Macromolecules **1999,** *32,* 1237−1243

Required Properties for Functional Monomers To Produce a Metal Template Effect by a Surface Molecular Imprinting Technique

Masahiro Yoshida, Kazuya Uezu, Masahiro Goto,* and Shintaro Furusaki

Department of Chemical Systems and Engineering, Graduate School of Engineering,
Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

Received March 25, 1998; Revised Manuscript Received November 18, 1998

ABSTRACT: We investigated the properties required to design functional monomers which produce an imprint effect in prepared metal-imprinted polymers. Novel organophosphorus functional monomers were synthesized, and zinc-imprinted polymers were prepared with the functional monomers by a surface molecular imprinting technique. The competitive adsorption behavior of zinc and copper ions on the surface-imprinted polymers was examined, and the template effect was characterized. A slight structural change in the functional monomers, which interact with target metal ions (zinc ions in this study), resulted in a favorable change in metal recognition by the zinc-imprinted polymers. It was found that the presence of aromatic rings and a suitable straight alkyl chain in the functional monomer in addition to a high binding affinity to the target metals renders molecular recognition on the surface of the imprinted polymers effective.

Introduction

Molecular imprinting technique[1−6] has recently emerged as a technique for embedding special recognition of various target materials in highly cross-linked synthetic polymers. The resultant imprint polymers contain a specific recognition site that can recognize the imprint molecule and hence exhibit a high selectivity for rebinding the imprint molecule. The recognition sites are concretely tailor-made by copolymerization with cross-linking monomers and functional monomers which interact with a target molecule. The concept of this imprinting technique was first demonstrated by Wulff and co-workers about 25 years ago.[7] This epoch-making methodology has been applied to the variety examples of organic-soluble biological substances.[8−22]

Although molecular imprinting technique is conceptually attractive, it has some fundamental drawbacks: for example, (1) slow rebinding kinetics which arises from the inner diffusion of imprint molecules toward the recognition sites into a polymer matrix, (2) difficulty in handling water-soluble substances which are important to biological and medical fields, and (3) a residue of a guest molecule into the polymer matrix.

In recent years, we have proposed a novel molecular imprinting technique, which is called “surface template polymerization technique”,[23−27] to overcome these defects with the conventional molecular imprinting technique. In the novel technique, an aqueous−organic interface in the water-in-oil (W/O) emulsions is utilized as the recognizing-field for a target molecule. A target molecule (a water-soluble substance) forms a complex with a functional monomer at the oil−water interface and orderly arrangement. The orientation of the functional monomer is controlled by the complexation with the target molecules. The complex between the functional monomer and the imprint metal ion is expected not to be totally hydrophobic nor hydrophilic, and a functional monomer which has an amphiphilic nature is required to yield a high template effect for the target molecule. The organic phase containing a matrix-forming monomer is polymerized to give a polymer so that the target-selective cavities are created on the polymer surface. This enables a rapid and reversible complexation of the target molecule for surface imprinted polymers. The concept of surface template polymerization technique is illustrated in Figure 1. The surface-imprinted polymer is prepared by a W/O emulsion polymerization using a functional monomer, an imprint molecule, an emulsion stabilizer, and divinylbenzene as a matrix-forming monomer.

For our first approach utilizing the surface template polymerization, we have succeeded in preparing highly selective metal-imprinted (zinc ions) polymers using an organophosphorus compound; dioleyl phosphoric acid (abbreviated as DOLPA), has two long alkyl chains in the hydrophobic moiety as a functional monomer.[24] The interfacial activity of the functional monomer was found to be one of the key factors to succeed in preparing an effective imprinted polymer. However, we could not always obtain an excellent template effect due to the difficulty in fixing the recognition site on the polymer surface sufficiently. Therefore, the Zn(II)-imprinted polymers with DOLPA were irradiated with γ-rays to make the polymer matrix rigid and also to allow the recognition sites attach firmly to the polymer matrix, which resulted in producing a remarkable selectivity to zinc ions over copper ions.[26] We have designed other novel bifunctional monomers, 1,12-dodecanediol-*O,O′*-diphenyl phosphonic acid (abbreviated as DDDPA), which have a 12-methylene alkyl spacer linking two phosphonic acid and two aromatic rings in the molecular structure to fix the recognition sites more rigidly and to create more stronger interactions between the functional monomer and the target metal ion.[25] The Zn(II)-imprinted polymer possessing the novel bifunctional monomer exhibited a tremendously a high selectivity toward zinc ions over copper ions in a wide pH range. Furthermore, we have investigated in detail the selectivity for zinc ions in competitive zinc−copper sorption test on the Zn(II)-imprinted polymers with some analogous functional monomers, each of which has a different

---

* To whom correspondence should be addressed.

10.1021/ma980472m CCC: $18.00

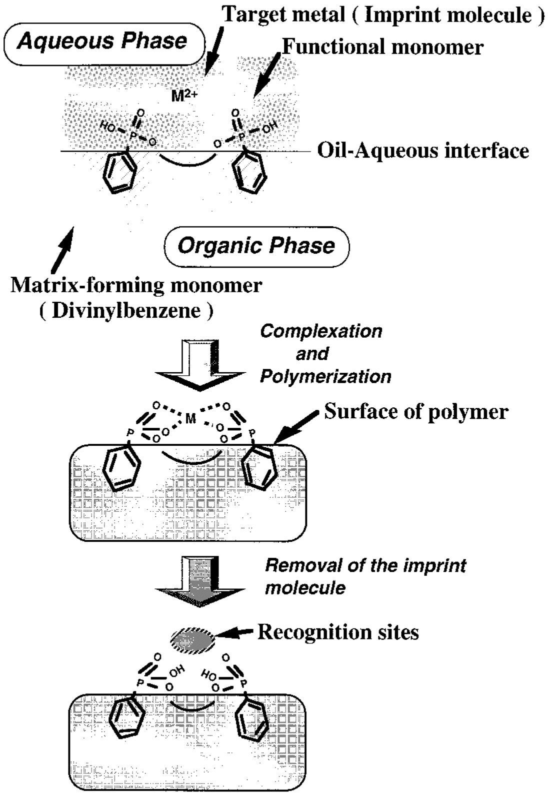

Figure 1. Schematic illustration of surface template polymerization technique.

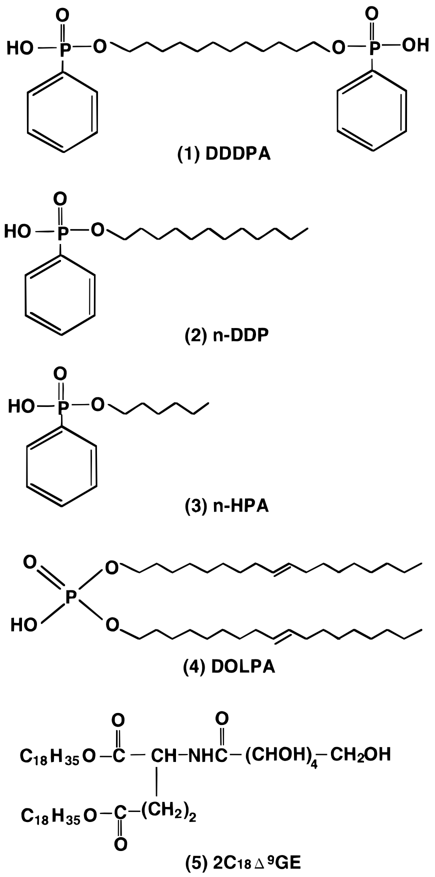

Figure 2. Structures of functional monomers (**1**−**4**) and an emulsion stabilizer (**5**).

length of methylene spacer ($-(CH_2)_n-$: $n = 4, 8, 12$) linking two phosphonic acid groups and two aromatic rings.[27] It was concluded that a suitable length for the alkyl spacer connecting the bifunctional phosphonic groups was a dominant factor to ensure the formation of effective recognition sites for a target metal on the surface of polymers. Moreover, we considered that in order to develop novel functional monomers for preparing highly selective surface-imprinted polymers it is necessary to explain the mechanism of the efficient template effect caused by the functional monomers.

In this paper, we introduce a few novel functional monomers which we have synthesized in order to elucidate the properties required to prepare metal-imprinted polymers successfully. The functional monomers are as follows: phenyl phosphonic acid monododecyl ester (abbreviated as *n*-DDP) containing a 12-methylene chain and one aromatic ring or phenyl phosphonic acid monohexyl ester (abbreviated as *n*-HPA) containing a six-methylene chain and one aromatic ring, each of which has a molecular structure similar to that of DDDPA[25,27] (a 12-methylene chain and two aromatic rings) or DOLPA[24,26] (only two oleyl chains) as shown in Figure 2 (structures **1**−**4**). Using synthesized functional monomers, we prepared a highly selective Zn(II)-imprinted polymer by surface template polymerization with the W/O emulsion. The competitive adsorption behavior of zinc and copper ions with the Zn(II)-imprinted polymers was investigated and the relationship between the structure of the functional monomers and the template effect toward zinc ions were characterized by (1) comparing the adsorption results to those from conventional liquid−liquid extraction bearing functional monomers, (2) measuring the rigidity of the surface-imprinted polymers, (3) carrying out a Langmuir analysis, and (4) calculating the interfacial activity of functional monomers. These detailed investigation provided us with useful information concerning properties of functional monomers required to prepare highly selective synthetic polymers.

Experimental Sections

Reagents. The novel organophosphorus functional monomers, *n*-DDP and *n*-HPA, were synthesized from phosphonic dichloride and the corresponding diol or alcohol. DDDPA, DOLPA, and L-gultamic acid dioleylester ribitol (abbreviated as $2C_{18}\Delta^9GE$) were synthesized according to the procedures reported in previous works.[27−29] Figure 2 shows the structures of DDDPA (**1**), *n*-DDP (**2**), *n*-HPA (**3**), DOLPA (**4**), and $2C_{18}\Delta^9GE$ (**5**), respectively. Divinylbenzene (abbreviated as DVB, Wako Pure Chemical Industries Co., Ltd.) was employed after treatment with silica gel to remove an inhibitor. Other reagents were of commercially available grades.

Synthesis of the Functional Monomers. The novel functional monomers were synthesized as follows.

(I) *n*-DDP. Under nitrogen atmosphere, 28.0 g (0.144 mol) of phosphonic dichloride was added to a mixture of 60 cm^3 dry tetrahydrofuran (THF) and 40 cm^3 pyridine placed in an ice−water bath. A solution of 22.4 g (0.120 mol) of lauryl alcohol in 100 cm^3 of dry THF and pyridine was slowly added dropwise to the above solution at 273 K. This mixture was stirred in an ice−water bath for 48 h and then poured into 350 cm^3 of iced water. A 30 cm^3 aliquot of concentrated hydrochloric acid was added to the solution until the pH of the aqueous solution reached a value between 1 and 2. Then 300 cm^3 of chloroform was added to the acidic solution in order to extract the product. The mixed liquor containing chloroform was stirred for 2 h. The organic phase was separated, washed twice with 250 cm^3 of 1 M hydrochloric acid, and dried with anhydrous magnesium sulfate. After the organic phase was evaporated, the final product was obtained. The crude product was finally purified by column chromatography.(silica gel, chloroform/methanol =

9/1, v/v). The final product assayed as follows: light yellow liquid, yield 98.0%; IR (neat) ν_{OH} 2628 cm^{-1}, $\nu_{P=O}$ and δ_{OH} 2288 cm^{-1}, ν_{P-OR} 1684 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$, TMS, 303 K) $\delta = 0.88$ (3H, t, $-CH_2-\mathit{CH_3}$), $\delta = 1.25$ (18 H, m, $-CH_2-(\mathit{CH_2})_9-CH_3$), $\delta = 1.63$ (2H, m, $-O-CH_2-\mathit{CH_2}-(CH_2)_9$), $\delta = 3.98$ (2H, m, $-O-\mathit{CH_2}-CH_2-(CH_2)_9$), $\delta = 7.49$ (3H, m, P$-$ArH (*m*,*p*-position)), $\delta = 7.79$ (2H, m, P$-$ArH (*o*-position)), $\delta = 11.0$ (1H, s, P$-$OH). Anal. Calcd for $C_{18}H_{31}O_3P$: C, 66.23; H, 9.57. Found: C, 66.52; H, 9.65.

(II) *n*-HPA. Under nitrogen atmosphere, 33.8 g (0.173 mol) of phosphonic dichloride was added to the mixture of 60 cm^3 dry THF and 18 cm^3 pyridine placed in an ice$-$water bath. A solution of 16.9 g (0.165 mol) of *n*-hexyl alcohol in 100 cm^3 of dry THF and pyridine was slowly added dropwise to the solution at 273 K. The above mixture was stirred for 48 h. The subsequent steps are similar to the procedures reported in synthesizing DDDPA or *n*-DDP. The final product assayed as follows: light yellow liquid, yield 97.0%; IR (neat) ν_{OH} 2620 cm^{-1}, $\nu_{P=O}$ and δ_{OH} 2269 cm^{-1}, ν_{P-OR} 1681 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$, TMS, 303 K) $\delta = 0.84$ (3H, t, $-CH_2-\mathit{CH_3}$), $\delta = 1.24$ (6H, m, $-CH_2-(\mathit{CH_2})_3-CH_3$), $\delta = 1.63$ (2H, m, $-O-CH_2-\mathit{CH_2}-(CH_2)_3$), $\delta = 3.99$ (2H, m, $-O-\mathit{CH_2}-CH_2-(CH_2)_3$), $\delta = 7.39$ (3H, m, P$-$ArH (*m*,*p*-position)), $\delta = 7.41$ (2H, m, P$-$ArH (*o*-position)), $\delta = 13.0$ (1H, s, P$-$OH). Anal. Calcd for $C_{12}H_{19}O_3P\cdot 0.22CHCl_3$: C, 58.14; H, 7.50. Found: C, 57.96; H, 7.60.

Preparation of Zn(II)-Imprinted Polymers. A metal ion-imprinted polymer was prepared by the surface template polymerization technique utilizing W/O emulsions. A 40 cm^3 of DVB, in which 60 mM DDDPA, *n*-DDP, or *n*-HPA and 20 mM $2C_{18}\Delta^9$GE were dissolved, was mixed with 20 cm^3 toluene containing 5 vol % 2-ethylhexyl alchohol. An aqueous solution (30 cm^3) of 10 mM $Zn(NO_3)_2$, which was buffered with 100 mM acetic acid$-$sodium acetate and maintained at the pH 3.0 to 3.5, was added. The mixture was sonicated for 4 min to yield W/O emulsions. After the addition of 0.36 g (1.4×10^{-3} mol) of the powder initiator (2,2′-azobis(2,4′-dimethylvaleronitrile)), 0.01 wt % for DVB), the mixture was polymerized at 328 K for 2 h under a flow of nitrogen. The bulk polymers were dried under vacuum and ground into an appropriate size. The particles were washed with 1 M hydrochloric acid to remove the target metals (zinc ions) and then filtered off. This procedure was repeated several times until zinc ions could not be detected in the filtrate. Finally, the Zn(II)-imprinted polymers were dried in vacuo for several days. Unimprinted polymers as a reference were similarly prepared without imprinting metal ions. A particle size analysis and a scanning electron microscopy were performed by means of a microtrac optical analyzer (Model 7995-10 SRA, Nikkiso Co., Ltd.) and an ABT-32 type microscopy (Akashi Beam Technology Co., Ltd.), respectively.

Competitive Adsorption Experiment for Zn(II) and Cu(II) on the Zn(II)-Imprinted and Unimprinted Polymers. The competitive adsorption experiments for zinc and copper ions were conducted batchwise using imprinted and unimprinted polymers. The polymers (0.1 g) were added to the 5 cm^3 of aqueous solution containing 0.1 mM $Zn(NO_3)_2$ and 0.1 mM $Cu(NO_3)_2$ and sealed in a test tube (10 cm^3 volume). The pH was adjusted to a desired value between 1.0 and 5.0 using 100 mM acetic acid$-$sodium acetate and 100 mM nitric acid. The mixture was shaken in a thermostated water bath at 303 K for 24 h. The polymers were then filtered off through a cellulose nitrate membrane (DISMIC-25, Tokyo Roshi Kaisha, Ltd.). The amounts of zinc and copper ions on the polymers were calculated by the residual concentrations of zinc and copper ions in the filtrated aqueous solution. The metal concentration was measured by means of an atomic absorption spectrophotometer (SAS-760, Seiko Instrument Inc.). The adsorption percentage defined as the percentage of the amount of adsorbed metal ions to that of initial one was calculated from the data.

Competitive Liquid$-$Liquid Extraction of Zn(II) and Cu(II) Using the Functional Monomers. An organic solution was produced, composed of 10 mM DDDPA, *n*-DDP, or *n*-HPA in toluene. An aqueous solution containing 0.1 mM $Zn(NO_3)_2$ and 0.1 mM $Cu(NO_3)_2$ had its pH adjusted to a desired value between 1.0 and 6.0 with 100 mM sodium acetate$-$acetic acid and 100 mM nitric acid. Equal volumes (10 cm^3) of the aqueous and organic solutions were shaken in a thermostated water bath at 303 K for 24 h. After phase separation, the equilibrium concentration of zinc and copper ions in the aqueous solution was analyzed by the atomic absorption spectrophotometer. The degree of extraction, *E*, was defined as the percentage of the extracted metal ions in the organic phase to the initial concentration in the aqueous phase.

Swelling Ratio of the Zn(II)-Imprinted Polymers. The swelling ratio of the Zn(II)-imprinted polymers was determined by volumetric measurement.[30] A 1.0 g sample of the Zn(II)-imprinted polymers was placed in a sealed Teflon tube and centrifuged for 30 min at 5000 rpm. The volume of the Zn(II)-imprinted polymers filled was measured as V_1. Excess toluene was added as a swelling solvent, and was vigorously shaken with polymers to ensure complete mixing. After the mixture was centrifuged for 30 min at 5000 rpm again, it was left intact for several hours. The volume of the swelled Zn(II)-imprinted polymers was remeasured as V_2. The swelling of the column volumes is the expansion of the Zn(II)-imprinted polymers due to the swelling solvent. The volumetric swelling ratio, *S*, was defined as follows:

$$S = \{(V_2 - V_1)/V_1\} \times 100$$

Interfacial Activities of the Functional Monomers. A 25 cm^3 aqueous solution buffered at pH 1.2 with 100 mM nitric acid$-$sodium nitrate was prepared. A 25 cm^3 toluene solution containing a dissolved functional monomer at desired concentration was prepared. Equal volumes of the aqueous and organic solutions of known concentrations were shaken in a lidded flask and allowed to attain equilibrium in a thermostated water bath at 303 K. The interfacial activity of the functional monomer between the aqueous and organic solutions was measured by the volume drop method at 303 K.

Effective Ion-Exchange Capacities and Adsorption Equilibrium Constants for the Zn(II)-Imprinted Polymers. The measurement of adsorption equilibrium constants of zinc ions on the Zn(II)-imprinted polymers was conducted batchwise. A 1.0 g sample of the polymers was immersed in a sealed test tube (10 cm^3 volume) to which was added a 5 cm^3 aqueous solution (pH 4.5: buffered with 100 mM acetic acid$-$sodium acetate) containing a known concentration of zinc ions in the range of 0.1$-$50 mM. The mixture was shaken in a thermostated water bath at 303 K for 24 h. The polymers were then filtered off through the cellulose nitrate membrane. The concentration of zinc ions in the filtrate was analyzed by the atomic absorption spectrophotometer. It was assumed that the adsorption behavior of zinc ions on the Zn(II)-imprinted polymers follows the Langmuir type in the liquid$-$solid phase. The Langmuir's equation is expressed as follows:

$$q = aq_s\, C/(1 + aC) \tag{1}$$

Here q_s is the effective ion-exchange capacity and a is the adsorption equilibrium constant. These two constants (q_s, *a*) were calculated by the relationship between the slope and the intercept on the Langmuir straight plots which is expressed by eq 1.

Results and Discussion

Characterization of the Functional Monomers. (I) Interfacial Activity of the Functional Monomers. The interfacial activity of functional monomers is one of the dominant factors required to succeed in preparing a surface imprinted polymer. The property is important to create an effective recognition cavity on the surface of W/O emulsions. The adsorption equilibrium constant for the functional monomers is expressed as follows:

$$F_{org} = F_{ad}, K_F \tag{2}$$

Table 1. Interfacial Adsorption Equilibrium Constants of Functional Monomers

functional monomers	interfacial adsorption equilibrium constants K_F (m^3/mol)
DDDPA	310
n-DDP	61
n-HPA	0.7
DOLPA[24]	48

Here K_F is the interfacial adsorption equilibrium constant, and F and the subscript ad denote the functional monomers and the adsorption states at the oil–water interface, respectively. The relationship between the interfacial tension and the amount of the functional monomer adsorbed at the oil–water interface is expressed by Gibb's adsorption equation. Assuming Langmuir adsorption isotherm between the amount of the functional monomer adsorbed and its bulk concentration C_F, the relationship between interfacial tension, γ, and C_F at temperature T is expressed as follows:[29]

$$\gamma = \gamma_0 - (RT/S_F)\ln(1 + K_F C_F) \tag{3}$$

Here γ_0 is the interfacial tension between the pure organic solvent and the aqueous solution, R is the gas constant, and S_F is the interfacial area occupied by a unit mole of the functional monomer. The interfacial adsorption equilibrium constant, K_F, can be obtained from the experimental results for the interfacial tension and eq 3 by a nonlinear regression method. The interfacial adsorption equilibrium constants for the functional monomers are summarized in Table 1. The higher the interfacial adsorption equilibrium constant the higher the interfacial activity. The interfacial activities of DDDPA and *n*-DDP possessing a 12-methylene chain and DOLPA[24] possessing two oleyl chains are much higher than that of *n*-HPA possessing a six-methylene chain. The functional monomers having either longer alkyl or two oleyl chains were found to have a high interfacial activity at the oil–water interface.

(II) Liquid–Liquid Extraction Behavior of Zn(II) and Cu(II) Using the Functional Monomers. The binding affinity between the functional monomer and the target metal ions is also one of the vital factors in preparing effective imprint polymers. We evaluated the degree of binding affinity of the functional monomers to zinc ions by utilizing the liquid–liquid extraction technique. Figure 3 shows extraction behavior of zinc and copper ions using the three different functional monomers. In the liquid–liquid extraction system, the functional monomer of DDDPA or *n*-DDP exhibited a high binding affinity for both zinc and copper ions as well as that of DOLPA.[26] However, effective separation between Zn(II) and Cu(II) by DDDPA, *n*-DDP, or DOLPA was not attained because the functional monomers freely changed their complex conformation to tetrahedral configuration for Zn(II) and a square planar configuration for Cu(II) owing to their high mobility in the organic solvent. On the other hand, the *n*-HPA surprisingly exhibits a preferential high affinity for zinc ions compared to that of copper ions. We found that all functional monomers show a high binding affinity to the target zinc ions.

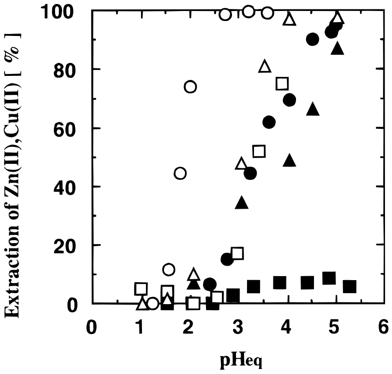

Figure 3. pH dependence in liquid–liquid extraction of zinc and copper ions using functional monomers: extraction of zinc (○) and copper (●) ions using DDDPA; extraction of zinc (△) and copper (▲) ions using *n*-DDP; extraction of zinc (□) and copper (■) ions using *n*-HPA.

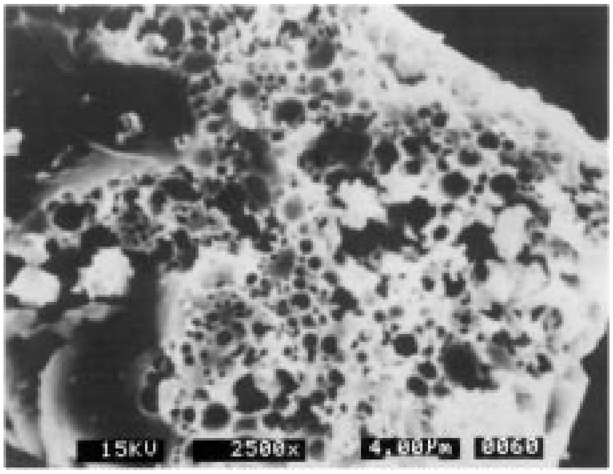

Figure 4. Typical SEM photograph of the Zn(II)-imprinted polymers.

Characterization of the Zn(II)-Imprinted Polymers. Highly cross-linked Zn(II)-imprinted polymers were prepared by surface template polymerization. In the present study, our target metal is zinc ions because our newly developed functional monomers have a high affinity toward the zinc ions. One of our objectives in this study is to enhance this selectivity toward the target metal ion by surface imprint technique. After polymerization, the bulk Zn(II)-imprinted polymers were ground into particles, whose volume-averaged diameters were ca. 40 μm in all experiments. The imprinted zinc ions were removed from the Zn(II)-imprinted polymers, on which selective recognition sites for zinc ions were introduced. All the Zn(II)-imprinted polymers were obtained at 80–90% yields. Figure 4 exhibits a typical scanning electron microscopy view of the Zn(II)-imprinted polymers. A number of traces of aqueous phases in the W/O emulsions, which seems to be a honeycomb, are observed in their polymers. The recognition sites for zinc ions are definitively constructed on the polymer surfaces.

In the surface template polymerization technique, it is important to make the polymer matrix rigid for fixing a functional monomer (recognition sites), and that results in creating a high selectivity between the functional monomer and an imprint molecule on the polymer surface. Therefore, we investigated the swelling ratio of the polymers to evaluate the rigidity of the polymer matrix. Table 2 summarized the swelling ratio of the Zn(II)-imprinted polymers with DDDPA, *n*-DDP, *n*-HPA, or DOLPA. The lower the value of the swelling ratio, the larger the fixing of the recognition sites for zinc ions on the polymer surface. The Zn(II)-imprinted polymer with DDDPA, which has two aromatic rings

Table 2. Swelling Ratios of the Zn(II)-Imprinted Polymers with DDDPA, *n*-DDP, *n*-HPA, or DOLPA in Toluene

Zn(II)-imprinted polymers	swelling ratio [%]
with DDDPA	9
with *n*-DDP	18
with *n*-HPA	27
with DOLPA[26]	35

and a 12-methylene chain, scarcely swelled compared to the swelling ratio of the Zn(II)-imprinted polymer with *n*-DDP or *n*-HPA, each of which has one aromatic ring and a 12- or six-methylene chain in the hydrophobic moiety. The Zn(II)-imprinted polymer with DOLPA[26] possessing two alkyl chains exhibited much higher swelling ratio than those of the other ones. It is considered that the high swelling ratio of *n*-HPA compared to that of *n*-DDP was caused by incorporating functional monomers to the polymer matrix owing to the small interfacial activity. *n*-DDP whose interfacial activity is similar to that of DOLPA,[24] which does not contain an aromatic ring, also exhibited a low swelling ratio compared to that of DOLPA.[26] Therefore, the aromatic ring was found to play an important role to fix the recognition sites on the polymer surface rigidly by a specific interaction such as $\pi-\pi$ stacking with the polymer matrix.

Adsorption Behavior of Zn(II) and Cu(II) and Adsorption Constants on the Zn(II)-Imprinted Polymers. Figures 5−7 show the pH dependence of competitive adsorption of zinc and copper ions on the Zn(II)-imprinted polymers with DDDPA, *n*-DDP, or *n*-HPA. Figure 5b also shows the adsorption result of unimprinted polymers with DDDPA. The difference in the adsorption performance between the imprinted and unimprinted polymers clearly shows the template effect to the target Zn(II) ions. The Zn(II)-imprinted polymers with DDDPA attained a high selective adsorption of zinc ions over copper ions compared to the corresponding unimprinted ones in a wide pH range (Figure 5, parts a and b). The selectivity is attributed to the zinc ions memorized cavities, whose formations have a tetrahedral configuration on the polymer surface. On the other hand, the Zn(II)-imprinted polymer with *n*-HPA, whose structure has a half-structure of DDDPA and a shorter six-methylene chain as compared to the structure of *n*-DDP, did not exhibit a high adsorption ability and selectivity for zinc and copper ions despite having a high binding affinity to zinc ions in the conventional liquid−liquid extraction (Figures 3 and 7). We considered that *n*-HPA having insufficient interfacial activity could not produce the recognition sites on the polymer surface due to the incorporation of functional monomers into the polymer matrix. These results are very interesting because they show that the template effect on the polymer surface is very sensitive to the structure of the functional monomer. It is worth noting that such smaller structural changes in the functional monomer could cause quite different adsorption results, even though they have similar extractive capabilities in liquid−liquid extraction operation. Thus a high binding affinity, the introduction of a straight and long chain, and the aromatic rings in the functional monomers facilitate the construction of effective recognition sites on the polymer surface.

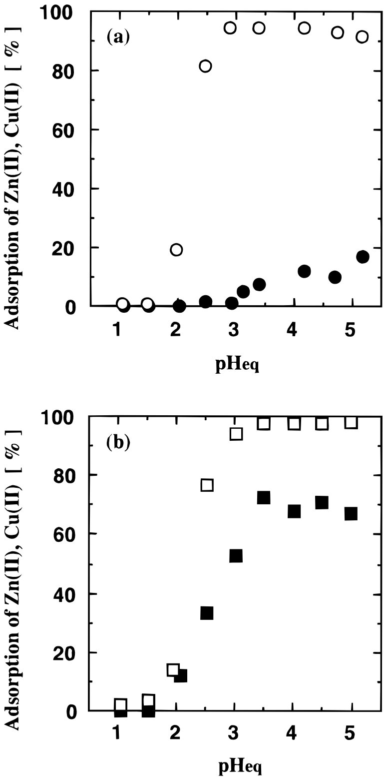

Figure 5. (a) pH dependence of the adsorption of zinc (○) and copper (●) ions on the Zn(II)-imprinted polymer with DDDPA. (b) pH dependence of the adsorption of zinc (□) and copper (■) ions on the unimprinted polymer with DDDPA.

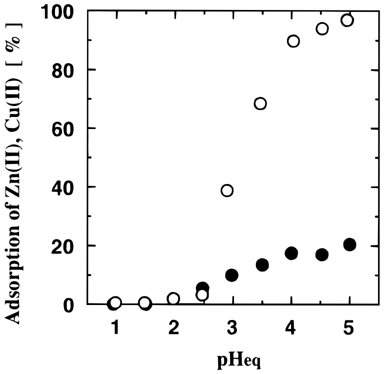

Figure 6. pH dependence of the adsorption of zinc (○) and copper (●) ions on the Zn(II)-imprinted polymer with *n*-DDP.

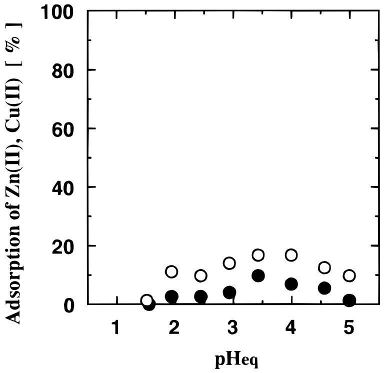

Figure 7. pH dependence of the adsorption of zinc (○) and copper (●) ions on the Zn(II)-imprinted polymer with *n*-HPA.

Furthermore, we characterized the template effect of the functional monomers for zinc ions on the Zn(II)-imprinted polymers by utilizing an effective ion-exchange capacity and an adsorption equilibrium constant. The results of adsorption constants of the Zn(II)-imprinted polymers with DDDPA, *n*-DDP, or *n*-HPA are

Table 3. Relationship between Effective Ion-Exchange Capacity and Adsorption Equilibrium Constants of the Zn(II)-Imprinted Polymers with DDDPA, *n*-DDP, or *n*-HPA

Zn(II)-imprinted polymers	effective ion-exchange capacity q_s (mmol/g)	adsorption equilibrium constants a (m^3/mol)
with DDDPA	2.1×10^{-2}	44
with n-DDP	2.5×10^{-2}	52
with n-HPA	1.9×10^{-2}	7.0

listed in Table 3. The effective ion-exchange capacity shows the adsorption ability including the nonimprinting sites on the polymer surface. In addition, the adsorption equilibrium constant is considered to be a measure of an affinity of the recognition sites for zinc ions. It can be seen that all the effective ion-exchange capacities of the Zn(II)-imprinted polymers with the functional monomers have a similar tendency. However, it was clarified that the adsorption equilibrium constants of the Zn(II)-imprinted polymer with DDDPA and *n*-DDP were much higher than that of *n*-HPA. Thus these results indicate that the Zn(II)-imprinted polymer using DDDPA or *n*-DDP possessing a 12-methylene chain, aromatic rings, and a high binding affinity toward zinc ions could successfully construct complementary recognition sites for the imprint metals in shape and in the positioning of the functional groups on the polymer surface.

Required Properties in Functional Monomers To Produce the Metal Template Effect. On the basis of the results, we found that the interfacial activity of the functional monomers and the swelling ratio of the imprinted polymers are predominant factors to produce a high imprint effect on the polymer surface. Figure 8 summarized the desirable range of both the swelling ratio (rigidity of the recognition sites) of the Zn(II)-imprinted polymers and the interfacial activity of the functional monomers for obtaining a high template effect. This relationship was obtained from the present results together with our previous studies.[26,27] Within the range of the dotted line (Figure 8), an effective template effect was observed for the target metal, zinc ions. The functional monomers possessing aromatic rings and a high interfacial activity such as DDDPA or *n*-DDP could affix the recognition sites rigidly on the polymer surface and consequently produce a template effect toward zinc ions. In our study, the bifunctional monomer, DDDPA, possessing two aromatic rings and an extremely high interfacial activity was the best functional monomer for realizing the template effect in the surface polymerization technique. In our initial study, we did not originally obtain an excellent template effect for zinc ions on the Zn(II)-imprinted polymer with DOLPA; however, the polymer was modified and moved to the range of dotted line by irradiating with γ-rays.[26] Although the Zn(II)-imprinted polymer with an analogous bifunctional monomer (ODP)[27] having two aromatic rings, a high interfacial activity, and a high affinity for zinc ions is located in the range of the dotted line, an exceptional and efficient template effect could not be obtained for zinc in the competitive adsorption tests for zinc and copper ions. It is considered that this was caused by the deficiency of a suitable alkyl chain length on the recognition sites of the polymer surface. Of course, a functional monomer is necessary to have the binding affinity for a target molecules, however, the existence of both a suitable alkyl chain producing a high interfacial activity (the interfacial adsorption constant: more than 40 m^3/mol) and an aromatic ring creating a matrix rigidity (the swelling ratio was less than 30%) in a functional monomer are realized to be essential properties in designing high performance functional monomers. The matrix rigidity was introduced by a specific interaction such as $\pi-\pi$ stacking with a matrix polymer, which is formed by divinylbenzene.

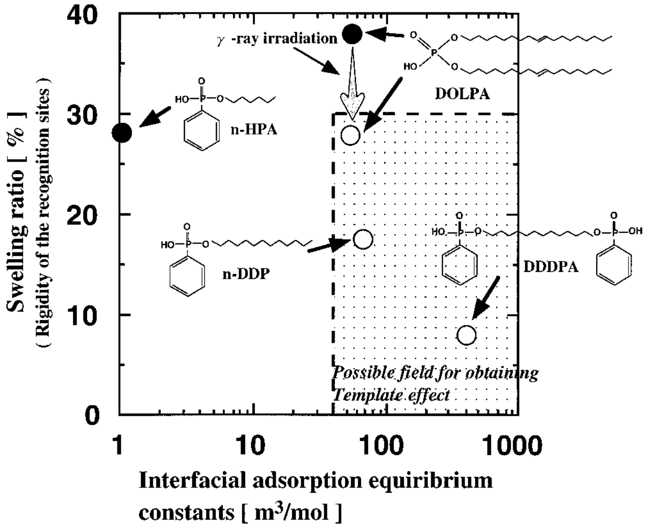

Figure 8. Preferable region of both the swelling ratio (rigidity of the recognition sites) of the Zn(II)-imprinted polymers and the interfacial adsorbability of the functional monomers (each functional monomer has a high affinity to zinc ions) for getting the excellent template effect to zinc ions: (○) Excellent template effect; (●) Poor template effect.

Conclusions. This work provides us with useful information for designing functional monomers required to develop highly selective synthetic polymers. The Zn(II)-imprinted polymers with organophosphorus functional monomers were characterized in terms of interfacial activity, swelling ratio, and binding affinity. A Zn(II)-imprinted polymer with DDDPA or *n*-DDP demonstrated high adsorption and separation efficiency of zinc ions compared to that of a Zn(II)-imprinted polymer with *n*-HPA or DOLPA. We found that the functional monomers possessing more than 40 m^3/mol as interfacial adsorption equilibrium constant and less than 30% swelling ratio showed an efficient template effect to the target molecule. Consequently, the presence of three essential factors—(1) longer alkyl chain yielding a high interfacial activity, (2) aromatic rings leading to rigidity of the recognition sites, and (3) organophosphorus groups producing a high binding affinity—ensure strong adsorption and high selectivity for target metal ions. The surface template polymers are easy to prepare and possess excellent chemical and physical stability. It is our belief that the use of the surface template polymerization technique for the preparation of the "recognition polymers" will find many applications in the future.

Acknowledgment. We are grateful for the Grant-in-Aid for Scientific Research (No. 09750842) from the Ministry of Education, Science, Sports, and Culture of Japan. M.Y. was supported by a Research Fellowship for Young Scientists from the Japan Society for the Promotion of Science (JSPS).

References and Notes

(1) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812.
(2) Wulff, G. *TIBTECH* **1993**, *11*, 85.

(3) Mosbach, K.; Ramstöm, O. *BIO/TECHNOLOGY* **1996**, *14*, 163.
(4) Shea, K. J. *TRIP* **1994**, *5*, 166.
(5) Vidyasankar, S.; Dhal, P. K.; Plunkett, S. D.; Arnold, F. H. *Biotechnol. Bioeng.* **1995**, *48*, 431.
(6) Kempe, M.; Mosbach, K. *J. Chromatogr.* **1995**, *694*, 3.
(7) Wulff, G.; Sarahan, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 341.
(8) Vidyasanker, S.; Ru, M.; Arnold, F. A. *J. Chromatogr.* **1997**, *775*, 51.
(9) Sellergen, B.; Ekberg, B.; Mosbach, K. *J. Chromatogr.* **1985**, *347*, 1.
(10) Andersson, L. I.; O'Shannessy, D. J.; Mosbach, K. *J. Chromatogr.* **1990**, *513*, 167.
(11) Fischer, L.; Müller, R.; Ekberg, B.; Mosbach, K. *J. Am. Chem. Soc.* **1991**, *113*, 9358.
(12) Whitocombe, M. J.; Rodrigez, M. E.; Villar, P.; Vulfson, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 7105.
(13) Cheong, S. H.; McNiven, S.; Rachkov, A.; Levi, R.; Yano, K.; Karube, I. *Macromolecules* **1997**, *30*, 1317.
(14) Wulff, G.; Minarik, M. *J. Liq. Chromatogr.* **1990**, *13*, 2987.
(15) Mathew-Krotz, J.; Shea, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 8154.
(16) Spivak, D. A.; Gilmore, M. A.; Shea, K. J. *J. Am. Chem. Soc.* **1997**, *119*, 4388.
(17) Matsui, J.; Nicholls, I. A.; Takeuchi, T.; Mosbach, K.; Karube, I. *Anal. Chim. Acta* **1996**, *335*, 71.
(18) Liu, X. C.; Mosbach, K. *Macromol. Rappid Commun.* **1997**, *18*, 609.
(19) Müller, R.; Andersson, L. I.; Mosbach, K. *Macromol. Chem. Rappid Commun.* **1993**, *14*, 637.
(20) Kriz, D.; Ramstöm, O; Svensson, A.; Mosbach, K. *Anal. Chem.* **1995**, *67*, 2142.
(21) Valtakis, G.; Andersson, L. I.; Müller, R.; Mosbach, K. *Nature* **1993**, *361*, 645.
(22) Kempe, M.; Glad, M.; Mosbach, K. *J. Mol. Recogn.* **1995**, *8*, 35.
(23) Tsukagoshi, K.; Yu, K. Y.; Maeda, M.; Takagi, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 114.
(24) Uezu, K.; Nakamura, H.; Goto, M.; Murata, M.; Maeda, M.; Takagi, M.; Nakashio, F. *J. Chem. Eng. Jpn.* **1994**, *27*, 436.
(25) Yoshida, M.; Uezu, K.; Goto, M.; Nakashio, F. *J. Chem. Eng. Jpn.* **1996**, *29*, 74.
(26) Uezu, K.; Nakamura, H.; Kanno, J.; Sugo, T.; Goto, M.; Nakashio, F. *Macromolecules* **1997**, *30*, 3888.
(27) Yoshida, M.; Uezu, K.; Goto, M.; Nakashio, F. *J. Polym. Sci. Part A* **1998**, *36*, 2727.
(28) Goto, M.; Kondo, K.; Nakashio, F. *J. Chem. Eng. Jpn.* **1989**, *22*, 79.
(29) Goto, M.; Matsumoto, M.; Kondo, K.; Nakashio, F. *J. Chem. Eng. Jpn.* **1987**, *20*, 157.
(30) Green, T. K.; Kovac, J.; Larsen, J. W. *Fuel* **1984**, *63*, 935.

MA980472M