd^{b}$	63.40	6.97	4.13
				Found	63.42	6.90	4.23
	TMDMA	26	99	Calcd	65.29	7.06	4.12
				Found	65.62	7.15	4.07
"	HMDMA	27	100	Calcd	64.06	7.29	3.65
				Found	63.94	7.26	3.51

Table IISynthesis of Copolymers of 4-VPy and MVBipy with Different Dimethacrylate Crosslinkers<sup>a</sup>at a 2 : 1Crosslinker/Chelating Monomer Molar Ratio

<sup>a</sup> See Figure 2 for structures of the crosslinkers.

<sup>b</sup> Calculated with 0.8 CH<sub>3</sub>OH per repeat unit.

of copolymers from the EGDMA crosslinker and 2-Vpy, 4-VPy, or MVBipy with AIBN as the freeradical initiator, EGDMA/chelating monomer ratios of 1: 1, 2: 1, 4: 1, and 8: 1 were utilized. An EGDMA homopolymer (13) also was prepared. Results from the polymer syntheses are presented in Table I. The elemental analysis data are in a good agreement with the molar ratios of the chelating monomer to the crosslinker in the feed. Also, the polymers were characterized by IR spectroscopy. Disappearance of the C=C stretching absorption in the IR spectrum verified complete conversion of the monomer(s) into the polymeric product.

To study the influence of the crosslinker/chelating monomer ratio in the copolymer on its metal ion sorption ability, Cu(II) sorption from



Figure 3 Dependence of Cu(II) sorption on the crosslinker/chelating monomer ratio for the EGDMA copolymers with ( $\bigcirc$ ) 4-VPy and ( $\bigcirc$ ) MVBipy at pH 4.6 and C<sub>Cu</sub> = 10.0 mM.



**Figure 4** Overlay of TGA graphs for (a) MVBipy-EGDMA copolymers with varied crosslinker/monomer ratios and (b) 4-VPy copolymers with different crosslinkers.

10.0 mM aqueous solutions of  $Cu(NO_3)_2$  at pH 4.6 (acetate buffer) by the 2-VPy, 4-VPy, and MVBipy copolymers with EGDMA was examined. The results are presented in Figure 3. No Cu(II) sorption was observed for any of the 2-VPy–EGDMA copolymers. Probably, the chelating groups in these polymers are inaccessible to the metal ions due to steric hindrance. For the 4-VPy– and MVBipy–EGDMA copolymers, the most efficient Cu(II) sorption was obtained when the ratio of the EGDMA crosslinker to the chelating monomer was 2: 1.

In view of this finding, a crosslinker/chelating monomer ratio of 2 : 1 was utilized to prepare a variety of copolymers of 4-VPy and MVBipy with different dimethacrylate crosslinkers whose structural formulas and abbreviations are shown in Figure 2. The elemental analysis data for these copolymers are presented in Table II.

The thermal properties of the polymers were examined by TGA (Fig. 4). All the polymers were found to decompose above 300°C. The thermal stability of the EGDMA copolymers **1–12** was found to vary with the crosslinker/chelating monomer ratio. An increase in the crosslinker/chelating monomer ratio decreased the temperature at which polymer decomposition is observed [Fig. 4(a)]. Apparently, increasing the content of EGDMA units relative to the thermostable heterocyclic moieties, Py or Bipy, leads to an overall reduction in the thermal stability of the copolymer.

The thermal stability of the 4-VPy and MVBipy copolymers with various crosslinkers (copolymers **14–27**) was found to be determined by the struc-

	Competitive Sorption of Cu(II), Co(II), and Ni(II) <sup>a</sup> (mmol/g)	Single Species Sorption of Cd(II) and Hg(II) (mmol/g)		
Copolymer	Cu(II)	Cd(II)	Hg(II)	
6	0.26	0.07	0.95	
14	0.04	0.00	0.49	
15	0.06	0.00	0.88	
16	0.00	0.00	0.57	
17	0.00	0.00	0.53	
18	0.22	0.01	0.81	
19	0.11	0.00	0.77	
20	0.20	0.00	0.67	
10	0.95	0.32	1.00	
21	0.49	0.02	0.76	
22	0.88	0.04	0.96	
23	0.41	0.00	0.81	
<b>24</b>	0.85	0.00	0.97	
25	0.80	0.00	0.98	
26	0.28	0.00	0.81	
27	0.27	0.00	0.77	
13 <sup>b</sup>	0.00	0.00	0.00	

Table III Competitive Sorption of Cu(II), Co(II), and Ni(II) and Singlespecies Sorption of Cd(II) and Hg(II) from 10.0 mM Aqueous Solutions at pH 4.6 by Copolymers Containing Pyridyl (6 and 14–20) and Bipyridyl (10 and 21–27) Groups

<sup>a</sup> No sorption of Co(II) or Ni(II) was detectable.

<sup>b</sup> The homopolymer of EGDMA.

ture of the crosslinker rather than by identity of the chelating monomer. For the copolymers of 4-VPy, this trend is illustrated in Figure 4(b). As would be anticipated, the highest decomposition temperatures were observed for copolymers 14 and 21, which contain thermostable aromatic rings in the crosslinker.

#### **Heavy Metal Ion Sorption**

Heavy metal ion sorption from aqueous solutions by copolymers **6**, **10**, and **14–27** and homopolymer **13** was investigated as described in the Experimental section. Results for competitive Cu(II), Co(II), and Ni(II) sorption from 10.0 mM (in each) aqueous solutions at pH 4.6 are presented in Table III. Since Co(II) and Ni(II) sorption was undetectable, all these copolymers were found to be highly selective for Cu(II) sorption. The homopolymer of EGDMA (**13**), which does not contain any heterocyclic amine chelating groups, was found to be ineffective for sorption of any of the three metal ion species.

The Cu(II)-sorption capacity of the copolymers clearly depends on the identity of the chelating

monomer. The Bipy-containing copolymers 10 and 21–27 are all more efficient Cu(II) sorbents than are the corresponding Py-containing copolymers. This can be rationalized in terms of a greater stability of the Cu(II) complexes formed by bidentate Bipy chelating ligands compared with those of the Cu(II) complexes with monodentate Py ligands.

Within both series of copolymers, the metal ion binding ability varied with the crosslinker structure. For the Py-containing materials, the Cu(II) sorption ability diminished as the alkylene spacer in the crosslinker was lengthened or the rigidity of the crosslinker was increased: 6 > 15 > 16> 14, 17. This suggests that Cu(II) is coordinated by two Py moieties in the copolymer. When the spacer separating the Py units is too long or contains a rigidifying unit, the stability of the metal ion complex should decrease as does the sorption capacity of the copolymer. The reduction in sorption ability of the copolymers with long alkylene spacers was somewhat lessened when additional donor atoms were incorporated into the spacer for copolymers **18–20**. Copolymer **18**, which contains



**Figure 5** Dependence of Cu(II) sorption by copolymer **10** on the initial Cu(II) concentration in the aqueous solution at pH 4.6.

an alcohol function in the spacer of the crosslinker, exhibited almost the same Cu(II)sorption capacity as that of **6**. Copolymers **19** and **20**, with oligoethylene glycol spacers in the crosslinkers, sorbed metal ions stronger than did copolymers **15** and **16** which have only alkylene spacers.

The Cu(II) sorption capacity of the Bipy copolymers also varied with the structure of the crosslinkers in the order: 10 > 22 > 24 > 21 > 23. However, for this series of copolymers, metal ion sorption was much less affected by the length or rigidity of the alkylene spacer than were the Pycontaining analogs. This contrasting behavior of the Bipy and Py copolymers may result from different compositions of their Cu(II) complexes, with the metal ion being coordinated by one bidentate Bipy unit or two monodentate Py units.

To determine the limiting Cu(II)-sorption capacity for the MVBipy–EGDMA copolymer **10**, single-species metal ion sorptions from aqueous solutions with differing concentrations of Cu(NO<sub>3</sub>)<sub>2</sub> at pH 4.6 were performed. As shown in Figure 5, the limiting Cu(II) sorption was 1.80 mmol/g, which is equal to the Bipy group content in the copolymer, as calculated from its elemental analysis data. This is consistent with the proposed formation of 1 : 1 Cu(II)–Bipy complexes in the Bipy-containing copolymers.

It is also noted that the introduction of oxygen donor atoms into the spacers of crosslinkers for the Bipy-containing copolymers **26** and **27** did not increase the Cu(II)-sorption ability, as was noted for the analogous Py-containing copolymers. It appears that the oxygen atoms in copolymers **26**  and **27** do not participate in the Cu(II) coordination.

Single-species sorptions of the chelating copolymers with the softer heavy metal ions of Cd(II) and Hg(II) was also examined (Table III). All the copolymers except **10** exhibited high to very high selectivity for Hg(II) sorption compared with Cd(II). For both the Py- and Bipy-containing copolymers, Hg(II) sorption is quite efficient with little influence on the crosslinker type. As was found for competitive Cu(II) sorption, single-species Hg(II) sorption by the copolymers containing bidentate Bipy units is somewhat more efficient than that by the analogous Py-containing copolymers.

The homopolymer poly(EGDMA) (13) was ineffective in sorbing Hg(II) and Cd(II), as it was for Cu(II), Co(II), and Ni(II).

## CONCLUSIONS

A series of new chelating copolymers containing Py or Bipy units as ligating centers with different dimethacrylate crosslinkers were synthesized and examined for heavy metal ion sorption from aqueous solutions. Both Py- and Bipy-containing polymers exhibited high selectivity for Cu(II) sorption in the presence of Co(II) and Ni(II) and for Hg(II) sorption compared with Cd(II). The copolymers with Bipy binding sites were generally more efficient metal ion sorbents than were the analogous Py-containing compounds. The metal ion sorption capacity of the copolymers varied with the structure of the crosslinker.

This research was supported by the Texas Higher Education Coordinating Board–Advanced Research Program and by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. We thank Dr. Zhi-Yi Zhang for synthesizing the 4-methyl-4'-vinyl-2,2'-bipyridine.

#### REFERENCES

- 1. Sahni, S. K.; Reedijk, J. Coord Chem Rev 1984, 59, 1.
- Correlations Prediction of Analytical Properties of Organic Reagents and Chelate Polymers; Basargin, N. N.; Isaev, E. I., Eds.; Nauka: Moscow, 1986 (in Russian); Chem Abstr 1987, 106, 112789c.
- Beauvais, R. A.; Alexandratos, S. D. React Funct Polym 1998, 36, 113.
- 4. Antokol'skaya, I. I.; Myasoedova, G. V.; Bol'shakova, L. I.; Ezernitskaya, M. G.; Volynets,

M. P.; Karyakin, A. V.; Savvin, S. B. Zh Anal Khim 1976, 31, 610.

- Danilova, F. I.; Fedotova, I. A.; Rozdukhova, I. A.; Myasoedova, G. V.; Antokol'skaya, I. I. Zh Anal Khim 1978, 33, 1681.
- Gupta, S. G.; Neckers, D. C. J Polym Sci 1982, 20, 1609.
- Myasoedova, G. V.; Antokol'skaya, I. I.; Bol'shakova, L. I.; Danilova, F. I.; Fedotova, I. A.; Varshal, E. B.; Rakovskii, E. E.; Savvin, S. B. Zh Anal Khim 1982, 37, 1427.
- Kubrakova, I. V.; Varshal, G. M.; Sedykh, E. M.; Myasoedova, G. V.; Antokol'skaya, I. I.; Shemarykina, T. P. Zh Anal Khim 1983, 38, 1703.
- G. V.; Antokol'skaya, I. I.; Kurbakova, I. V.; Belova, E. V.; Mezhirov, M. S.; Varshal, G. M.; Grishina, O. N.; Zhukova, N. G.; Danilova, F. I.; Savvin, S. B. Zh Anal Khim 1986, 41, 1261.
- Myasoedova, G. V.; Antokol'skaya, I. I.; Dmitrieva, G. A.; Kubarev, S. V.; Moiseeva, G. A.; Danilova, F. I.; Grishina, O. N.; Zhukova, N. G.; Savvin, S. B. Zh Anal Khim 1988, 43, 531.

- Morozova, L. V.; Markova, M. V.; Mikhaleva, A. I.; Golentovskaya, I. P.; Shaulina, L. P. Zh. Prikl Khim 63, 2022 1990) (in Russian); Chem Abstr 1991, 114, 123127b.
- Chessa, G.; Marangoni, G.; Pitteri, B. React Funct Polym 1990, 12, 219.
- Skujins, A.; Rassa, R.; Klavins, M.; Zicmanis, A. Latv Khim Zh 1991, 79.
- Vorina, O. G.; Abamova, N. D.; Shaulina, L. P.; Musorin, G. K.; Foroshcha, G. I. Zh Prikl Khim 1991, 64, 141 (in Russian); Chem Abstr 1991, 115, 233607m.
- Chen, Y.; Yuan, X. Gaofenzi Xuebao 1993, 225 (in Chinese); Chem Abstr 1985, 122, 82625g.
- Huan, X.; Chen, Y. Trans Nonferrous Met Soc China 1995, 5, 57.
- Tomasik, P.; Ratajewicz, Z. Heterocyclic Compounds, Pyridine–Metal Complexes; Wiley: New York, 1985; Vol. 14, Parts 6A and B.
- Ghosh, P. K.; Spiro, T. G. J Am Chem Soc 1980, 102, 5543.