Preparation and Selective Binding Characterization of Bisphenol A Imprinted Polyethersulfone Particles

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ABSTRACT: Bisphenol A (BPA) imprinted polyethersulfone (PES) particles were prepared for the recognition of BPA by means of phase inversion method. During the preparation of the BPA-imprinted particles, acetone, ethanol and acetone/ethanol solutions were used to extract the template BPA molecules. The SEM morphology and the recognition experiments suggested that the acetone/ethanol provided an efficient way to extract the BPA from the imprinted PES particles. The binding and recognition ability for the imprinted particles disappeared under alkali condition, and they recovered as soon as possible when the solution changed from alkali condition to neutral or acid condition. With the addition of Na^+, Mg^{2+}, and Cl^-, the binding amounts for the imprinted particles and non-imprinted particles were not changed heavily, which suggested the potential application of the particles in seawater. In the BPA/BPA analogue mixed solution, the imprinted particles showed selectivity for the template molecules BPA. The FTIR results suggested that the PES and BPA interacted through hydrogen bonds. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2791–2799, 2007

Key words: molecular imprinting; Bisphenol A; poly(ether sulfones); particles; separation techniques

INTRODUCTION

The technique of molecular imprinting imparts molecular recognition ability to polymer materials because it memorizes template molecules with respect to its shape and functionality.[1–3] It has been shown that molecularly imprinted polymers (MIPs) possess high selectivity and sensitivity for template molecules including drugs,[4] environmental contaminants,[5] nucleotide bases,[6] protein,[7] even chemical warfare agents.[8] These MIPs demonstrate very good thermal and mechanical stability and can be used in aggressive media.[9] MIPs possess several advantages over their biological counterparts including low cost and easy preparation, besides the good physical and chemical stability.

Since people have faced severe endocrine disruptor problems, some methods to treat endocrine disruptor polluted river and wastewater are essential.[10] Bisphenol A (BPA), which is known as one of the endocrine disruptors, affects the reproduction and development of animal organism even at a extra-diluted concentration.[11] Therefore, the materials having high recognition and selective capture to BPA are surely required in the viewpoint of environmental conservation in near future. For development of BPA adsorbents, molecular imprinting has been very useful as alternative methods,[12] though porous carbon, polymer-activated carbon hybrid particles, DNA-films, and DNA hybrid microspheres could also be used in the removal of the endocrine disruptors.[13–16]

To develop a novel type of highly selective adsorbing materials with artificial host sites of both specificity and high capacity, BPA-imprinted polyethersulfone (PES) microspheres were first prepared by liquid–liquid phase separation method in our previous studies.[17] However, it took more than 20 days for the template molecules in the microspheres to be extracted in ethanol during the preparation, which limited the commercial application of the BPA-imprinted PES microspheres effectively. Furthermore, in the previous studies, the recognition and selectivity ability were only studied in the BPA aqueous and water/ethanol solutions. The mechanism of the binding and recognition were not studied clearly.

To extend the research and application of BPA-imprinted PES particles, in the present work, we aimed at the preparation of BPA-imprinted PES particles with novel extraction technique to improve the extraction efficiency. Furthermore, the BPA-imprinted PES particles were further studied under more practical conditions. The selectivity of the BPA-imprinted PES particles was tested in BPA and its analogue mixed solutions in detail. Also the mechanism of the BPA binding and recognition were studied by Fourier transform infrared (FTIR).

EXPERIMENT

Materials

Polyethersulfone (PES, Ultrason E 6020P, CAS Number: 25608-63-3) was purchased from BASF chemical company (Germany), and was used to prepare the porous particles. Bisphenol A (BPA) was purchased from Shanghai Chemical Reagent (China) and was used as the template. Dimethyl acetamide (DMAc), acetone, ethanol, phenol, and biphenyl were obtained from Chengdu Kelong Chemical Reagent (China). All the chemicals were reagent grade and used without further purification unless otherwise described. Distilled water passed through ion-exchange columns was used throughout the studies.

Preparation of the imprinted microspheres

PES and BPA were dissolved in DMAc with a concentration of 24 and 5 wt %, respectively. The resultant polymer solution was dropped into distilled water by using a 0.6-mm-diameter syringe needle at room temperature to prepare particles. These particles were incubated in water for over 24 h to elute the DMAc from the particles. Then, extraction of the template molecules from the solidified polymer particles was carried out in ethanol, acetone, acetone/ethanol solutions for several days. Using an UV–VIS spectrophotometer (SP-752, Shanghai Spectrum Instruments, Shanghai, China), the extraction was confirmed with the disappearance of the BPA absorption peak at the wave length of 276 nm in the extracted solutions. Simultaneously, PES solution with a concentration of 24 wt % was used to prepare nonimprinted PES particles, then the particles were extracted respectively in ethanol, acetone, acetone/ethanol solutions in the same manner.

Scanning electron micrograph and Fourier transform infrared

For scanning electron micrograph (SEM) observation, the particle samples were dried at room temperature. Then the particles were quenched by liquid nitrogen, cut with a single-edged razor blade, attached to the sample supports, and coated with a gold layer. A scanning electron microscope (JSM-5900LV, JEOL) was used for the morphology observation of the particle cross-sections.

FTIR spectroscopy was also used for the characterization of the imprinted and nonimprinted particles by using a FTIR spectrophotometer (Nicolet FTIR170).

Effect of extraction on the BPA recognition

For the preparation of BPA solution, the BPA was dissolved in ethanol with a concentration of 5 wt % first. Then, the BPA ethanol solution was dissolved in water to prepare the BPA aqueous solution (the concentrations were 50, 100, and 200 μM, respectively).

To study the effect of extraction technique on the recognition, the imprinted particles were extracted in ethanol, acetone, and acetone/ethanol, respectively. Then, 30 mg of the imprinted porous particles which were extracted in ethanol, acetone, acetone/ethanol (V : V = 25 : 75), respectively, were placed in 6 mL of the solutions containing various concentrations of BPA. The concentration of the BPA at different time intervals was monitored by an UV–VIS spectrophotometer at the wavelength of 276 nm. Binding amounts of the template to the particles, $[S]_b$ (μmol g^{-1}), were calculated by the following equation[18]

$$[S]_b = (C_0 - C_t)V/W \qquad (1)$$

where C_0 and C_t were the template concentrations (μM) in the solutions, which were measured initially and after interval time, t, respectively. V (L) was the volume of the bulk solution and W (g) was the weight of the particles.

Recognition coefficient (α) was used to evaluate the recognition ability, and can be defined as following :

$$\alpha = [S]_{(imprinted)}/[S]_{(nonimprinted)} \qquad (2)$$

where $[S]_{(imprinted)}$ was the BPA binding amount to the imprinted particles (μmol g^{-1}), and $[S]_{(nonimprinted)}$ was the binding amount to the nonimprinted particles (μmol g^{-1}).

Binding of BPA to imprinted particles under acid, neutral, and alkali conditions

To study the effect of pH value on the recognition, 24 mg of the particles were applied in 4.8 mL, 150 μM BPA aqueous solution, 0.1M HCl solution, and 0.1M NaOH solution, respectively. Then, the concentrations of BPA at different time intervals were

monitored by an UV–VIS spectrophotometer at 276 nm. Binding amounts and recognition coefficient were calculated from eqs. (1) and (2).

Binding of BPA to imprinted particles in solutions with different metal ions

To study the effect of ions on the recognition, 30 mg of the particles were applied in 6.0 mL, 200 μM BPA aqueous solution, $0.1M$ NaCl solution, $0.01M$ NaCl solution, 1.0 mM NaCl solution, $0.05M$ MgCl$_2$ solution, 5.0 mM MgCl$_2$ solution, and 0.5 mM MgCl$_2$ solution respectively. Then, the concentrations of BPA at different time intervals were monitored by an UV–VIS spectrophotometer at 276 nm. Binding amounts and recognition coefficient were calculated from eqs. (1) and (2). The particles applied in this experiments were extracted in acetone/ethanol (V : V = 25 : 75).

Selectivity of the imprinted particles

Selectivity of the imprinted particles was studied by immersing the particles in the BPA/phenol (100 μM/100 μM) mixed aqueous solution and BPA/biphenyl (50 μM/50 μM) mixed water/ethanol (V : V = 90 : 10) solution at 20°C, respectively. Then, the concentrations of these compounds at different time intervals were monitored by an UV–VIS spectrophotometer for BP at 246 nm, phenol at 270 nm, and BPA at 276 nm. Binding amounts and recognition coefficient (α) can be calculated by the eqs. (1) and (2), and were used to evaluate the selectivity.

Furthermore, the binding amounts by the recognition sites ($[S]_{(sites)}$) to the imprinted particles can be calculated from the following equation:

$$[S]_{(sites)} = [S]_{(imprinted)} - [S]_{(nonimprinted)} \quad (3)$$

RESULT AND DISCUSSION

Characterization of the imprinted particles

A phase inversion technique was used to fabricate the BPA imprinted PES particles from the PES-DMAc-BPA solution. In the preparation process, nonsolvent water was selected as the coagulation medium, which was commonly used in preparing polymeric membranes.[19–21] Here, water showed high miscibility for DMAc but was not soluble for PES and BPA. Therefore, when the PES-BPA-DMAc solution was dropped into water, phase inversion that was caused by the rapid exchange of the solvent DMAc and water occurred. Simultaneously, due to the poor solubility of BPA in water, the template BPA was retained in the solidified particles. With the completion of the exchange between the solvent

and the nonsolvent, the particles were prepared. After the extraction of the template molecules, the imprinted particles were prepared. The diameter and the specific surface areas of the particles depended on the diameter of the syringe needle and the polymer solution.[17] In this study, the particles were 2.3 ± 0.1 mm in diameter for both the imprinted and nonimprinted particles. The specific surface areas, which were determined using the mercury porosimetry, were 119.5 and 122.3 m^2 g^{-1}, respectively, for the nonimprinted and imprinted particles. Clearly, the specific surface area, which was a significant factor related to the binding, was similar for the imprinted and the nonimprinted particles.[17]

Extraction of BPA from the particles was carried out by immersing the imprinted particles into ethanol, acetone, and acetone/ethanol (V : V = 25 : 75), respectively. As shown in Figure 1(a,b), SEM was used to characterize the cross sections of the imprinted particles extracted in ethanol. A finger-like structure was found under a skin layer as shown in Figure 1(a). Between the finger-like macrovoids, lots of small pores were distributed inside the PES porous particles as shown in Figure 1(b). This structure was very useful when the particles were used to bind and recognize the BPA.[22–24] Figure 1(c,d) show the cross sections of the imprinted particles extracted in acetone. Clearly, the finger-like structures are different from what is described earlier. The surface of the porous structures became smooth as shown in Figure 1(c). Meanwhile, in Figure 1(d), which was magnified 2000×, the small pores in the finger-like macrovoids disappeared. This was caused by the PES swelling in the acetone.[22]

The result of the SEM indicates that PES was swelled in the acetone while not swelled in the ethanol. Thus a series of ratios of ethanol/acetone were applied in the experiments to find out the optimum condition (details not shown). When the ratio of acetone/ethanol (V/V) is less than 30/70, no obvious change in the porous structure was observed.

In the ethanol/acetone (V : V = 25 : 75), the finger-like structure and the pores as shown in Figure 1(e,f) are similar to that in the Figure 1(a,b), respectively. Obviously, the ethanol/acetone mixed solution did not destroy the inside structure of the imprinted particles. The SEM morphology suggested that the acetone destroyed the inside structure while the ethanol and acetone/ethanol solution (V : V = 25 : 75) can extract the template molecule without changing the porous structure in the imprinted particles. This may be due to the interaction between the BPA and PES decreased due to the slight swollen interaction, which facilitated the
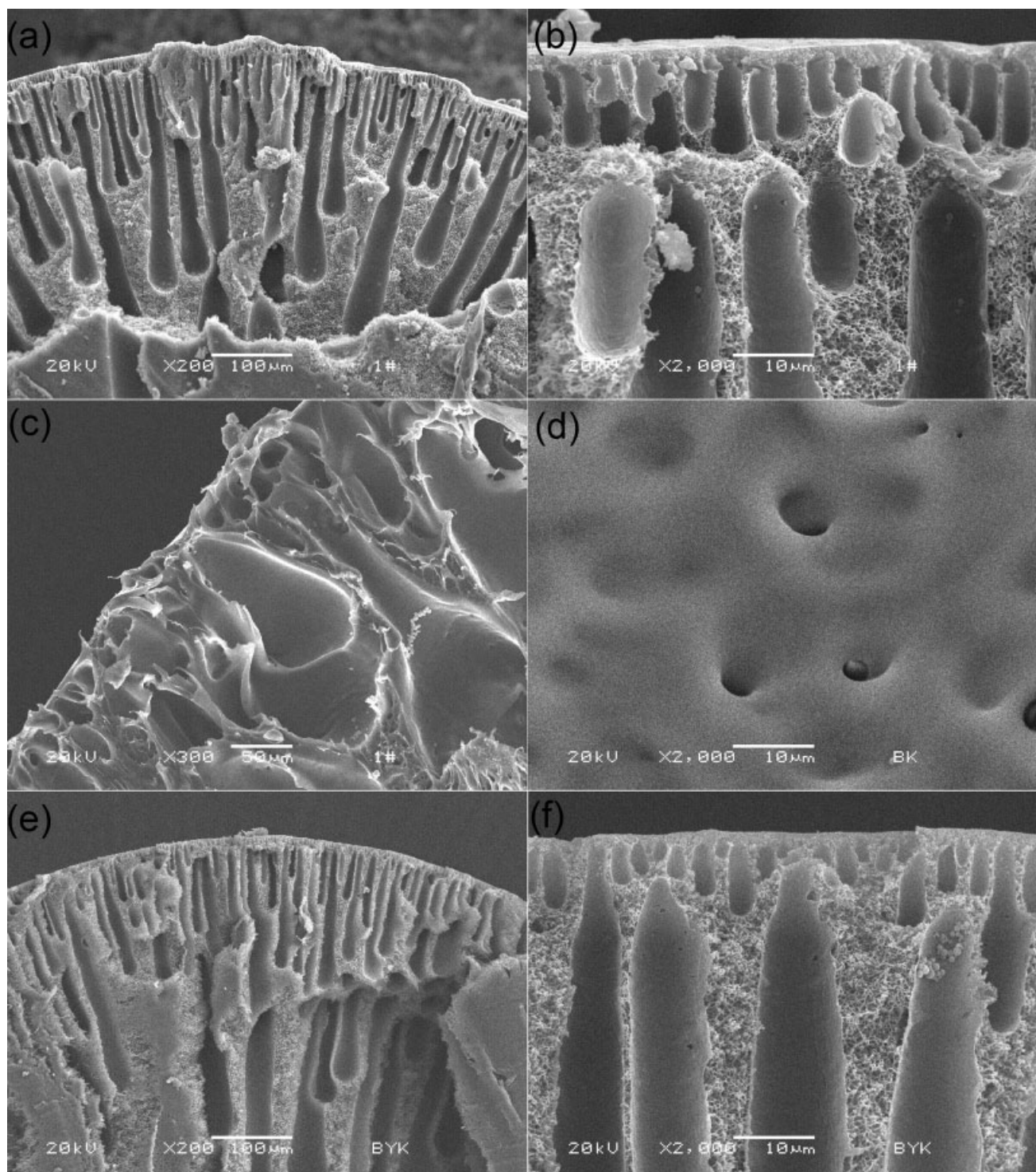
Figure 1 SEM photographs of the cross-sections of the particles. (a) and (b) were extracted in ethanol; (c) and (d) were extracted in acetone; (e) and (f) were extracted in acetone/ethanol (V : V = 25 : 75).

extraction of the template and protected the recognition sites.

Effect of extraction on the BPA recognition

To further study the effect of the extraction method on the recognition, the imprinted particles and the nonimprinted particles were applied in binding and recognition experiments. As shown in Figure 2(a), for the particles extracted in acetone, the binding amounts for the imprinted and nonimprinted particles are both very low. In 300 hours, nearly no binding and recognition was found in 100 µM BPA aqueous solution for the imprinted particles with the
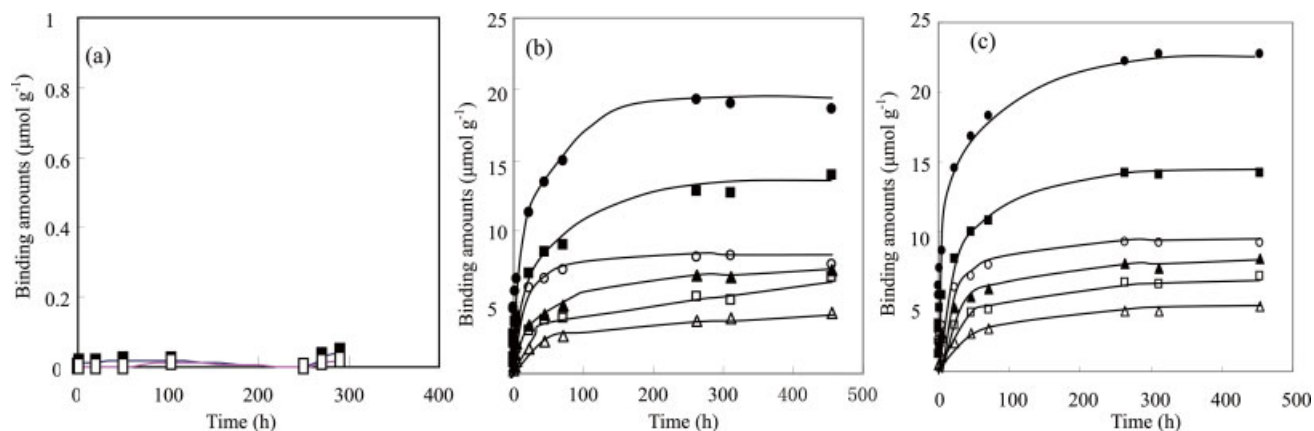
Figure 2 Time course of binding to the imprinted and the nonimprinted particles with different extraction methods. (a) was extracted in acetone, (b) was extracted in ethanol, (c) was extracted in acetone/ethanol (V : V = 25 : 75). In 50 μM, for the imprinted (▲) and the nonimprinted (△); in 100 μM, for the imprinted (■) and the nonimprinted (□); in 200 μM, for the imprinted (●) and the nonimprinted (○).

extraction of acetone. It is well-known that both the imprinted PES particles and the nonimprinted particles can bind BPA due to the hydrophobic interaction between the BPA and the PES, and the large porosity.[25] Here, for the particles with the extraction of acetone, since the matrix polymer, PES, could swell in the acetone, the inside structures became smooth as shown in Figure 1(c,d); and the specific surface area became smaller (12.1 m^2 g^{-1}, determined by the mercury porosimetry). Therefore, no binding was observed for the nonimprinted and imprinted particles. Thus, it can be concluded that acetone should not be used as an extractor for the preparation of the BPA-imprinted particles.

Figure 2(b) shows the binding amounts of BPA to the imprinted and nonimprinted PES particles with the extraction of ethanol in 50, 100, 200 μM BPA aqueous solutions. The binding amounts (μmol g^{-1}) increased with time and reached an equilibrium value at about 70 h. It was noted that the amounts of the BPA binding to the imprinted PES particles was higher than that to the nonimprinted ones in all the three concentrations. The saturated binding amounts of BPA were 7.29, 13.94, and 18.59 μmol g^{-1} for the imprinted PES particles in 50, 100, 200 μM BPA aqueous solutions, respectively, while the values were 4.26, 6.80, and 7.71 μmol g^{-1} for the nonimprinted PES particles, respectively. The recognition coefficients were 1.71, 2.05, and 2.41, respectively, which were calculated from eq. (2).

Figure 2(c) shows the binding amounts of BPA to the imprinted and nonimprinted PES particles with the extraction of acetone/ethanol (V : V = 25 : 75) in 50, 100, 200 μM BPA aqueous solutions, respectively. The trends of the binding amounts in Figure 2(c) are similar to Figure 2(b). The saturated binding amounts of BPA were 8.05, 14.21, and 22.76 μmol g^{-1} for the

imprinted PES particles in 50, 100, 200 μM BPA aqueous solutions, respectively, while the recognition coefficients were 1.72, 2.07, and 2.47. Clearly, the binding amounts of the particles with the extraction of ethanol/acetone were slightly higher than that with the extraction of ethanol. However, there was no significant difference among the recognition coefficients.

Furthermore, it took more than 20 days for the ethanol to complete the extraction, but it took only 4 days for the acetone/ethanol. Comparing the two extraction methods, no significant differences were found on the binding amounts and the recognition coefficients. Clearly, using the acetone/ethanol to extract the template molecules was far more effective than the use of ethanol. The swelling of PES decreased the interaction between the BPA and PES in the initial imprinted particles, but the inside structure was not destroyed because of the existence of ethanol. Therefore, it is easier for the acetone/ethanol to extract the BPA. It is well-known that the extraction of template molecules is a time-consuming and difficult process during the preparation of molecularly imprinted polymer.[17] These results indicated that acetone/ethanol mixture may be a good method to extract BPA from the PES particles.

Binding of BPA to imprinted particles under acid, neutral, and alkali condition

To study the effect of pH value on the recognition, the imprinted and nonimprinted particles were applied in 150 μM BPA acid, neutral, and alkali solutions, respectively. Figure 3(a) shows the binding amounts of BPA to the imprinted and nonimprinted PES particles in various BPA aqueous solutions with different pH. The values of the binding amounts
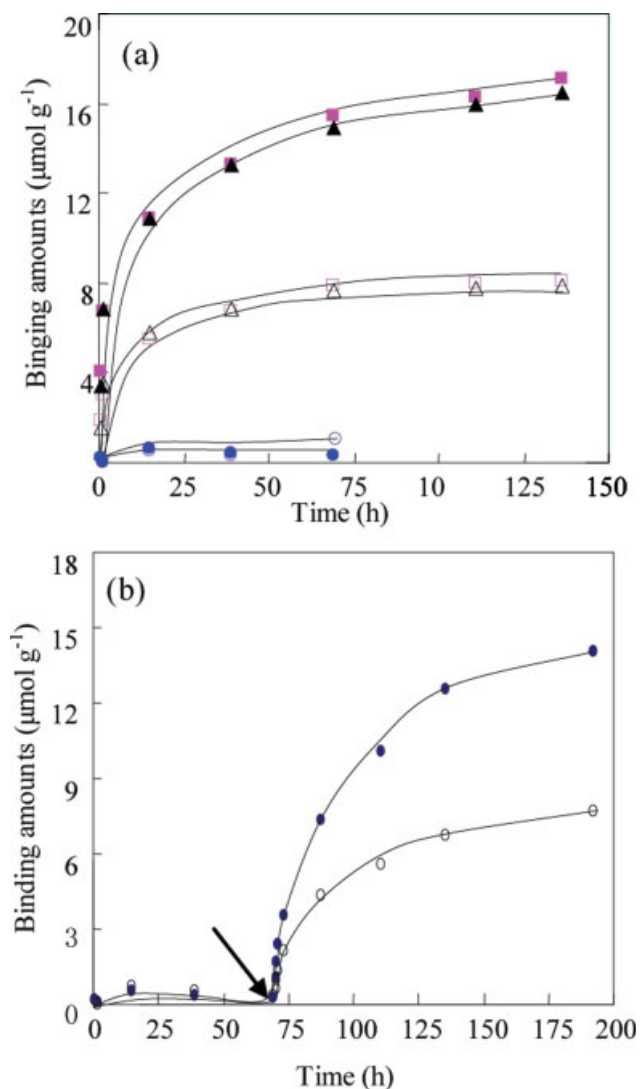
Figure 3 Time course of BPA binding to the imprinted particles and the nonimprinted particles in 150 μM BPA acid, neutral, and alkali solution. In 0.1M HCl solution for the imprinted (▲) and the nonimprinted (△); in neutral solution for the imprinted (■) and the nonimprinted (□); in 0.10M NaOH solution for the imprinted (●) and the nonimprinted (○). In the (b), the point of arrowhead (→) mean the time of addition of 0.50M HCl solution into 150 μM BPA alkali solution, then the pH of the solution is 1.1. Duplicate experiments gave the similar results. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

from each solution increased with time and the saturated binding were observed in 60–160 hours. It was noted that the amounts of BPA binding to the imprinted PES particles was higher than that to the nonimprinted ones in neutral and alkali BPA solutions, while few BPA binding was found in the BPA alkali solution for both the imprinted and nonimprinted particles. The BPA binding amounts for the imprinted and nonimprinted particles were 17.14 and 8.05 μmol g^{-1}, respectively, under neutral condi-

tions, while they were 16.43 and 7.86 μmol g^{-1}, respectively, in acid solution. Clearly, there were no significant differences between the acid solution and neutral solution in term with the binding amounts. However, in the BPA alkali solution, the binding amounts for the imprinted and nonimprinted particles were only 0.28 and 0.37 μmol g^{-1}, respectively. This indicated that the OH$^-$ in the solution interacted with the —OH in the BPA molecule, which prevent the interaction between BPA and PES recognition sites.[5,17]

Interestingly, as shown in Figure 3(b), the binding and recognition behavior recovered as soon as possible, when 0.50M HCl solution was added into the BPA alkali solution, and the pH value of the solution changed to 1.1. The amounts of BPA binding to the imprinted PES particles were higher than that to the nonimprinted ones. This can be deduced that the HCl solution neutralize the NaOH in the BPA solution, then the recognition sites recovered to bind the BPA. After 120 hours, the BPA binding amounts for the imprinted and nonimprinted particles were 13.99 and 7.71 μmol g^{-1}, respectively. The binding amounts were a little smaller than that in acid and neutral solutions as shown in Figure 3(a). In our previous studies, the binding amounts to the microspheres decreased with the decrease of the BPA concentrations.[17] In this case, when 1M HCl solutions were added into 150 μM BPA alkali solution, the initial BPA concentration decreased to 106 μM. Thus the recognition and binding ability of the imprinted
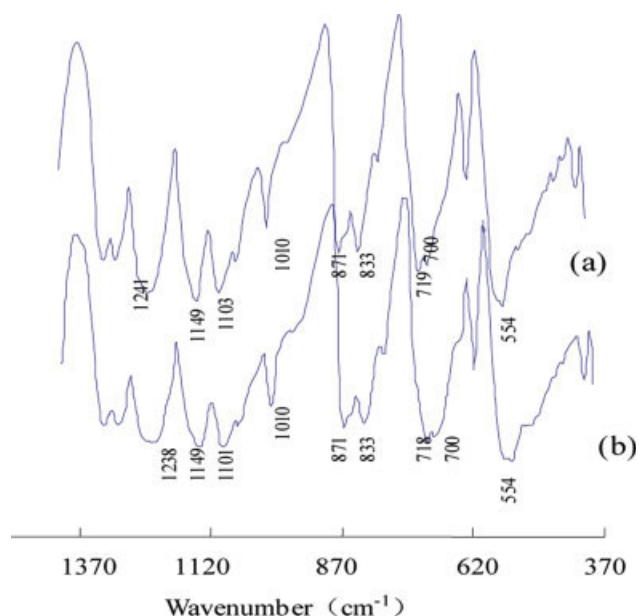

Figure 5 FTIR spectra of the nonimprinted PES particles (a) and imprinted PES particles (b). [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

TABLE I
The Binding Amounts of BPA to the Imprinted Particles ($[S]_{(imprinted)}$), to the Nonimprinted Particles ($[S]_{(nonimprinted)}$), and the Recognition Coefficients (α) in 200 μM BPA Solutions with Different Concentrations of Na^+, Cl^-, and Mg^{2+}

Solutions	$[S]_{(imprinted)}$ (μmol g^{-1})	$[S]_{(nonimprinted)}$ (μmol g^{-1})	α
BPA aqueous solution	22.77	9.20	2.47
BPA solution with 0.10M NaCl	25.94	11.92	2.18
BPA solution with 0.010M NaCl	19.63	8.87	2.21
BPA solution with 1.0 mM NaCl	19.74	9.72	2.03
BPA solution with 0.050M MgCl$_2$	22.29	11.02	2.02
BPA solution with 5.0 mM MgCl$_2$	20.11	10.42	1.93
BPA solution with 0.50 mM MgCl$_2$	19.14	9.03	2.12

All the particles were extracted in the mixed solvent of acetone/ethanol (V : V = 25 : 75).

particles slightly decreased. This interesting pH-sensitive phenomenon suggested that for advanced recognition and separation, a controllable result may be obtained by changing the pH value.

Binding of BPA to imprinted particles in solutions with different ions

Since people have faced severe BPA problems in seawater,[26] it is necessary to detect and remove BPA in seawater, a system with different ions. In the seawater, Na^+, Mg^{2+}, and Cl^- constitute nearly 95% of all the ions in the seawater. The binding amounts for the imprinted particles and nonimprinted particles were measured in the solutions with different concentrations of Na^+, Mg^{2+}, and Cl^-. As shown in Table I, with the addition of Na^+, Mg^{2+}, and Cl^-, the binding amounts for the imprinted particles and nonimprinted particles were not changed heavily. And the recognition coefficients were slightly decreased in solutions with different concentrations of Na^+, Mg^{2+}, and Cl^- compared to that in aqueous solution, this can be deduced that the ions in the BPA solutions have interactions with the PES residue, which contributed to the recognition of BPA.[17] These results suggested that the BPA-imprinted PES particles can be applied in the binding and recognition of the endocrine disruptor, BPA, in seawater.

Selectivity of the imprinted particles

To study the selectivity of the BPA-imprinted particles, binding experiments were carried out in the

BPA/phenol (100 μM/100 μM) mixed aqueous solution and BPA/biphenyl (50 μM/50 μM) mixed water/ethanol (V : V = 90 : 10) solution, respectively. Both the phenol and biphenyl (BP) were BPA structurally related organic compounds and were regarded as endocrine disruptors.[14,17] Figure 4(a) shows the amounts of BPA and phenol bound to the BPA-imprinted PES particles and the nonimprinted PES particles. The binding amounts for each substrate increased with time and the saturated bindings were observed in 50–100 hours. The BPA binding amounts to the imprinted particles and nonimprinted particles were 13.90 and
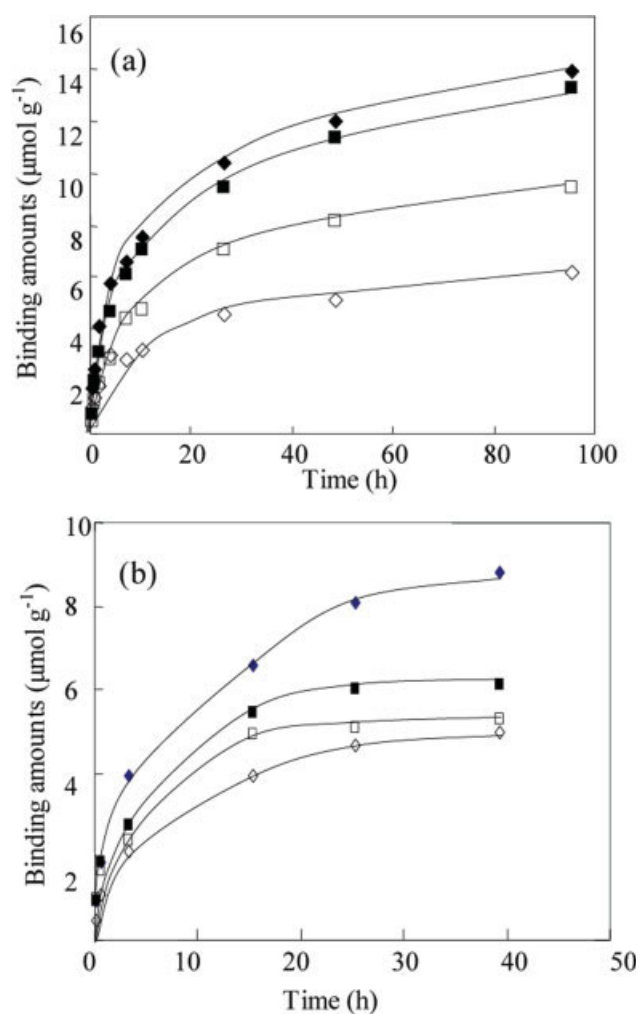

Figure 4 Time course of binding to the imprinted particles and the nonimprinted in the BPA/phenol (100 μM/100 μM) mixed aqueous solution and BPA/biphenyl (50 μM/50 μM) mixed water/ethanol (V : V = 90 : 10) solution. In the BPA/phenol solution (a), for BPA binding to the imprinted (◆) and nonimprinted particles(◇), for phenol binding to the imprinted (■) and nonimprinted particles (□).In the BPA/BP solution (b), for BPA binding to the imprinted (◆) and nonimprinted particles (◇), for BP binding to the imprinted (■) and nonimprinted particles (□). Duplicate experiments gave the similar results.

6.43 µmol g^{-1}, respectively. Meanwhile, the phenol binding amounts to the BPA-imprinted particles and the nonimprinted particles were 13.47 and 9.41 µmol g^{-1}, respectively. Though the BPA binding amounts to the imprinted particles ($[S]_{(imprinted)-BPA}$) are close to that of the phenol binding amounts ($[S]_{(imprinted)-phenol}$), the BPA binding amounts to the nonimprinted particles ($[S]_{(nonimprinted)-BPA}$) are smaller than that of the phenol binding amounts ($[S]_{(nonimprinted)-phenol}$). The recognition coefficient can be calculated as 2.16 and 1.43, respectively, for BPA and phenol. According to the eq. (3), the BPA binding amounts to the recognition sites ($[S]_{(sites)-BPA}$) was 7.47 µmol g^{-1}, while the phenol binding amounts to the recognition sites ($[S]_{(sites)-phenol}$) was 4.06 µmol g^{-1}. $[S]_{(sites)}$ can quantified the specific binding and was absent from the denominator effect, by which we can investigated the behavior of the recognition sites straightforwardly and quantitatively.[17] In this case, the recognition sites select more BPA than phenol.

Selectivity coefficient ($\beta_{A/B}$) was used to evaluate the selectivity of the recognition sites for substance A, based on substance B. It can be defined as following:

$$\beta_{A/B} = [S]_{(sites)-A}/[S]_{(sites)-B} \qquad (4)$$

where $[S]_{(sites)-A}$ was the A binding amount to the recognition sites (µmol g^{-1}), and $[S]_{(sites)-B}$ was the B binding amount to the recognition sites (µmol g^{-1}).

Clearly, when $\beta_{A/B}$ is larger than 1, the recognition sites show selectivity for A. The larger the $\beta_{A/B}$ is, the stronger selectivity for A is shown. The value of $\beta_{BPA/phenol}$ was calculated as 1.84, which indicated that the recognition sites show strong selectivity for BPA in BPA/phenol mixed solution.

Figure 4(b) shows the amounts of BPA and BP bound to the BPA-imprinted PES particles and the nonimprinted PES particles in BPA/biphenyl (50 µM/50 µM) mixed water/ethanol solution (V : V = 90 : 10). Because of the poor solubility for biphenyl in water, the ethanol was employed to facilitate the dissolution of biphenyl in the solution. Similarly as Figure 4(a), the binding amounts of each substrate increased with time. It is noted that the binding amounts of BPA to the imprinted particles were higher than that to the nonimprinted particles, while the BP binding amounts to the imprinted particles was close to that to the nonimprinted particles. The BPA binding amounts to the imprinted particles and the nonimprinted particles were 8.81 and 4.96 µmol g^{-1}, respectively. Meanwhile, the BP binding amounts to the BPA-imprinted particles and the nonimprinted particles were 6.12 and 5.30 µmol g^{-1}, respectively. Though the BPA binding amounts to the nonimprinted particles ($[S]_{(nonimprinted)-BPA}$) are close to that of the BP binding amounts ($[S]_{(nonimprinted)-BP}$), yet the BPA binding amounts to the imprinted particles ($[S]_{(imprinted)-BPA}$) are larger than the BP binding amounts

to the imprinted particles ($[S]_{(nonimprinted)-phenol}$). The recognition coefficient can be calculated as 1.78 and 1.15, respectively, for BPA and BP. According to the eq. (3), the BPA binding amounts to the recognition sites ($[S]_{(sites)-BPA}$) was 3.85 µmol g^{-1}, whereas the BP binding amounts to the recognition sites ($[S]_{(sites)-BP}$) was 0.82 µmol g^{-1}. According to the eq. (4), the selectivity coefficient, $\beta_{BPA/BP}$, was calculated as 4.70, which indicated that the recognition sites show stronger selectivity for BPA in the BPA/biphenyl (50 µM/50 µM) mixed water/ethanol solution (V : V = 90 : 10) than that in BPA/phenol mixed solution. This was presumably caused by the hydrogen bond interaction between the —OH in the BPA and the S(=O)$_2$ in the PES molecular chains when the coagulation process occurred in the water. After the extraction of the BPA from the PES particles, the specific recognition sites were exposed. These sites can also recognize the phenol due to the —OH in the molecules.

Interaction between PES and BPA

BPA-imprinted PES particles showed high binding of BPA in contrast to nonimprinted PES particles. It is proved that the morphology and porous structure of the imprinted and nonimprinted are similar to each other. It is the recognition sites that lead to the difference of imprinted and nonimprinted. To study the recognition sites and BPA interaction, FTIR analysis was carried out. The difference in FTIR spectra of the nonimprinted (a) and the imprinted PES (b) are shown in Figure 5. In the spectra of PES (a), the bands at 1241 cm^{-1} corresponded to the S(=O)$_2$ asymmetric stretching, and 1149 and 1103 cm^{-1} to the symmetric stretching.[4] Also, C—O—C stretching of the main chain of the PES appeared near 1010 cm^{-1}. IR bands between 800 and 900 cm^{-1} were for S—O—C stretching. Aromatic bending peaks at 719, 700, and 554 cm^{-1} were assigned to out-of-plane CH bending.[4] A difference between spectrum (a) and (b) was apparently observed in PES bands. The 1241 cm^{-1} S(=O)$_2$ of the PES peak shifted to 1238 cm^{-1} in the imprinted PES. From this change, it can be deduced that the electronic state of the S(=O)$_2$ in PES is influenced by the neighboring BPA. This result suggested that the S(=O)$_2$ in the PES molecules can interact with the —OH in the BPA molecules through hydrogen bond,[27] when the PES and BPA were dissolved in the DMAc simultaneously. Then this interaction was solidified in the initial particles. After the BPA was extracted from the solidified particles, this interaction was memorized in the imprinted particles, which was indicated by the red shift of S(=O)$_2$ in the Figure 5. Through this process, the recognition sites formed and had special binding to BPA.[18,28] In addition, when BPA was bound in

the imprinted sites, the $>S(=O)_2$ peak appeared at 1238 cm^{-1}. For the nonimprinted PES, the $>S(=O)_2$ peak appeared at 1241 cm^{-1}. This slight shift toward the low wave number side could also imply the interaction between the —OH and the $>S(=O)_2$.

CONCLUSION

BPA imprinted PES particles were prepared for the recognition of BPA by means of phase inversion. Different extraction methods were used by using acetone, ethanol, and acetone/ethanol solutions. The SEM morphology suggested that the acetone destroy the inside structure while the ethanol and acetone/ethanol mixed solution (V : V = 25 : 75) can extract the template molecules but not change the porous structure in the imprinted particles. No recognition behavior was found in the imprinted particles extracted by the acetone, while the imprinted particles which were extracted by acetone/ethanol (V : V = 25 : 75) had similar recognition ability with ethanol-extracted particles. But it took much more time for the ethanol extraction than the acetone/ethanol extraction. Therefore the acetone/ethanol mixed solution provided an efficient way to extract the BPA from the imprinted PES particles. The binding and recognition ability for the imprinted particles disappeared under alkali condition, and they recovered as soon as possible when the solution changed from alkali condition to neutral or acid condition. With the addition of Na$^+$, Mg^{2+}, and Cl$^-$, the binding amounts for the imprinted particles and nonimprinted particles were not changed heavily. In BPA and BPA-related compounds mixed solutions, the imprinted particles showed selectivity for the template molecule BPA. The FTIR results suggested that the PES and BPA interacted by hydrogen bonds. These results suggested that the BPA-imprinted PES porous particles might be prepared at ease and have the potential to be used in environmental applications and chromatography.

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