Metal Ion-Imprinted Polymer Prepared by the Combination of Surface Template Polymerization with Postirradiation by γ-rays

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ABSTRACT: Zinc ion-imprinted polymers were prepared by the combination of surface template polymerization and irradiation by γ-rays. Dioleyl phosphate, which has two C−C double bonds in the oleyl chains, and divinylbenzene were employed as a functional monomer and a cross-linking agent, respectively. After the surface template polymerization with water-in-oil emulsions, the imprinted resins were irradiated with γ-rays to make the polymer matrices more rigid and also to allow the functional monomer to attach firmly to the matrices. The irradiated imprinted resin exhibits a tremendously high selectivity toward zinc ions over copper ions. Thus it is understood that the postirradiated imprinted polymers are characterized by stable and highly specific recognition sites. The combination of surface template polymerization with irradiation with γ-rays offers a potential technique to construct highly selective molecular-recognizing polymers applicable to the adsorption of various water-soluble substances.

Introduction

Molecular imprinting is a technique for preparing polymeric materials for applications in molecular recognition. The approach to preparing imprinted polymers involves interactive preorganization of functional monomers such that specific chemical interactions occur between functional monomers and "print" molecules, followed by polymerization in the presence of a large excess of cross-linking agents. The resulting polymer contains specific binding sites that recognize the print molecule, and such a polymer exhibits a high selectivity for rebinding the print with which it was prepared. Because the print molecule itself directs the organization of the functional groups, specific knowledge of the imprinted structure is not necessary. Wulff et al.[1] first demonstrated this approach by designing a polymeric receptor using reversible covalent bonds for monomer−print interactions. Mosbach et al.,[2] Shea et al.,[3] and Arnold et al.[4] have reported the preparation of a variety of imprinted polymers.

Although these imprinting techniques are conceptually attractive, few practically useful materials have been reported. Problems encountered include low binding selectivities, loss of selectivity with time, and slow rebinding kinetics. Common fundamental problems with these conventional imprinting techniques stem from the recognition sites that are usually formed within the hydrophobic polymer matrix. Particularly, difficulties arise when handling water-soluble substances such as components of biological origin like proteins.

We have developed a novel molecular imprinting technique, which is called "surface template polymerization", to overcome the drawbacks of conventional imprinted polymers.[5,6] Surface-templated polymers are prepared by emulsion polymerization utilizing a functional monomer, an emulsion stabilizer, a polymer matrix-forming comonomer, and a print molecule. A functional monomer which is amphiphilic in nature forms a complex with the print molecule at the interface of the emulsion, and the complex so formed remains stationary at the reaction surface. After the matrix is polymerized, the coordination structure is "imprinted" at the polymer surface. Uezu et al.[6] previously showed that a Zn(II)-imprinted polymer prepared by this technique manifested the imprinting effect as far as the amount of metal ions adsorbed is concerned. The adsorption results showed that the interfacial activity of the functional monomer was vital toward the assessment of a suitable metal ion-binding amphiphile. Notwithstanding, the Zn(II)-imprinted polymers had shown poor selectivity for Zn(II) in a Cu(II) component system. In order to fix the recognition sites more rigidly and to create stronger interactions between the functional monomers and imprint molecules, Yoshida et al.[7] designed a functional monomer which has two phosphonic acid ester groups and two benzene rings in the molecular structure. The Zn(II)-imprinted polymers possessing multifunctional monomers exhibited a tremendously high selectivity toward zinc ions over copper ions. The imprinted polymers combine both rigid polymer matrices and the strong binding ability owing to the specificity of the multifunctional monomer. However, in general it is difficult to realize for uncomplexed functional monomers which have satisfactory interfacial activity and strong binding characteristics. Therefore, it is necessary to develop a technique for creating rigid polymer matrices alongside with the development of highly stable and interactive functional monomers.

In the present study, the Zn(II)-imprinted polymers were irradiated with γ-rays to make the polymer matrices rigid and also to allow the functional monomer to attach firmly to the matrices. The separation of zinc and copper ions with the imprinted polymer was conducted, and the template effect of the polymer was characterized by comparing it with the unimprinted polymer and also with the conventional solvent extraction method for the same metal ions.

Experimental Section

Materials. The syntheses of dioleyl phosphate (DOLPA) and N-ribitol L-glutamic acid dioleyl diester ($2C_{18}\Delta^9GE$) have been reported previously.[8,9] Figure 1 shows the structures of DOLPA and $2C_{18}\Delta^9GE$. Divinylbenzene (DVB, Wako Pure

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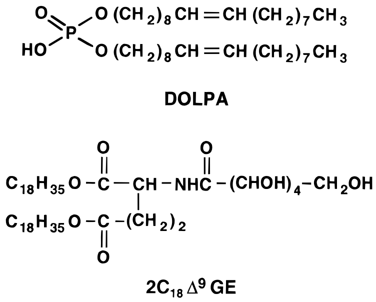

Figure 1. Structures of dioleyl phosphate (DOLPA) and N-ribitol L-glutamic acid dioleyl diester ($2C_{18}\Delta^9GE$).

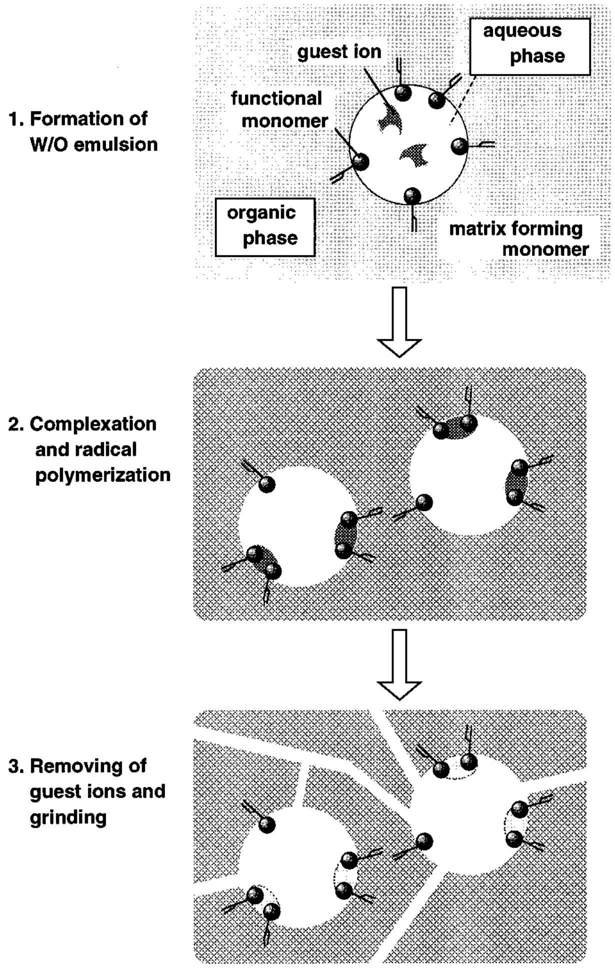

Figure 2. Schematic illustration of surface template polymerization with W/O emulsions.

Chemical Industries, Ltd.) was used after treatment with silica gel to remove an inhibitor. Other reagents were of commercially available grades.

Preparation of Zn(II)-Imprinted Polymer. The scheme for preparation of the Zn(II)-imprinted polymer by surface-template polymerization is shown in Figure 2. A 2.9-g (4.8×10^{-3} mol) portion of DOLPA and 0.25 g (3.0×10^{-4} mol) of $2C_{18}\Delta^9GE$ were dissolved in 60 mL of toluene/DVB 1/2 (v/v). A 30-mL aqueous solution of 1.0×10^{-2} mol/L Zn(II), which was buffered with acetic acid/sodium acetate and was maintained at pH 3.8, was added, and the mixture was sonicated for 3 min to give a water-in-oil (W/O) emulsion. Subsequently, by the addition of 0.36 g (1.4×10^{-3} mol) of 2,2′-azobis(2,4-dimethylvaleronitrile) [1 wt % with respect to DVB (36.56 g, 2.8×10^{-1} mol), Wako Pure Industries, Ltd.], polymerization was carried out at 55 °C for 2 h in a stream of nitrogen. The bulk polymer was dried under vacuum and ground into particles. Finally, the particles were washed with 1.0 mol/L hydrochloric acid solution to remove Zn(II) and then filtered. This procedure was repeated until Zn(II) in the filtrate became negligible. The Zn(II)-imprinted polymer was dried in vacuo and is designated as EIP. Similarly, a reference polymer was prepared but without the imprinting of Zn(II) and is referred to as EP.

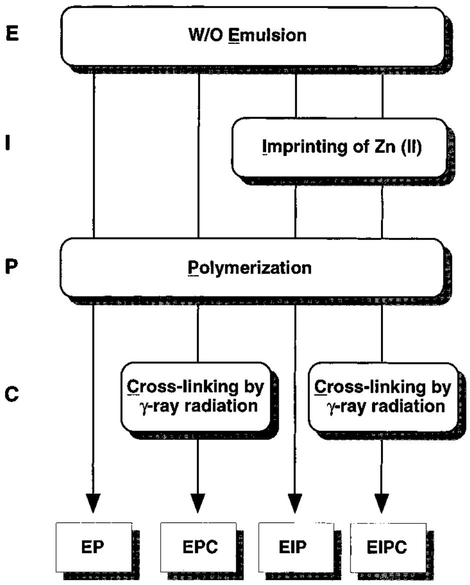

Figure 3. Preparation scheme for EP, EPC, EIP, and EIPC polymers.

Irradiation by γ-rays of Zn(II)-Imprinted Polymer. Before removal of Zn(II), the Zn(II)-imprinted polymer (EIP) was irradiated with γ-rays at ambient temperature in a nitrogen atmosphere to induce cross-linking (hereinafter abbreviated EIPC). The dose for cross-linking was 1820 kGy. A reference polymer, EP, was equally subjected to γ-ray radiation and is hereinafter referred to as EPC. The preparation of the above mentioned processes for EP, EPC, EIP, and EIPC are summarized in Figure 3.

Analyses of the Polymer. FT-IR spectra of samples dispersed in KBr in the range of 400–2000 cm^{-1} were recorded on a Perkin-Elmer Series PARAGON 1000 FTIR spectrophotometer. The swelling ratio was determined by a volumetric measurement.[10] Tetrahydrofuran (THF) was employed as a swelling solvent. To assess how rigidly DOLPA fixes on polymer matrices, the amount of phosphorus contained in DOLPA released from the matrices into the acid washing solution was measured using an ICP atomic emission spectrometer (ICPS-5000, Shimadzu Corp.).

Adsorption of Zn(II) and Cu(II). The adsorption equilibrium of Zn(II) and Cu(II) onto the imprinted polymers was determined batchwise. A quantity of 0.1 g of polymer was immersed in a 5-mL solution of 1.0×10^{-4} mol/L $Zn(CH_3COO)_2$ and 1.0×10^{-4} mol/L $Cu(NO_3)_2$. The pH was adjusted to a desired value between 1 and 5 with 5.0×10^{-2} mol/L acetic acid/sodium acetate and 1.0 mol/L nitric acid. The mixture was shaken in a thermostatted water bath at 303 K for 24 h. The polymers were filtered through a cellulose nitrate membrane (DISMIC-25, Toyo Roshi Kaisha, Ltd.). The amount of Zn(II) and Cu(II) adsorbed on the polymers was calculated from the decrease in Zn(II) and Cu(II) concentration in the filtrate. Zn(II) and Cu(II) concentrations were analyzed using an atomic absorption spectrophotometer (SAS 760, Seiko Instruments Inc.).

Solvent Extraction of Zn(II) and Cu(II). An organic and an aqueous solution were prepared in a way similar to the preparation of the polymer. A mixture of 10 mL organic solution and 5 mL aqueous solution was shaken in a thermostatted water bath at 303 K for 24 h. After phase separation, the equilibrium concentration of zinc or copper ions in the aqueous solution was analyzed with the atomic absorption spectrophotometer.

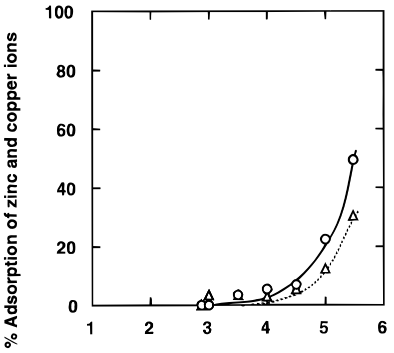

Figure 4. pH dependence of the adsorption of zinc (○) and copper (△) ions with an unimprinted polymer (EP).

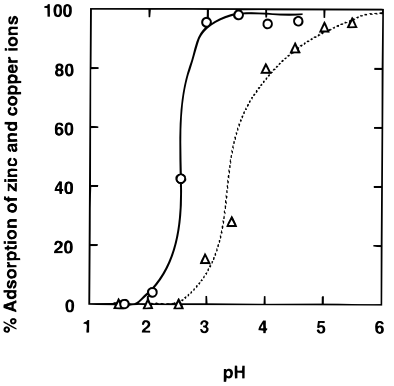

Figure 5. pH dependence of the adsorption of zinc (○) and copper (△) ions with a Zn(II)-imprinted polymer (EIP).

Results and Discussion

A Zn(II)-imprinted polymer was prepared by surface template polymerization with W/O emulsions. DVB, toluene, DOLPA, and $2C_{18}\Delta^9GE$ were used as a cross-linking agent, diluent, a Zn(II)-binding amphiphile, and an emulsion stabilizer, respectively. After the polymerization, the bulk polymer was ground into particles whose diameter was ca. 10 μm throughout the experiments. After drying under vacuum the Zn(II)-imprinted particles were subjected to γ-ray radiation to bind DOLPA thoroughly and to cross-link the polymer matrices. Zn(II) was completely removed from the polymer particles using 1.0 mol/L hydrochloric acid. The particles were then dried. The yield was ca. 70%.

Figures 4 and 5 show the pH dependence of competitive adsorption of Zn(II) and Cu(II) on EP and EIP polymers, respectively. The amount of metal ions for rebinding was set up to be below the maximum capacity of Zn(II)-imprinted sites (1.1×10^{-6} mol for 0.1g of polymer) in order to evaluate the binding affinity of polymers. EIP polymers adsorbed both Zn(II) and Cu(II) much more effectively than did EP polymers over the entire pH range. It follows from this that EIP polymers exhibit the template effect concerning the amount of metal ions adsorbed. However, even EIP polymers show less selectivity for Zn(II) and Cu(II). In the solvent extraction system (Figure 6), an effective selectivity was not observed because the functional monomers (extractants) can take both the tetrahedral configuration for zinc ions and the square planar configuration for copper ions due to their high mobility in organic solvent. Thus EIP polymers have a selectivity for metal ions equivalent only to that of the functional monomer, as is the case for other conventional imprinted polymers.[11-13]

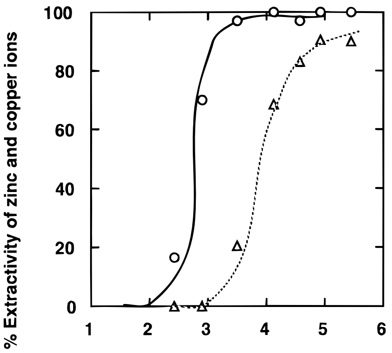

Figure 6. pH dependence of the solvent extraction of zinc (○) and copper (△) ions using DOLPA.

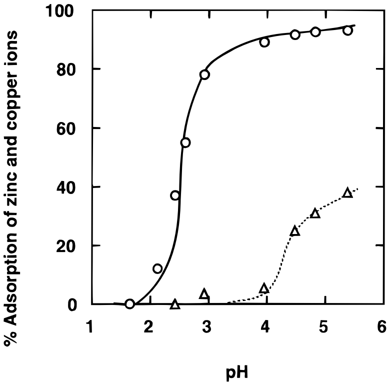

Figure 7. pH dependence of the adsorption of zinc (○) and copper (△) ions with a γ-ray-irradiated Zn(II)-imprinted polymer (EIPC).

Table 1. Swelling Ratio of Polymers in THF

polymers	swelling ratio (%)
EP	27
EPC	22
EIP	37
EIPC	27

Figure 7 shows the pH dependence of the competitive adsorption of Zn(II) and Cu(II) on EIPC polymers. The difference was not observed between EIP and EIPC polymers with respect to their ability for Zn(II) binding. An irradiated blank polymer, which does not include DOLPA, adsorbed no metal ions. These results clearly show that irradiation of γ-rays does not destroy the Zn(II)−DOLPA complex and produces few functional groups such as carbonyl group within the dose range used. In contrast with Zn(II) binding, the Cu(II) binding ability of EIPC polymers was drastically decreased; EIPC polymers can distinguish the coordination of Zn(II) from that of Cu(II). Comparison of the IR spectra for both EIP and EIPC or EP and EPC shows that the peak at 1630 cm^{-1} , associated with $RHC{=}CH_2$ ($\nu_{C=C}$), was diminished owing to the cross-linking by the irradiation. From the swelling ratio in THF for all polymers (Table 1) , the irradiated polymers were found to be swollen much less than nonirradiated polymers. The rate of DOLPA released from each polymer matrix during acid-washing operations (Table 2) was remarkably reduced by irradiation with γ-rays. The improvement in the selectivity of EIPC was attributed to the induced cross-linking in the polymer matrices by irradiation with γ-rays, which renders the polymer matrices rigid, consequently making the binding sites stable enough to recognize zinc ions. Furthermore, the double bond in the oleyl chains of DOLPA was reduced, and DOLPA

Table 2. Ratio of Functional Monomer (DOLPA) Released from Each Polymer Matrix during Acid-Washing Operations

polymers	release ratio[a] (%)
EP	1.5
EPC	1.3
EIP	3.1
EIPC	1.5

[a] (Amount of DOLPA released)/(total amount of DOLPA added) × 100%.

combined rigidly with the polymer matrices. Therefore, the application of γ-ray irradiation is considered to be a very convenient way for fixing the binding sites of target metal ions.

These results show that rigid and dimensionally stable metal-imprinted polymers which recognize metal coordination by anchoring a functional monomer such as DOLPA to the polymer surface can be prepared. It is well-known that properties such as matrix rigidity bring about poor mass transfer in conventional imprinted polymers in which the recognition sites exist, although this is an advantage in surface template polymerization. Furthermore, the combination of surface template polymerization with irradiation by γ-rays offers a potential technique to construct highly selective molecular-recognizing polymers applicable to the adsorption of various water-soluble substances.

Conclusions

Zn(II)-imprinted polymers with the functional monomer, DOLPA, were irradiated with γ-rays to make polymer matrices rigid and also to allow the functional monomer to attach firmly to the matrices. The irradiated, imprinted polymer exhibits a tremendously high selectivity toward zinc ions over copper ions. It is concluded that the irradiation with γ-rays enables recognition sites to be rigid. The combination of surface template polymerization with γ-ray irradiation will be an ideal method to construct new molecular-recognizing materials for various water-soluble substances.

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