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Evaluation of the Capture of Metal Ions by
Cross-Linked Poly(vinylcatechol)Osamu SHIMOMURA*, Kohei KURAMOTO*, Masaki KAWAGUCHI*,
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Abstract

A cross-linked poly(vinylcatechol) was prepared by a suspension copolymerization of 5-vinyl-1,3-benzodioxol (1) with divinylbenzene (a), 1,2-bis(4-vinylphenyl)ethane (b), or 1,4-bis(4-vinylphenyl)butane (c) and the successive ring-opening of the acetals with boron tribromide/dimethylsulfide. The cross-linked poly(vinylcatechol)s **3a-c** showed good swelling in DMF, methanol, ethanol, and THF. Their capture abilities towards metal ions in organic solvents were investigated. The sorption of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{3+} , and Pd^{2+} with 6 equiv of cross-linked poly(vinylcatechol)s **3a-c** were carried out in methanol and DMF.

In methanol the cross-linked polymers: **3a-c** showed more than 80% of the capture ratios for Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} except for Ni^{2+} with **3c**. For Fe^{3+} , **3a-c** showed under 15%. In DMF the cross-linked polymers: **3a-c** showed around 90% of the capture ratios for Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} . For Pd^{2+} , **3a-c** showed about 70% and for Fe^{3+} **3a**, **3b**, and **3c** showed 13%, 28%, and 57% of the capture ratio, respectively.

The prepared cross-linked polymers: **3a-c** showed enough capacity for Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Pd^{2+} , whereas for Fe^{3+} they show poor capacity in both solvents.

Key words : Poly(vinylcatechol), Suspension polymerization, Cross-linked polymer, Metal ion

1. Introduction

One of the most striking features of the cross-linked polymers such as poly(styrene-co-divinylbenzene)s is their infusible and insoluble characteristics. Owing to the characteristics, poly(styrene-co-divinylbenzene)s are applied to supports in solid-phase organic syntheses (SPOS)¹⁾. Numerous conventional organic reactions have been employed in SPOS using these supports. In SPOS the polymer supports are needed to work well under a reaction media with a variety of polarities. Especially, improvement of their swelling properties in polar media has been the most urgent subject and cross-

linker modifications have been reported^{2~7)}. In view of these points, we have reported novel tailor-made polymer supports for SPOS^{8~10)}.

In SPOS under polar media, metal ions derived from reagents and catalysts were sometimes dissolved, which caused some synthetic difficulties. Therefore, development of new polymeric scavengers for the metal ions is strongly needed. Branger et al. suggested that catechol functionality should be effective for the purpose and they prepared porous poly(vinylcatechol-co-divinylbenzene) from 1,2-dimethoxy-4-vinylbenzene^{11~13)}. However, the sorption ability of the poly(vinylcatechol) resin was low, because of its low swelling property to the polar media.

In this paper we report that novel preparation of cross-linked poly(vinylcatechol)s: **3a-c**, their swelling property to some organic polar solvents, and

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scavenging performance for transition metal ions: Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{3+} , Pd^{2+} .

2. Experimental Section

2.1 Materials

Styrene was distilled under reduced pressure. 5-Vinyl-1,3-benzodioxole **1**¹⁴⁾ and 1,2-bis(4-vinylphenyl) ethane **b**¹⁵⁾ were prepared by the reported methods. Gum arabic was dissolved in water and the solution was filtered off to remove the insoluble materials on Celite 545, dried under freeze-drying. Divinylbenzene was purchased from Aldrich, catalog number 414565. 4-Bromostyrene and 2,2-azobisisobutyronitrile were purchased from TCI, catalog numbers B1980 and A0566. All other chemicals and solvents were used without further purification.

2.2 Measurements

¹H- and ¹³C-NMR spectra were recorded with a Varian Unity-300 spectrometer using tetramethylsilane (TMS) as an internal standard. FT-IR spectra were obtained with a Thermo Scientific Nicolet is10 infrared spectrometer equipped with a Smart Orbit. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out on a Shimadzu QP-2010 mass spectrometer using J&W GC Column (30 m × 0.250 mm × 0.25 μm). Atomic absorption spectrophotometer (AAS) analyses were carried on a Shimadzu AA-6800 spectrophotometer. Melting points (mp) were measured by a Yanaco micro melting point apparatus.

Preparation of 1,4-bis(4-vinylphenyl)butane (c).

The cross-linker (c) was prepared by a slight modification of the reported procedure for 1,6-bis(4-vinylphenyl) hexane¹⁶⁾. To prepare a Grignard reagent, 4-bromostyrene (25.00 g, 136 mmol) was added dropwise to magnesium turnings (6.64 g, 273 mmol) in THF (250 mL) at ambient temperature. End of the addition, stirring was kept for 0.5 h. After the reaction, this suspension was added dropwise to the mixture of 1,4-dibromobutane (8.31 g, 38.5 mmol) and CuI (0.89 g, 4.69 mmol) in THF (100 mL). The resulting mixture was kept stirring another 48 h. After the reaction, was added saturated NH_4Cl solution (200 mL) and stirred for additional 0.5 h. The resulting mixture was filtered off by celite and the THF in solution was evaporated. The resultant was extracted with three 200 mL portions of

diethyl ether. The collected organic layer was washed with three 300 mL portions of water, dried over MgSO_4 , and filtered off. After evaporation of the solvent, the residue was recrystallized from methanol to give pure **c** in 31% (3.09 g) yield.

¹H-NMR (300 MHz, CDCl_3) δ 7.32 (d, 4H, $J=8.1$ Hz), 7.12 (d, 4H, $J=8.1$ Hz), 6.69 (dd, 2H, $J=17.7$, 10.8 Hz), 5.70 (dd, 2H, $J=17.7$, 0.9 Hz), 5.19 (dd, 2H, $J=10.8$, 0.9 Hz), 2.62 (m, 4H), 1.65 (m, 4H); ¹³C NMR (75 MHz, CDCl_3) δ 141.4 (Ar), 136.6 (vinyl- $\text{CH}=\text{CH}_2$), 135.3 (Ar), 128.6 (Ar), 126.2 (Ar), 113.0 (vinyl- $\text{CH}=\text{CH}_2$), 37.5 (methylene $\text{Ph}-\text{CH}_2-\text{CH}_2$), 31.0 (methylene $\text{Ph}-\text{CH}_2-\text{CH}_2$); MS (m/z):262 [M^+]; mp 60.3 - 62.0°C (Ref: 60.5 - 61.8°C)¹⁷⁾.

Suspension copolymerization of a-c with 1.

The conditions of suspension polymerization were slightly modified for reported method³⁾. A mixture of **1** (22.22 g, 150 mmol), **a** (0.40 g, 3.06 mmol, 2.0 mol% for overall monomers), and AIBN (0.18 g, 1.04 mmol) was dissolved in chlorobenzene (16.88 g, 15.3 mL). Aqueous phase was prepared by the following procedure. A solution of NaCl (12.50 g) and gum arabic (30.00 g) in water (500 mL) was stirred until the solute dissolved. The organic solution was added dropwise to aqueous phase (210 mL) under N_2 at 65°C. After 24 h, insoluble beads of **2a** were filtered off from the reaction mixture, and successively washed with hot water. Then **2a** was washed with THF and hexane, and dried under vacuum. Yield: 18.33 g (81%). Suspension copolymerization of **b** and **c** with **1** were done under the similar conditions and given in 20.48 g (89%) and 19.52 g (84%) yields, respectively.

¹³C NMR (75 MHz, CDCl_3) **2a**: δ 147.7 (Ar), 139.8 (Ar), 121.0 (Ar), 108.0 (Ar), 100.9 (O- CH_2 -O), 44.2 (methine), 40.0 (methylene of the main chain). **2b**: δ 147.7 (Ar), 145.7 (Ar), 140.1 (Ar), 121.2 (Ar), 108.0 (Ar), 101.1 (O- CH_2 -O), 44.7 (methine), 40.5 (methylene of the main chain). **2c**: δ 147.7 (Ar), 145.8 (Ar), 138.4 (Ar), 140.0 (Ar), δ 121.2 (Ar), 108.0 (Ar), 101.0 (O- CH_2 -O), 44.0 (methine), 42.2 (methylene of the main chain). FT-IR **2a**: 2899 cm^{-1} (ν C-H), 2774 cm^{-1} (ν C-H), 1038 cm^{-1} (ν O-C-O), **2b**: 2898 cm^{-1} (ν C-H), 2773 cm^{-1} (ν C-H_{st}), 1034 cm^{-1} (ν O-C-O), **2c**: 2915 cm^{-1} (ν C-H), 2776 cm^{-1} (ν C-H), 1035 cm^{-1} (ν O-C-O).

Deprotection of 2a-c.

Deprotection of **2a-c** were carried out with respect to the reported method¹⁴⁾. A solution of 1M boron tribromide in dichloromethane (66 mL) was added to the solution of methyl sulfide (4.95 g, 80 mmol) in dichloromethane (100 mL) at 0 °C. The resulting mixture was kept stirring for 2h and allowed to warm to room temperature. After an additional stirring for 1 h, the solvent of the mixture was evaporated to obtain the white powder of boron tribromide dimethyl sulfide complex. Polymer **2a** (4.00 g) and dichloromethane (100 mL) were added under N₂, and refluxed for 24 h and then cooled to room temperature. To quench the reaction, methanol (40 mL) was added to the reaction mixture, and transferred to filtration syringe. The polymer residue was washed with methanol, dichloroethane, THF, hot water, methanol, THF, and hexane and dried under vacuum. Yield: 2.69 g. The deprotection of **2b** (2.00 g) and **2c** (2.00 g) was carried out by the similar procedure to **2a** in **3b**:1.65 g and **3c**:1.79 g yields, respectively.

Measurement of swelling volume⁸⁾.

The beads of **3a-c** were then sieved off (212 - 355 μm) and placed in 1 mL syringes with filter and various types of solvents (0.8 mL) respectively. The syringes were set on a shaker for 2 h and the volume of the resin was measured.

Preparation of metal solution.

Cu(OAc)₂ · H₂O (31.7 mg) was added to a 100 mL volumetric flask and methanol was added to obtain the 100 mgdm⁻³ Cu(II) ion methanol (1.59 mmoldm⁻³) solution. Other metal salts, Co(OAc)₂ · 4H₂O (42.3 mg), Ni(OAc)₂ · 4H₂O (43.3 mg), Zn(OAc)₂ · 2H₂O (33.9 mg), FeCl₃ (30.6 mg), Pd(OAc)₂ (21.1 mg) were used to prepare the several 100 mgdm⁻³ ion solutions (Co:1.71 mmoldm⁻³, Ni:1.74 mmoldm⁻³, Zn:1.54 mmoldm⁻³, Fe:1.89 mmoldm⁻³, Pd:0.94 mmoldm⁻³) in methanol and DMF. Pd(OAc)₂ (21.1 mg) was not dissolved in methanol, only DMF was adapted for Pd(II) solution.

Sorption of Cu(II) with 3a-c.

A mixture of **3a** (13.1 mg; 6 equiv for Cu(II) calculated from the theoretical loading of monomer feed of **1** and **a**: **3a** (7.2 mmol/g) and 10 mL of Cu(II) methanol solution was stirred at room temperature. After 24 h,

the reaction mixture was filtered off and 1 mL of the filtrate was diluted to 50 mL with 0.02 moldm⁻³ HNO₃ aq. The solution mixture was used for AAS analysis. Alternatively, Cu(II) in DMF solution was used by the same method. The resins **3b** (theoretical loading: 7.1 mmol/g, 13.3 mg; 6 equiv) and **3c** (theoretical loading: 7.1 mmol/g, 13.4 mg; 6 equiv) were estimated by the same procedure to **3a**.

Sorption of various metal ions with 3a-c.

The removal of various metal ions with **3a** was carried out for Co(II), Ni(II), Zn(II), Fe(III), and Pd(II). A mixture of 6 equiv of **3a** (14.1 mg for Co(II), 14.2 mg for Ni(II), 12.7 mg for Zn(II), 14.9 mg for Fe(III), 7.8 mg for Pd(II)) was used to absorb from several metal solutions in methanol and DMF except for Pd(II) in methanol. The experimental procedure for the sorption of the metals was used for Cu(II) described above. The resins **3b** and **3c** were estimated by the same procedure to **3a**.

Sorption of mixed metal ions with 3a-c.

The sorption of mixed metal ion solution of several 100 mgdm⁻³ of Cu(II), Co(II), Ni(II), and Zn(II) with **3a-c**: ca 50 mg were carried out by the similar procedure described above.

3. Results and Discussion

3.1 Syntheses of poly(vinylcatechol)s

Slightly cross-linked poly(vinylcatechol)s with different cross-linkers were prepared by the suspension copolymerization of **1** with 2 mol% of divinylbenzene (**a**), 1,2-bis(4-vinylphenyl)ethane (**b**), or 1,4-bis(4-vinylphenyl)butane (**c**) as cross-linkers (**Scheme 1**). The polymerization reactions were performed by reported method⁴⁾. The yields of the resins were 81% (**2a**), 89% (**2b**), and 84% (**2c**), respectively. The resins obtained were confirmed by ¹³C-NMR and FT-IR measurements. The ¹³C-NMR spectrum of **2a** was shown in **Fig. 1**¹⁸⁾. The methylene carbons of acetals was observed at δ 100.9. The C-H stretching of O-CH₂-O was confirmed at 1038 cm⁻¹ by FT-IR spectrum shown in **Fig. 2** (a). Similarly, the confirmation of the methylenes of acetals in resins **2b** and **2c** were observed at δ 101.6 and δ 101.1 by ¹³C-NMR measurements and the C-H stretching of O-CH₂-O at 1034 cm⁻¹ and 1035 cm⁻¹ by FT-IR spectra. To prepare the poly(vinylcatechol)s by the

Scheme 1 Suspension copolymerization of **1** with cross-linker **a-c**.

Fig. 1 ^{13}C -NMR spectrum of **2a**.

Fig. 2 FT-IR spectrum of **2a** and **3a**.

deprotection of acetals, **2a-c** were treated with boron tribromide dimethyl sulfide complex in dichloroethane under reflux condition for 24 h (Scheme 2). The

Scheme 2 Syntheses of poly(vinylcatechol)s.

resulting polymers were confirmed by ^{13}C -NMR and FT-IR. ^{13}C -NMR spectrum of **3a** is shown in Fig. 3. The resin **3a** wasn't swelling in CDCl_3 , CD_3OD was used as a solvent for NMR measurement. The methylenes of acetals at δ 100.9 in Fig. 1 was completely disappeared in Fig. 3. FT-IR spectrum of **3a** was shown in Fig. 2 (b). The C-O stretching of $\text{O}-\text{CH}_2-\text{O}$ at 1038 cm^{-1} was disappeared and the broad peaks of O-H stretching at $3000\text{--}3600\text{ cm}^{-1}$ was appeared. These results showed the complete conversion from **2a** to **3a**. Deprotection of **2b** and **2c** were carried out with the same procedure to **2a**. Similarly, the disappearance of the methylenes of acetals and of the C-O stretching of $\text{O}-\text{CH}_2-\text{O}$, and the appearance of the O-H stretching at $3000\text{--}3600\text{ cm}^{-1}$ were observed for **2b** and **2c**.

3.2 Swelling ability

Good swelling ability of polymer supports in various solvents employed as reaction media are essential. We examined the swelling ability of cross-linked polymer

Fig. 3 ^{13}C -NMR spectrum of 3a.

Table 1 Swelling volume of 2a-c and 3a-c in various solvents.

Solvent	volume ratio (swollen/dry ^a)					
	2a	2b	2c	3a	3b	3c
Water				1	1	1
Acetonitrile	2	2	2	5	6	6
DMF	11	7	8	10	10	10
Methanol	2	2	2	8	8	9
Ethanol	2	2	2	8	8	8
THF	10	6	8	8	7	8
Diethylether	2	2	2	2	2	2
Toluene	4	2	2	2	1	2

^a) Dry volume of resins were approximately 1 mLg⁻¹.

resins. These results were summarized in Table 1. After the deprotection of acetals, the swelling ability of 3a-c was improved in acetonitrile, methanol, and ethanol. The resins of 3a-c prepared here showed good swelling in DMF, methanol, ethanol, and THF. As commercial divinylbenzene cross-linked polystyrene resin such as Merrifield resin is not swollen in polar solvent⁴⁾, polar *vic*-dihydroxyl groups in the resin 3a-c were attributed to high affinity to polar solvents. However, the difference of the swelling ability among 3a-c wasn't clearly found.

3.3 Sorption of various metal ions with 3a-c.

To remove the metal cation of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Fe³⁺, and Pd²⁺ with 6 equiv of 3a-c in methanol and DMF was observed. After 24 h, the reaction mixture of several solution was filtered off and the filtrate was quantified by AAS. The results were shown in Fig. 4. Pd was examined only DMF solution because of Pd(OAc)₂ was not dissolved in methanol. In the case of Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺, the capture ratio of 3a-c in methanol were over 80% except for Ni²⁺ with 3c in

Fig. 4 Capture ratio of metal ions with 3a(□), 3b(■), and 3c(▨) in methanol (a) and DMF (b). Initial concentrations in methanol: Cu²⁺ 103 mgdm⁻³, Ni²⁺ 91 mgdm⁻³, Co²⁺ 137 mgdm⁻³, Zn²⁺ 96 mgdm⁻³, Fe³⁺ 102 mgdm⁻³ and DMF: Cu²⁺ 121 mgdm⁻³, Ni²⁺ 105 mgdm⁻³, Co²⁺ 112 mgdm⁻³, Zn²⁺ 107 mgdm⁻³, Fe³⁺ 99 mgdm⁻³, Pd²⁺ 165 mgdm⁻³.

70% (Fig. 4 (a)). The capture ratio of 3c was slightly lower than that of 3a and 3b. However the capture

ratio of the Fe^{3+} with **3a-c** were lower than 15%. The similar capturing ratio were observed for Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} in DMF (Fig. 4 (b)). Whereas the difference of the capture ratio of **3a-c** in DMF was not clearly observed. In the case of Fe^{3+} , the low capture ratio of **3a** (14%), **3b** (28%), and **3c** (57%) were observed¹⁹. The metal of Pd was widely used for catalytic organic reaction. Scavenging of Pd ion from organic solution is of importance for recycling of Pd catalyst. The capture ratio of **3a-c** for Pd cation was over 70%. The resins **3a-c** could be used for the scavenger of Pd(II).

3.4 Sorption of the mixture of metal ions with **3a-c**.

The scavenging ability of **3a-c** (ca 50 mg) for mixed metal ion solution was examined (Fig. 5). The mixture of several 100 mgdm^{-3} solution of Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} , Cu^{2+} in methanol was completely removed (Fig. 5 (a)). The order of the capture ratio in methanol,

Fig. 5 Capture ratio of mixed metal ions of Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} with **3a**(□), **3b**(■), and **3c**(▨) in methanol (a) and DMF (b). Initial concentrations in methanol: Cu^{2+} 118 mgdm^{-3} , Ni^{2+} 102 mgdm^{-3} , Co^{2+} 104 mgdm^{-3} , Zn^{2+} 107 mgdm^{-3} . Initial concentrations in DMF: Cu^{2+} 115 mgdm^{-3} , Ni^{2+} 99 mgdm^{-3} , Co^{2+} 134 mgdm^{-3} , Zn^{2+} 100 mgdm^{-3} .

$\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} \approx \text{Ni}^{2+}$, the good correlation was shown for the equilibrium constant of catechol and metal ions²⁰. Similarly, the scavenging ability in DMF was examined (Fig. 5 (b)). The capture ratios of metals were ca. 40 - 60%. The difference of metal ions in DMF was not clearly observed. These results show the resins **3a-c** could be functioned for scavenging of mixed metal ions.

4. CONCLUSION

A cross-linked poly(vinylcatechol) was prepared by a suspension copolymerization of 5-vinyl-1,3-benzodioxol with divinylbenzene (a), 1,2-bis(4-vinylphenyl)ethane (b), or 1,4-bis(4-vinylphenyl)butane (c) to obtain the corresponding polymer in 81%, 89%, and 84%, respectively. To deprotect from acetals to catechols, boron tribromide/dimethylsulfide was treated with **2a-c** to obtain **3a-c**. The sorption of metal ions of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{3+} , and Pd^{2+} with **3a-c** were carried out. These resins could be used as good metal scavenger except for Fe^{3+} . The sorption of other metal ions with **3a-c** will be investigated further.

References

- For example, see: (a) M. R. Buchmeiser "Polymeric Materials in Organic Synthesis and Catalysis", WILEY-VCH, Weinheim (2003). (b) B. A. Bunin "The combinatorial index" vol 5, Academic Press, London (1998). (c) F. Z. Dörwald "Organic Synthesis on Solid Phase: Supports, Linkers, Reactions", WILEY-VCH, Weinheim (2000).
- M. E. Wilson, K. Paech, W.-J. Zhou, M. J. Kurth, *J. Org. Chem.*, **63**, 5094 (1998).
- P. H. Toy, K. D. Janda, *Tetrahedron Lett.*, **40**, 6329 (1999).
- P. H. Toy, T. S. Reger, P. Garibay, J. C. Garno, J. A. Malikayil, G.-y. Liu, K. D. Janda, *J. Comb. Chem.*, **3**, 117 (2001).
- M. C. McCairn, S. R. Tonge, A. J. Sutherland, *J. Org. Chem.*, **67**, 4847 (2002).
- N. Murthy, Y. X. Thng, S. Schuck, M. C. Xu, J. M. J. Frechet, *J. Am. Chem. Soc.*, **124**, 12398 (2002).
- M. A. Siyad, A. S. V. Nair, G. S. V. Kumar, *J. Comb. Chem.*, **12**, 298 (2010).
- O. Shimomura, B. S. Lee, S. Meth, H. Suzuki, S. Mahajan, R. Nomura, K. D. Janda, *Tetrahedron*, **61**, 12160 (2005).
- O. Shimomura, T. Hosokawa, R. Nomura, *Trans. Mater. Res. Soc. Jpn.*, **33**, 1293 (2008).
- O. Shimomura, Y. Ishino, T. Imada, A. Ohtaka, R. Nomura, *Nippon Setchaku Gakkaishi*, **48**, 97 (2012).
- J. Bernard, C. Branger, I. Beurroies, R. Denoyel, A. Margaillan, *React. Funct. Polym.*, **72**, 98 (2012).
- J. Bernard, C. Branger, I. Beurroies, R. Denoyel, S. Blanc, A. Margaillan, *Polymer*, **51**, 2472 (2010).
- J. Bernard, C. Branger, T. L. A. Nguyen, R. Denoyel, A. Margaillan, *React. Funct. Polym.*, **68**, 1362 (2008).
- T. Ishizone, A. Mochizuki, A. Hirao, S. Nakahama,

- Macromolecules*, **28**, 3787 (1995).
- 15) H. Huang, H. Niu, J.-Y. Dong, *J. Polym. Sci., Part A Polym. Chem.*, **48**, 5783 (2010).
- 16) S. Amou, S. Yamada, A. Nagai, T. Miwa, M. Tomoi, *Kobunshi Ronbunshu*, **61**, 474 (2004).
- 17) R. H. Wiley, G. L. Mayberry, *J. Polym. Sci.*, **1**, 217 (1963).
- 18) The ^{13}C -NMR measurement of swollen resin was shown here, see: F. Lorge, A. Wagner, C. Mioskowski, *J. Comb. Chem.*, **1**, 25 (1999).
- 19) The low ratio of capturing might be caused with the oxidation of catechol to quinone with Fe^{3+} , see: P. Sanchez, N. Galvez, E. Colacio, E. Minones, J. M. Dominguez-Vera, *Dalton Trans.*, p. 811 (2005).
- 20) R. Griesser, H. Sigel, *Inorg. Chem.*, **10**, 2229 (1971).

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架橋ポリ（ビニルカテコール）を用いた金属イオンの捕捉

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要 旨

架橋ポリ（ビニルカテコール）は、5-ビニル-1,3-ベンゾジオキソール (1) とジビニルベンゼン (a), 1,2-ビス（4-ビニルフェニル）エタン (b), あるいは 1,4-ビス（4-ビニルフェニル）ブタン (c) を懸濁共重合し、得られたポリマーのアセタール構造をボロントリブROMID/ジメチルスルフィドで処理することにより合成した。得られたポリ（ビニルカテコール）3a-c は DMF, メタノール, エタノール, THF に高い膨潤性能を示した。3a-c の有機溶媒中での金属イオン捕捉能について検討した。金属イオンとして Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{3+} , Pd^{2+} に対し 6 当量の 3a-c を用いメタノール, および DMF 溶媒中でのイオンの捕捉を試みた。メタノール中では 3 種の架橋ポリマー 3a-c いずれも Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} に対し, 3c を用いた Ni^{2+} の場合を除いて 80% 以上の捕捉率を示した。 Fe^{3+} の場合は, 3a-c のいずれも 15% 以下であった。DMF 溶媒中では, Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} に対して 3a-c はいずれも 90% 程度の捕捉率を示した。 Pd^{2+} の場合は 3a-c いずれも約 70% となり, Fe^{3+} に対しては, 3a で 13%, 3b で 28%, 3c で 57% の捕捉率となった。合成した架橋ポリマー 3a-c は Fe^{3+} イオンを除く Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Pd^{2+} に対し十分な捕捉能を示した。

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