Metal Ion Imprinted Microsphere Prepared by Surface Molecular Imprinting Technique Using Water-in-Oil-in-Water Emulsions

MASAHIRO YOSHIDA, KAZUYA UEZU, MASAHIRO GOTO, SHINTARO FURUSAKI

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

ABSTRACT: A novel metal ion imprinted polymer was prepared by the surface molecular imprinting technique. Trimethylolpropane trimethacrylate (TRIM), zinc ions, and 1,12-dodecanediol-O,O'-diphenyl phosphonic acid (DDDPA) were used as the matrix-forming monomer, imprint molecule, and functional monomer, respectively. We have prepared Zn(II)-imprinted microspheres utilizing water-in-oil-in-water emulsions, which are spherically well defined and uniform. TRIM comprises of three polymerizable groups that serve to align the recognition sites produced on the polymer surface with better template effect. We conducted diagnostic zinc adsorption tests by using the Zn(II)-imprinted and unimprinted polymers in order to make an assessment on the effectiveness of TRIM-based and divinylbenzene-based imprinted polymers. The template effect of the TRIM-based polymer was enhanced by the high rigidity of the polymer matrix compared to that of the imprinted polymer whose matrix is divinylbenzene. In addition, the adsorption equilibrium constant was evaluated on the basis of the Langmuir analysis for the adsorption data. The method to prepare metal-imprinted microspheres on the surface of polymers crosslinked by TRIM is easy, and the adsorbent produced can be readily used without subsequent grinding or sieving. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1223–1230, 1999

Key words: molecular imprinting; surface template polymerization; metal ion exchange resin; microspherical particle; adsorption

INTRODUCTION

The molecular imprinting technique[1–3] is an attractive strategy because it provides a direct approach to design artificial binding sites in a polymer. The recognition sites are tailor-made *in situ* by copolymerizing the functional monomers and crosslinkers around the organic-soluble print molecules. The print molecules are subsequently extracted from the polymer leaving behind complementary recognition sites in the polymer network. To date several polymers have been prepared by the molecular imprinting technique and applied as stationary phases in the high performance liquid chromatography,[4–12] artificial antibodies,[13,14] and catalysts.[15–17] Although the molecular imprinting technique is conceptually attractive, it has some fundamental drawbacks; for example: (1) slow rebinding kinetics that arise from the inner diffusion of imprint molecules toward the recognition sites in a polymer matrix, (2) difficulty in handling water-soluble substances that are generally important in the biological field,

---

Figure 1 Schematic illustration of the surface template polymerization technique.

and (3) presence of residual target molecules in the imprinted polymer matrix.

Recently, we have proposed a novel molecular imprinting technique, called the "surface template polymerization technique,"[18–24] to overcome the weak points associated with the conventional molecular imprinting technique. The general idea of the surface template polymerization technique is illustrated in Figure 1. The surface-imprinted polymer is prepared by emulsion polymerization with a functional monomer, an imprint molecule, an emulsion stabilizer, and a matrix-forming monomer. In this novel technique, the aqueous–organic interface in emulsions is utilized as a recognition field for a target molecule. The target molecule (water-soluble substances) forms a complex with the functional monomer at the oil–water interface and rearranges in a regular pattern. The orientation of the functional monomer is controlled through the complex formation with a target molecule at the interface. The complex between the functional monomer and the target molecule is desired not to be totally hydrophobic nor hydrophilic—that is, the functional monomer that has an amphiphilic nature such as a surfactant is required to yield a high template effect for

a target molecule. The organic phase containing the matrix-forming monomer is polymerized so that target-selective cavities are left on the polymer surface. The surface-imprinted polymers enable a rapid and reversible complexation of the target molecules.

In our previous studies concerning surface template polymerization, we clarified that there are three essential factors that promote the template effect of functional monomers: a long alkyl chain that leads to a high interfacial activity, presence of aromatic rings that yield enhanced rigidity in both the recognition sites, and the metal recognition groups producing a high binding affinity for the target metal ion.[22,23] For this purpose, we synthesized the novel bifunctional monomer, 1,12-dodecanediol-O,O′-diphenyl phosphonic acid (DDDPA), possessing two aromatic rings, an extremely high interfacial activity, and high binding affinity to the target zinc ions, and proved that the bifunctional monomer was suitable for realizing the template effect.[20,22,23] However, we realized that the rigidity of the polymer matrix was another vital factor to produce a template effect for target molecules.[21,23] Therefore, in the present study, the matrix-forming monomer trimethylolpropane trimethacrylate (TRIM)[25–27] possessing the three polymerizable groups, is introduced to make the polymer matrix more rigid. As a result, the recognition sites produced on the polymer surface were expected to be better defined and of better quality, which would be reflected in the higher selectivity. The first aim of the study was to create a metal-imprinted polymer that showed a high selectivity to a target metal ion. The recognition capabilities of the metal-imprinted polymers were evaluated through the selective adsorption test of zinc over copper ions. The corresponding template effect was characterized by carrying out the Langmuir analysis.

The second objective was to prepare the DDDPA-immobilized Zn(II)-imprinted macroporous sphere, spherically well defined and uniform, by using the surface template polymerization technique with the water-in-oil-in-water (W/O/W) emulsions. The obtained polymer beads were then applied as metal adsorbents without either grinding or sieving. In the basic fundamental research, we succeeded in forming a stable microspheric polymer using divinylbenzene (DVB).[24] Therefore, our next objective in this project was to add highly selective recognition sites to the surfaces of the microspheric polymers by utilizing the surface template polymerization

technique. Therefore, we focused on the TRIM, which has three polymerizable groups to make the polymer matrix more rigid. The TRIM offers better prospects of preparing macroporous spheres in a single step and to form superior metal-recognition sites. The recognition capability of the Zn(II)-imprinted spherical polymer was systematically investigated along with those of the polymers prepared by W/O emulsions.

EXPERIMENTAL

Reagents and Apparatus

DDDPA and L-gultamic acid dioleylester ribitol ($2C_{18}\Delta^9GE$) were synthesized according to the procedures reported in previous works.[22,28] Dodecylsulfate (SDS) purchased from Wako Pure Chemical Industries Co., Ltd., was used without further purification. TRIM (Kishida Chemical Co., Ltd.) was employed after treatment with silica gel to remove an inhibitor. Figure 2(a–d) show the structures of (a) DDDPA, (b) TRIM, (c) $2C_{18}\Delta^9GE$, and (d) SDS, respectively. The other reagents were of commercially available special grades. The particle size analysis and electron scanning 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. The metal concentration was measured by means of atomic absorption spectrophotometer (SAS–760, Seiko Instrument Inc.).

Preparation of Zn(II)-Imprinted Polymer with W/O Emulsions

A metal-imprinted polymer was prepared by surface template polymerization technique utilizing W/O emulsions. The amount of 40 cm^3 of TRIM, in which 60 mol/m^3 DDDPA and 20 mol/m^3 $2C_{18}\Delta^9GE$ were dissolved, was mixed with 20 cm^3 toluene containing 5 vol % 2-ethylhexyl alcohol as a solubility modifier. An aqueous solution (30 cm^3) of 10 mol/m^3 Zn(NO$_3$)$_2$, which was buffered with 100 mol/m^3 acetic acid–sodium acetate and maintained at pH 3.5, was added. The mixture was sonicated for 4 min to give W/O emulsions. After the addition of 0.42 g (1.4×10^{-3} mol) of the powder initiator [2,2′-azobis(2,4′-dimethylvaleronitrile), 0.01 wt % for TRIM], the mixture was polymerized at 55°C for 2 h under a flow of nitrogen. The resultant bulk polymer was dried under

Figure 2 Structures of (a) functional monomer, (b) matrix-forming monomer, (c) emulsion stabilizer, and (d) scattering stabilizer.

vacuum and ground into an appropriate size. The particles were washed with 1000 mol/m^3 hydrochloric acid to remove the target metal ions (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. An unimprinted polymer was similarly prepared as a reference polymer without zinc ions.

Preparation of Zn(II)-Imprinted Polymer with W/O/W Emulsions

A metal ion imprinted polymer was prepared by surface template polymerization technique utilizing W/O/W emulsions. The amount of 40 cm^3 of

TRIM, in which 60 mol/m^3 DDDPA and 20 mol/m^3 2C$_{18}$Δ^{9}GE were dissolved, was mixed with 20 cm^3 toluene containing 5 vol % 2-ethylhexyl alcohol. An aqueous solution (30 cm^3) of 10 mol/m^3 Zn(NO$_3$)$_2$, which was buffered with 100 mol/m^3 acetic acid–sodium acetate and maintained at pH 3.5, was added. The mixture was sonicated for 4 min to give W/O emulsions. The emulsions were put into a 500 cm^3 aqueous phase containing 15 mol/m^3 SDS and 10 mol/m^3 Mg(NO$_3$)$_2$ as an ionic strength controller (pH 3.5, buffered with 100 mol/m^3 acetic acid–sodium acetate) stirring at the rate of 500 rpm, and W/O/W emulsions were formed. The next polymerization step was similar to the procedure described above. The unimprinted polymer used was prepared in a similar way to act as a standard polymer without zinc ions.

Competitive Adsorption Experiment of Zn(II) and Cu(II) on the Zn(II)-Imprinted or Unimprinted Polymers

The batchwise selective adsorption experiments of zinc and copper ions were conducted using imprinted and unimprinted polymers. The polymers (0.1 g) were added to a 5 cm^3 of aqueous solution containing 0.1 mol/m^3 Zn(NO$_3$)$_2$ and 0.1 mol/m^3 Cu(NO$_3$)$_2$ and placed in a sealed test tube (10 cm^3 volume). The pH was adjusted to the desired value between 1.0 and 4.0 with 100 mol/m^3 acetic acid–sodium acetate and 100 mol/m^3 nitric acid. The mixture was shaken in a thermostated water bath at 30°C for 24 h. The polymers were then filtered off through a polyethylene membrane (Sumplep LCR25-LG, Nippon Millipore, Ltd.). The amounts of zinc and copper ions adsorbed to the polymers were calculated from the residual concentrations of zinc and copper ions in the filtrate solution. The metal concentration was measured by atomic absorption spectrophotometer. The percent adsorption defined as the amount of adsorbed metal ions relative to that initially added in the material phase was calculated from the data.

Adsorption Constants for the Zn(II)-Imprinted Polymers

Adsorption constants (effective ion-exchange capacity and adsorption equilibrium constants) of zinc ions on the Zn(II)-imprinted polymers were measured in a batchwise method. One gram of the polymers was immersed in a sealed test tube (10

cm^3 volume). Then, a 5 cm^3 aqueous solution (pH 4.5, buffered with 100 mol/m^3 acetic acid–sodium acetate) containing zinc ions adjusted to the desired concentration between 0.1 and 50 mol/m^3 was added. The mixture was shaken in a thermostated water bath at 30°C for 24 h. The polymers were then filtered off through the polyethylene membrane. The concentration of zinc ions in the filtrate was analyzed by means of atomic absorption spectrophotometer. It was assumed that the adsorption behavior of zinc ions on the Zn(II)-imprinted polymers followed Langmuir's isotherms on the liquid-solid phase. The Langmuir's equation is expressed as follows:

$$q = aq_sC/(1 + aC)$$

where q_s is the effective ion-exchange capacity and a is the adsorption equilibrium constant. These two constants (q_s, a) can be evaluated from the relationship between the slope and the intercept of the Langmuir straight plots.

Swelling Ratio of the Zn(II)-Imprinted Polymers

A swelling ratio of the Zn(II)-imprinted polymers was determined by volumetric measurement.[29] One gram 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 the mixture was vigorously shaken to ensure complete mixing. After the mixture was centrifuged for 30 min at 5000 rpm again, it was left to stand intact for several hours. The volume of the swollen 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:

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

RESULT AND DISCUSSION

Physicochemical Characterization of Zn(II)-Imprinted Polymers

Highly crosslinked Zn(II)-imprinted polymers were prepared by surface template polymerization with W/O or W/O/W emulsions. When the

W/O emulsion was used, the recognition sites were formed on the inner surfaces of water droplets. Therefore, grinding operation of bulk polymer was required to obtain a particle adsorbent. On the other hand, polymer beads are directly produced by introducing the W/O/W emulsion.

In the present study, zinc ions, DDDPA, TRIM, $2C_{18}\Delta^9GE$, SDS, and toluene were employed as the imprint molecule, functional monomer, matrix-forming monomer, emulsion stabilizer, dispersion stabilizer, and diluent, respectively. After polymerization, the bulk Zn(II)-imprinted and unimprinted polymers utilizing W/O emulsions were ground into particles, whose volume-averaged diameter was ca. 40 μm. While the Zn(II)-imprinted and unimprinted polymers utilizing W/O/W emulsions are obtained as uniform-size spheres whose volume-averaged diameters was ca. 25 μm. About 95% yield of all the Zn(II)-imprinted and unimprinted polymers was obtained. Figure 3 shows a typical view of (I) Zn(II)-imprinted polymers prepared from W/O emulsions and (II) Zn(II)-imprinted polymers utilizing W/O/W emulsions by scanning electron microscopy. For polymers (I) utilizing W/O emulsions, substantial traces of aqueous phases in the emulsions are observed in the polymer. The recognition sites for zinc ions are constructed on the surfaces of inner cores of the polymer. The polymers (IIa, addition of SDS) utilizing W/O/W emulsions are spheres such as commercially available ion-exchange beads. However, the polymers (IIb) which are SDS free could not yield uniform-size spheres. Hence, we found that a dispersion stabilizer (SDS) which is added to the outer aqueous phase plays a prominent role in maintaining uniform-size spheres.[24] The recognition sites are formed on the surface of the particles and the surface of micropores into the particles. A number of micropores in the polymers facilitate diffusion of the target metal ions into the polymer.

In the surface template polymerization technique, it is important to make the polymer matrix rigid to allow a solid attachment of the functional monomer (recognition sites), and this results in creating a high selectivity potential for the target metal ions (zinc ions).[20–23] We measured the swelling ratio of the polymers, which is an indicator of the rigidity of the polymer matrix. Table I summarizes the swelling ratio of the prepared polymers; (a) Zn(II)-imprinted polymers utilizing W/O emulsions (the polymer matrix is TRIM or DVB) and (b) Zn(II)-imprinted polymers utilizing W/O/W emulsion (the polymer matrix is TRIM).

Figure 3   A typical SEM photograph; (I) Imprinted polymer utilizing W/O emulsions, (II) Imprinted polymer utilizing W/O/W emulsions; (a) Addition of SDS, (b) SDS free.

The lower swelling ratios means that the recognition sites are fixed more rigid on the polymer surface. In the previous study, we clarified that the polymer possessing less than 30% swelling ratio was able to produce a high template effect toward a target metal.[23] The polymers utilizing W/O emulsions did not swell compared to those utilizing W/O/W emulsions. Further, the polymers utilizing W/O emulsions, whose matrices comprised of TRIM possessing three polymerizable groups, scarcely swelled compared to those whose matrix was DVB. This result indicates that the matrix-forming monomer possessing many

Table I   Swelling Ratio; (a) Zn(II)-Imprinted Polymers Utilizing W/O Emulsions (The polymer matrix is TRIM or DVB) and (b) Zn(II)-Imprinted Polymer Utilizing W/O/W Emulsions (The polymer matrix is TRIM)

Polymers	Swelling Ratio S (%)
(a) Zn(II)-imprinted polymer (TRIM, W/O)	≤ 0
Zn(II)-imprinted polymer (DVB, W/O)[23]	9
(b) Zn(II)-imprinted polymer (TRIM, W/O/W)	22

Figure 5   The pH dependence of the adsorption of zinc (closed square) and copper (closed circle) ions on the unimprinted polymer (W/O).

crosslinking points facilitates the creation of polymer-matrix rigidity. In spite of employing TRIM, the polymer utilizing W/O/W emulsions swelled compared to those of W/O emulsions. However, as the Zn(II)-imprinted TRIM-based polymers were of less than 30% swelling ratio, an efficient template effect was expected for the target zinc ions.

Competitive Adsorption Behavior of Zn(II) and Cu(II) on the Zn(II)-Imprinted and Unimprinted Polymers Utilizing W/O or W/O/W Emulsions

Figures 4, 5, 6, and 7 show the pH dependence of the competitive adsorption of zinc and copper ions on the Zn(II)-imprinted and unimprinted TRIM-

based polymers with DDDPA utilizing W/O or W/O/W emulsions, respectively. The percent adsorption increased with increasing pH on all polymers. This result means that the phosphonic acid groups of the functional monomer play an important role in metal binding. The Zn(II)-imprinted polymer prepared in the presence of zinc ions exhibited better selective adsorption of zinc ions over copper ions in the whole pH range (1–4). On the other hand, unimprinted polymers prepared in the absence of zinc ions did not show selectivity

Figure 4   The pH dependence of the adsorption of zinc (open square) and copper (open circle) ions on the Zn(II)-imprinted polymer (W/O).

Figure 6   The pH dependence of the adsorption of zinc (open square) and copper (open circle) ions on the Zn(II)-imprinted polymer (W/O/W).

Figure 7   The pH dependence of the adsorption of zinc (closed square) and copper (closed circle) ions on the unimprinted polymer (W/O/W).

to zinc ions, and showed different adsorption profiles for both metal ions. The results clearly verify that the zinc ions-template effect was due to the phosphonic groups of DDDPA implanted on the surface of the Zn(II)-imprinted polymers. A desirable coordination (tetrahedral coordination) was considered to be formed on the surface to facilitate their interaction with the templated zinc ions. The memorized recognition sites should have a high affinity to zinc ions and must not favor the accommodation of copper ions. Furthermore, in the unimprinted polymers, the phosphonic groups could be randomly distributed on the polymer surface where metal ions show similar tendencies of adsorption behavior. Although the imprinted polymer using W/O emulsions exhibited a higher template effect than that prepared by W/O/W emulsions, the W/O/W emulsions are advantaged by the formation of spherical particles not obtainable in W/O emulsions.

Adsorption Constants on the Zn(II)-Imprinted Polymers

We characterized the template effect quantitatively in the Zn(II)-imprinted polymers by measuring the adsorption constants (the effective ion-exchange capacity and the adsorption equilibrium constant). Table II lists the results of the adsorption constants for the Zn(II)-imprinted polymers; (a) TRIM or DVB-based polymers utilizing the W/O emulsions and (b) TRIM-based polymer utilizing the W/O/W emulsions. The effective ion-exchange capacity (q_s) corresponds to the adsorption ability on the polymer involving the nonimprinting sites, while the adsorption equilibrium constant (a) is an indicator to express an adsorption affinity of recognition sites for the target metal ions. Both the Zn(II)-imprinted TRIM- and DVB-based polymers exhibit a similar ability of effective ion-exchange capacity [Table II(a)]. However, the TRIM-based polymer has much higher adsorption equilibrium constant than that of the DVB-based polymer. This results suggest that the rigidity of the polymer matrix formed by TRIM leads to the formation of favorable recognition sites with respect to the shape and position of the functional groups on the polymer surface. Hence, TRIM was found to be one of the best matrix-forming monomers for maintaining the recognition sites for the target metals. Although the adsorption behavior of the TRIM-based Zn(II)-imprinted polymer utilizing W/O/W emulsions showed a template effect toward zinc ions, the adsorption constants fell short of the values of

Table II   Effective Ion-Exchange Capacity and Adsorption Equilibrium Constants; (a) Zn(II)-Imprinted Polymer Utilizing W/O Emulsions (The polymer matrix is TRIM or DVB) and (b) Zn(II)-Imprinted Polymer Utilizing W/O/W Emulsions (The polymer matrix TRIM)

Imprinted Polymers	Effective Ion-Exchange Capacity q_s (mmol/g)	Adsorption Equilibrium Constants a (m^3/mol)
(a) Zn(II)-imprinted polymer (TRIM, W/O)	4.7×10^{-2}	150
Zn(II)-imprinted polymer (DVB, W/O)[22]	4.8×10^{-2}	60
(b) Zn(II)-imprinted polymer (TRIM, W/O/W)	3.1×10^{-2}	30

polymers prepared by W/O emulsions [Table II(b)]. The low ion-exchange capacity is considered to be caused by the loose polymer-matrix at the preparation step. However, the polymer beads prepared by the W/O/W emulsions will be more useful in industrial applications because they can be directly used without grinding into finer particles.

CONCLUSIONS

The Zn(II)-imprinted polymers were prepared using TRIM as the matrix-forming monomer by applying the surface template polymerization technique with W/O or W/O/W emulsions. The Zn(II)-imprinted polymers exhibited a high selectivity toward the imprinted zinc ions over copper ions. The rigidity of the matrix polymer was found to be a crucial factor to produce the high molecular imprinting effect. Unlike DVB, the high rigidity of TRIM resulted in the superior adsorption performance of imprinted polymers. compared to the DVB-based polymer. In addition, we succeeded in preparing the metal-imprinted microspherical particles, by utilizing W/O/W emulsions, which can be readily applied as metal recognition adsorbents without either grinding or sieving.

REFERENCES

1. Wullf, G. In Polymeric Reagents and Catalysts; Ford, W. T., Ed.; ACS Symposium Series 308; American Chemical Society: Washington, DC, 1986; p186.
2. Wullf, G. Angew Chem Int Ed Engl. 1995, 34, 1812.
3. Mosbach, K.; Ramstöm, O. Bio/Technology 1996, 163, 14.
4. Sellergren, B.; Lepistö, M.; Mosbach, K. J Am Chem Soc 1988, 110, 5853.
5. Sellergren, B. Macromol Chem 1989, 190, 2703.
6. Andersson, L. I.; O' Shannessy, D. J.; Mosbach, K. J Chromatogr 1990, 513, 167.
7. Shea, K. J.; Spivak, D. A.; Sellergren, B. J Am Chem Soc 1993, 115, 3368.
8. Ramstöm, O.; Nicholls, I. A.; Mosbach, K. Tetrahedron Asymmetry 1994, 5, 649.
9. Sellergren, B.; Shea, K. J. J Chromatogr A 1995, 690, 29.
10. Matsui, J.; Miyoshi, Y.; Doblhoff-Dier, O.; Takeuchi, T. Anal Chem 1995, 67, 4404.
11. C.; Yu, K.; Mosbach, J Org Chem 1996, 62, 4057.
12. Cheong, S. H.; McNiven, S.; Rachkov, A.; Levi, R.; Yano, K.; Karube, I. Macromolecules 1997, 30, 1317.
13. Valtakis, G.; Andersson, L. I.; Müller, R.; Mosbach, K. Nature 1993, 361, 645.
14. Andersson, L. I.; Müller, R.; Valtakis, G.; Mosbach, K. Proc Natl Acad Sci USA 1993, 14, 637.
15. Müller, R.; Andersson, L. I.; Mosbach, K. Macromol Chem Rapid Commun 1993, 14, 637.
16. Beach, J. V.; Shea, K. J.; Mosbach, K. J Am Chem Soc 1994, 116, 379.
17. Leonhardt, A.; Mosbach, K. React Polym1987, 6, 285.
18. Tsukagoshi, K.; Yu, K. Y.; Maeda, M.; Takagi, M. Bull Chem Soc Jpn 1993, 66, 114.
19. Uezu, K.; Nakamura, H.; Goto, M.; Murata, M.; Maeda, M.; Takagi, M.; Nakashio, F. J Chem Eng Jpn 1994, 27, 436.
20. Yoshida, M.; Uezu, K.; Goto, M.; Nakashio, F. J Chem Eng Jpn 1996, 29, 436.
21. Uezu, K.; Nakamura, H.; Kanno, J.; Sugo, T.; Goto, M.; Nakashio, F. Macromolecules 1997, 30, 3888.
22. Yoshida, M.; Uezu, K.; Goto, M.; Nakashio, F. J Polym Sci Part A 1998, 36, 2727.
23. Yoshida, M.; Uezu, K.; Goto, M.; Furusaki, S. Macromolecules 1999, 32, 1237.
24. Uezu, K.; Nakamura, H.; Goto, M.; Nakashio, F.; Furusaki, S. J Chem Eng Jpn 1999, in press.
25. Kempe, M.; Mosbach, K. Tetrahedron Lett 1995, 36, 3563.
26. Kempe, M. Anal Chem 1995, 68, 1948.
27. Dahl, P. K.; Vidyasankar, S.; Arnold, F. H. Chem Mater 1995, 7, 154.
28. Goto, M.; Matsumoto, M.; Kondo, K.; Nakashio, F. J Chem Eng Jpn 1987, 20, 157.
29. Green, T. K.; Kovac, J.; Larsen, J. W. Fuel 1984, 63, 935.