

Effect of the Template Molecules and Nonsolvent Additives on the Recognition Property of Molecular Imprinted Polyethersulfone Particles

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ABSTRACT: In this study, molecular imprinted polyethersulfone (PES) particles were prepared by phase inversion technique. Bisphenol A, 4,4'-biphenol, and phenol were used as the template molecules, and the functional binding performance in aqueous medium towards the template molecules was investigated. The nonsolvent additives such as ethanol, water, chloroform, and toluene had no effect on the recognition property of the PES particles. The resultant BPA imprinted particles showed the highest BPA recognition coefficient, which was 2.14 times higher than that for the nonimprinted ones. The 4,4'-biphenol imprinted particles showed

the highest binding ability towards the template which was 28.4 $\mu\text{mol/g}$. Scatchard analysis showed that there were two classes of binding sites formed in the imprinted particles, and the equilibrium dissociation constant of the highest affinity binding sites was estimated to be 9.2 μM . Finally, the interaction between PES and the templates was studied by Fourier transform infrared (FTIR) and NMR. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3859–3866, 2008

Key words: molecular recognition; imprinted polyethersulfone particles; bisphenol A; scatchard analysis

INTRODUCTION

Molecular imprinting technology for creating specific molecular recognition ability for the target molecule in polymer matrix has attracted much attention lately.^{1,2} The molecularly imprinted polymers (MIPs) were widely used in solid-phase extraction,^{3,4} chiral separation,^{5,6} sorbent^{7,8} and other analytical chemistry^{9,10} field. To prepare MIPs, two different approaches have been developed: the covalent¹¹ and non-covalent methods.¹² For the covalent method, functional monomers, cross-linkers and the template molecules are arranged in a mixture. The binding sites in the resultant polymers originated from the polymerization reaction according to the shape and chemical properties of the template molecules. For the second one, the noncovalent interactions usually are hydrogen bonds, ionic interactions, hydrophobic interactions and dipole–dipole interactions.¹³ After

the removal of the template molecules, the MIPs exhibited high affinity and selectivity for the template molecules.

In the last three decades, liquid–liquid phase inversion process has always been used for the preparation of membranes such as ultrafiltration or microfiltration membrane.^{14,15} Recently, Kabayashi and coworkers have developed an ease noncovalent imprinting method with the use of phase inversion technique, and theophylline (THO)-imprinted poly(acrylonitrile-*co*-acrylic acid) [P(AN-*co*-AA)] membrane was prepared.¹⁶ Now, phase inversion technique has been demonstrated as an effective method to prepare molecularly imprinting membranes with selective recognition properties.^{17–19} Common features to the template molecules used in the method are the small solubility in water and polar function groups in their structure.

Bisphenol A (BPA)-imprinted polyethersulfone (PES) particles were firstly prepared by the liquid–liquid phase inversion in our earlier study.²⁰ To prepare the BPA-imprinted PES particles, it will take a long time to extract the template BPA, since the imprinting sites not only exist on the surface but also in the deep polymer matrix. BPA is known as one of the endocrine disruptors, and affects the reproduction and development of animal organism even at an extra-diluted concentration.²¹ Our aim in this study is to find a method to prepare imprinted PES particles without directly using BPA as the

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template molecule. Yoshizako et al.²² investigated the porogen imprinting effects, and found that using toluene or benzene as the porogenic solvent, molecular imprinted polymer matrix could be prepared.

In the present work, we attempted to study the effect of BPA homologues on the adsorption performance to extend the research and application of template-imprinted PES particles. In addition, the effect of ethanol, water, chloroform, toluene as non-solvent additives (NSA) on the recognition property was investigated in aqueous medium. SEM was used to characterize the morphology of the template-imprinted PES particles. Finally, Fourier transform infrared (FTIR) and NMR were used to investigate interaction between the PES matrix and the template molecule in an effort to understand the mechanism of different recognition property.

EXPERIMENTAL

Materials

PES (Ultrason E 6020P) was purchased from BASF chemical company (Germany). BPA, 4,4'-Biphenol (BPhe) and phenol (Phe), which were used as the template molecules, were purchased from Shanghai Chemical Reagent (China). Dimethyl acetamide (DMAC), ethanol, chloroform, and toluene were purchased from Chengdu Chemical Reagent (China). All the reagents used in the experiments were of reagent grade unless otherwise described, and used without further purification. Double distilled water passed through ion-exchange columns was used throughout the studies.

Preparation of imprinted PES particles

Molecular imprinted particles were prepared by means of a liquid-liquid phase inversion method.²⁰ Template molecules (BPA, BPhe, or Phe) and one kind of non-solvent additive were mixed in DMAC at glass flask. Dried PES was added into the mixture and stirred until the solution became homogenous. The concentration of the template molecules or the non-solvent additives was 5 wt %, while the concentration of PES was 21 wt %. After being degassed, the resultant polymer solution was dropped into distilled water by using a 0.6-mm-diameter syringe needle at room temperature to prepare the particles. The injection speed was controlled at about 80 drops/min. The air gap from the needle head to the water was 15–20 cm. The particles were incubated in water for over 24 h to elute the residual DMAC from the particles, and the water was changed every 4 h. The template molecules were removed by alcohol with Soxhlet extractor. Nicolet 560 (Nicol, American) FTIR spectra and UV-vis (U-200A Shanghai

Spectrum Instruments, China) spectrophotometer were used to confirm the complete extraction of the template molecules. Simultaneously, PES solution with a concentration of 21 wt % was used to prepare nonimprinted PES particles in the same manner.

Characterizations of PES particles

The morphology of the crosssection of the particle was characterized with a scanning electron microscope (SEM, JSM-5900LV JEOL). For the SEM observation, the particle samples were dried at room temperature. Then the particles were quenched in liquid nitrogen, cut with a microtome knife and sputtered with gold.

Infrared spectra were recorded with Fourier transform infrared spectra (FTIR, Nicolet 560) from 4000 to 800 cm^{-1} . ^1H NMR (Unity INVO-400 MHz NMR spectrometer) was also used to study the interaction of PES and the template in d_6 -Dimethyl sulfoxide (DMSO).

Calculation of the particle porosity

The porosity of the particles was calculated from the density of the polymer and the sample weight change before and after drying,²³ using the following formula:

$$\text{Porosity} = \frac{(W_B - W_A)/\rho_w}{W_A/\rho_P + (W_B - W_A)/\rho_w} \times 100\% \quad (1)$$

where W_A and W_B is the weight of the sample after and before drying (g), respectively; ρ_w and ρ_P is the density of water (1.00 g/cm^3) and PES (1.43 g/cm^3),²⁴ respectively.

Recognition experiments

Template and substrate recognition were studied by binding experiments at 25°C. For the experiments, about 40.0 mg PES particles were added into 10 mL of the solutions containing various concentrations of the template molecules. The concentration of the template at different time intervals was monitored by using an UV-vis spectrophotometer at the wavelength of 276 nm for BPA, 269 nm for Phe and 274 nm for BPhe. Binding amounts, $[S]_b$ ($\mu\text{mol}/\text{g}$ of polymer), were calculated by the following equation:

$$[S]_b = (C_0 - C_t)V/W \quad (2)$$

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

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

$$\alpha = [S]_{(\text{imprinted})} / [S]_{(\text{non-imprinted})} \quad (3)$$

where $[S]_{(\text{imprinted})}$ is the binding amount to the imprinted particles ($\mu\text{mol/g}$); and $[S]_{(\text{non-imprinted})}$ is the binding amount to the nonimprinted particles ($\mu\text{mol/g}$).

Scatchard analysis

The polymer particles (40.0 mg) were applied to 10 mL BPA aqueous solutions with different concentrations (varied from 50 μM to 0.6 mM), and incubated for over 120 h with continuous stirring at room temperature. It had been confirmed that under these conditions, the BPA adsorption had already reached the equilibrium. The concentration of the free BPA, $[\text{BPA}]$, in the equilibrium solution was detected using an UV-vis spectrophotometer at 276 nm. The amount of the BPA bound to the polymer, $[B]_{\text{bound}}$, was then calculated. The average data of triplicate independent results were used for the Scatchard analysis. Binding data can be linearly transferred according to the Scatchard equation,

$$[B]_{\text{bound}} / [\text{BPA}] = (B_{\text{max}} - [B]_{\text{bound}}) / K_D \quad (4)$$

where K_D is an equilibrium dissociation constant and B_{max} is an apparent maximum number of the binding sites. $[B]_{\text{bound}} / [\text{BPA}]$ is plotted versus $[B]_{\text{bound}}$, then K_D and B_{max} can be estimated from the slope and the intercept, respectively.²⁵

RESULTS AND DISCUSSION

Characterization of the PES particles

Molecular imprinted PES particles were prepared through direct phase inversion method from PES-template-DMAC solution. During the imprinting process, non-solvent water was selected as the coagulation medium, which was commonly used.^{26,27} Here, water show high solubility for DMAC but not for PES and the template molecules. Thus, the imprinting occurred immediately during the PES solidification in water, and the template molecules were retained in the solidified particles. That is, the specific binding sites of the template molecules were introduced into the polymer matrix during the precipitation process in water.

Figure 1 shows the SEM pictures of the cross-section of the BPA-imprinted PES particles. A skin layer was found on the surface of the particle, under which was a finger-like structure as shown in Figure

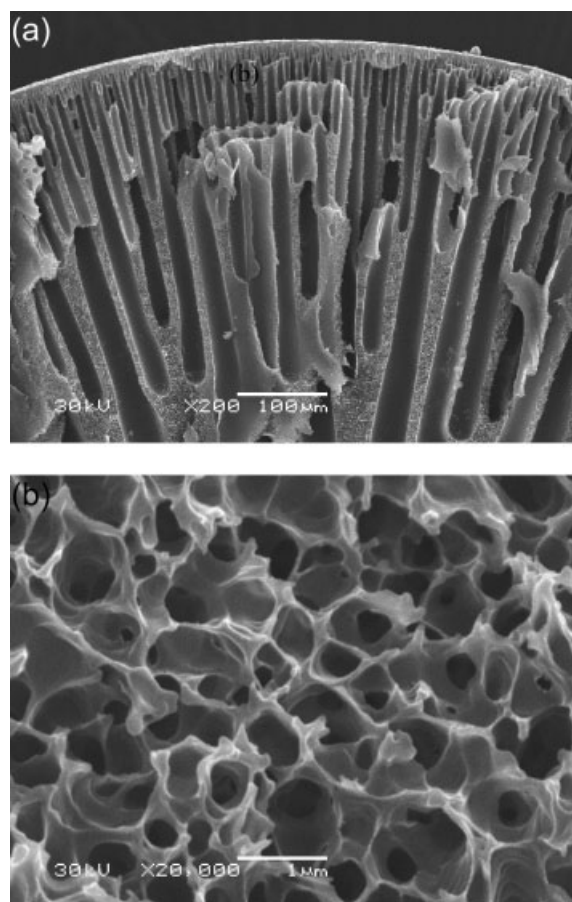


Figure 1 SEM images of the cross-section of the BPA-imprinted PES particle Voltage: 30 KV; Magnification: (a) 200 \times (b) 20,000 \times .

1(a), which was magnified 200 \times . Significant pores (about 1 μm) were observed in the porous sublayer of the particles as shown in Figure 1(b), which were magnified 20,000 \times . Similar morphology was observed for the BPhe-imprinted PES particles (not shown). The SEM morphology suggested that the PES transformation from polymer solution to the solid state occurred quickly in the poor solvent water. Instantaneous demixing during the phase inversion process reflected the typical behavior when the solvent and non-solvent showed high affinity.^{20,28}

Figure 2 shows the SEM photograph of the cross-section of the phenol (Phe)-imprinted PES particles. Compared with Figure 1, significant difference was observed. The finger-like structure disappeared; instead, round macrovoids were found inside the particles, as shown in Figure 2(a). And the diameter of the macrovoids was about 3 μm , as shown in Figure 2(b). The possible reason was due to the better solubility of phenol than that of BPA and BPhe in water.

For the blank PES particles, there was no difference in the morphology when the magnification was

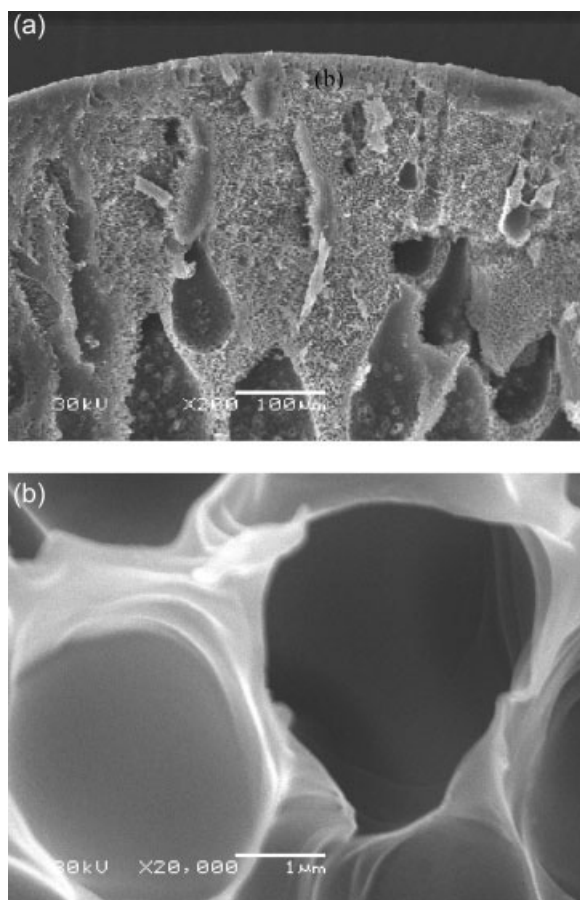


Figure 2 SEM images of the cross-section of the Phe-imprinted PES particle Voltage: 30 KV; Magnification: (a) 200 \times (b) 20,000 \times .

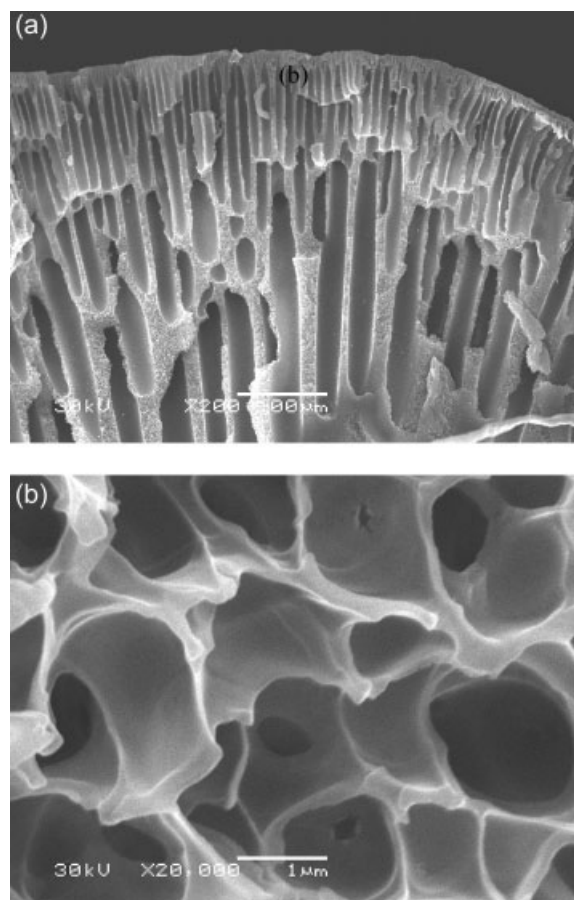


Figure 3 SEM images of the cross-section of the blank PES particle Voltage: 30 KV; Magnification: (a) 200 \times (b) 20,000 \times .

200 \times , as shown in Figure 3 (a). The pore size [as shown in Fig. 3(b)] distributed in the porous PES networks was about 2 μm in diameter, which was larger than that of the BPA-imprinted particles and less than that of the Phe-imprinted particles.

Moreover, the porosity of the particles can be calculated according to the Eq. (1), and were listed in Table I. The porosity for the blank PES particles was about 73.1%, while that was slightly increased for the imprinted particles. Since the porosity was the total volume of the macro-voids and the micro pores, thus there was no significant difference in the pores between the particles prepared using template and nonsolvent. Here, both the template and nonsolvent also play the action of porogens. In fact, the porosity of the particles mainly depended on the PES concentration, the preparation conditions and the composition of the polymer solution.²⁹ The surface area, which was a significant factor to the binding, is about 100 m^2/g for all the particles determined by the mercury porosimeter. And in this study, the diameter of the particles was about 2.0 ± 0.1 mm.

Binding behavior of various particles

To study the recognition ability of the template-imprinted particles, binding experiments were carried out in 100 μM template solutions at 25 $^\circ\text{C}$. In batch experiments, the various template-imprinted particles were soaked in aqueous BPA solution, BPhe solution and Phe solution, respectively. And the concentration of the bulk solution was determined at various time intervals.

TABLE I
Particle Porosities and the Binding Amounts in 100 μM BPA Aqueous Solution

Particles	Porosity (%)	[S] _b ($\mu\text{mol}/\text{g}$ of polymer)
BPA-imprinted	76.5 \pm 2%	18.3
BPhe-imprinted	77.4 \pm 2%	21.7
Phe-imprinted	75.4 \pm 2%	7.3
Toluene as nonsolvent	76.8 \pm 2%	6.7
Chloroform as nonsolvent	78.3 \pm 2%	8.3
Ethanol as nonsolvent	75.5 \pm 2%	9.0
Blank	73.1 \pm 2%	8.6

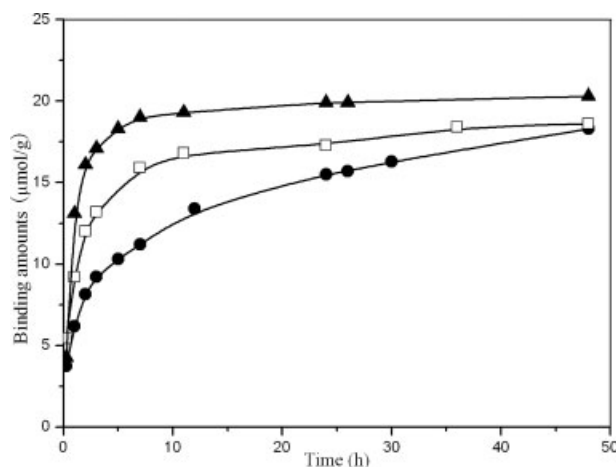


Figure 4 Time course of binding to the BPA-imprinted particles in various substance aqueous solutions ($100 \mu\text{M}$) at 25°C : (▲) BPhe aqueous solution; (●) BPA aqueous solution; (□) Phe aqueous solution. Duplicate experiments gave the similar results.

Figure 4 shows the binding amounts of BPA and its analogues by the BPA-imprinted PES particles. The value of the binding amounts ($\mu\text{mol/g}$) increased with time and the saturated binding was observed in about 30–48 h. The saturated binding amounts by the BPA-imprinted particles were about 20.3, 18.3, 18.6 $\mu\text{mol/g}$ for the BPhe, BPA, and Phe aqueous solutions respectively. It was noted that the binding amounts of BPhe and Phe were higher than that of BPA. This can be explained by the fact that the molecular volume of BPhe and Phe is smaller than that of BPA. Also, it was observed that the BPhe binding rate was somewhat larger than that of the BPA, which was attributed to the BPhe molecular structure with smaller steric hindrance. Both

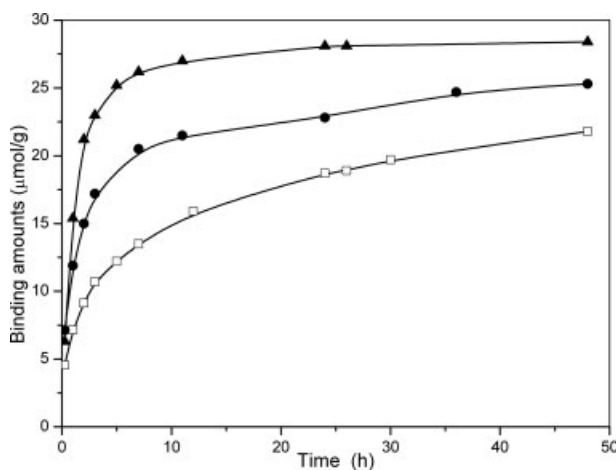


Figure 5 Time course of binding to the BPhe-imprinted particles in various substance aqueous solutions ($100 \mu\text{M}$) at 25°C : (▲) BPhe aqueous solution; (●) BPA aqueous solution; (□) Phe aqueous solution. Duplicate experiments gave the similar results.

BPhe and BPA molecules, have hydroxyl at 4- and 4'- position of the phenyl ring, which are easy to form inter- or intramolecular hydrogen bonding. The similar binding behavior by the BPhe-imprinted particles was also observed, as shown in Figure 5. The binding amounts were larger than that to the BPA-imprinted particles; and the saturated binding amounts were 28.3, 21.8, 25.3 $\mu\text{mol/g}$ for the BPhe, BPA, and Phe, respectively.

For the imprinted particles, specific recognition sites had a great influence on the substance binding at lower concentration.³⁰ It is noted that the binding amount of BPA by the BPhe-imprinted particles was larger than that of BPA-imprinted ones; this may be attributed to the larger amounts of the recognition sites when BPhe was used as the template. Since the BPhe molecular weight ($M_w = 186$) was smaller than that of the BPA. Considering the molecular weights and the mol value of the BPA and BPhe, there was no significant difference for the BPA binding amounts to the BPA and BPhe imprinted particles.

Phe-imprinted particles and blank particles were also applied to BPA, BPhe, and Phe aqueous solutions, respectively; data are shown in Figures 6 and 7. Comparing with the binding to the BPhe-imprinted particles (Fig. 5), the binding amount and binding rate of the Phe-imprinted ones were smaller. For the Phe-imprinted particles, the specific sites in the polymer matrix were hard to form, because the solubility of phenol in water is very large. When the solvent (DMAC) and water exchange, the phenol molecules dissolved in water, that is, less imprinting sites were formed.

For the blank PES particles, the binding was attributed to the large porosity^{31,32} (as shown in Table I) and the hydrophobic interaction between the tem-

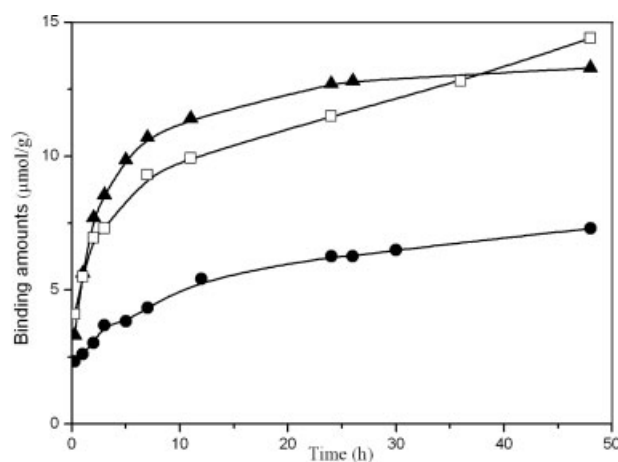


Figure 6 Time course of binding to the Phe-imprinted particles in various substance aqueous solutions ($100 \mu\text{M}$) at 25°C : (▲) BPhe aqueous solution; (●) BPA aqueous solution; (□) Phe aqueous solution. Duplicate experiments gave the similar results.

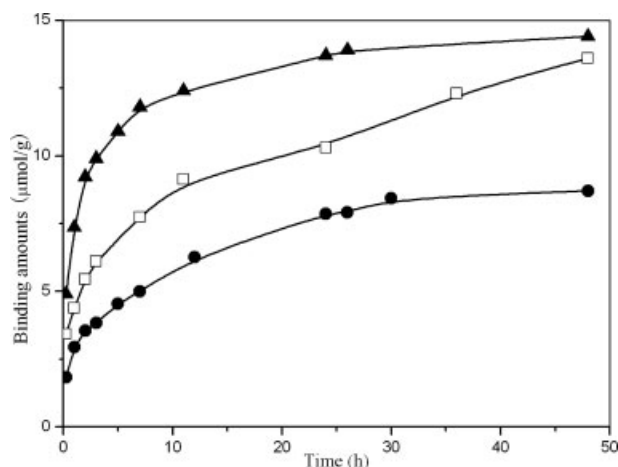


Figure 7 Time course of binding to the Blank PES particles in various substance aqueous solutions (100 μM) at 25°C: (▲) BPhe aqueous solution; (●) BPA aqueous solution; (□) Phe aqueous solution. Duplicate experiments gave the similar results.

plate molecules and PES. Also, there was no significant difference in the BPA binding amounts between the particles prepared from the PES solution when toluene, chloroform or ethanol was added, as shown in Table I. The results indicated that these compounds as non-solvents had no contribution to the binding and recognition.

The relative recognition coefficients (see Experiment Section) are listed in Table II. It was found that the Phe-imprinted particles had the lowest recognition coefficient, which was caused by the higher solubility in water. The BPhe-imprinted particles showed the highest binding amounts. It is probably because of the larger amounts of the recognition sites.

Affinity of the BPA-imprinted polymer

In order to investigate the binding performance of the BPA-imprinted polymer, saturation adsorption experiments were carried out, and the data were used for Scatchard analysis. Figure 8 shows the Scatchard plots for BPA binding by the BPA-imprinted, BPhe-imprinted and non-imprinted particles, respectively. From the plots of $[B]_{\text{bound}}/C$ versus $[B]_{\text{bound}}$, the K_D , an average equilibrium dissociation constant, can be calculated from the negative

TABLE II
Recognition Coefficient (α) of the Template-Imprinted PES Particles

Particles	α_{BPA}	α_{BPhe}	α_{phe}
BPA-imprinted	2.13	1.41	1.36
BPhe-imprinted	2.52	1.97	1.85
Phe-imprinted	0.84	0.93	1.05

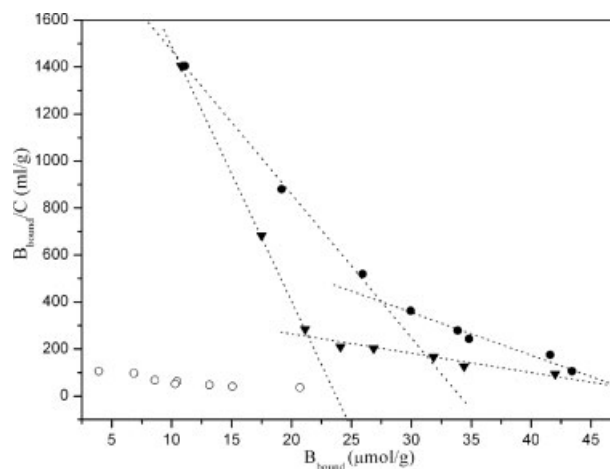


Figure 8 Scatchard plots to estimate the binding nature of the P (BPA) in the particles, (●) BPA imprinted, (▼) BPhe imprinted, (○) blank. Dashed lines shows the region which can be assumed to the two classes of the binding sites of P (BPA).

slope; and the B_{max} , the number of the binding sites can be obtained from the intercept. In the resultant plots, two straight line regions were obtained, except for the nonimprinted particles. It is reasonable to assume that two different sites (specific and nonspecific binding sites) for the BPA molecules existed.

From the straight area in the range of 1–30 $\mu\text{mol/g}$ of binding amounts, the equilibrium dissociation constants (K_{D1}) were calculated (Table III). The K_{D1} for the BPA-imprinted and BPhe-imprinted particles, were 16.7 and 9.2 μM , respectively. For the non-imprinted particles, the K_{D1} showed the highest value of 135.6 μM ; and the K_{D1} equal to the K_D . Therefore, the BPhe-imprinted particles exhibited the most effective binding ability to BPA. In the 100 μM BPA aqueous solution, the binding amounts for the BPhe imprinted particles would correspond to 86% of the calculated maximum binding sites. From the higher binding amounts area, the resulting K_{D2} was bigger than that obtained from lower binding amount region. It may due to the non-specific bind-

TABLE III
Equilibrium Dissociation Constants (K_D) and the Maximum Binding Sites (B_{max}) for BPA Adsorption to the Particles

Particles	K_{D1}^a (μM)	$B_{\text{max}1}$ ($\mu\text{mol/g}$)	K_{D2}^b (μM)
BPA-imprinted	16.7	34.4	58.4
BPhe-imprinted	9.2	25.2	117.6
Phe-imprinted	135.6	18.0	135.6

^a The values in specific binding region.

^b As nonspecific parameter, the value of equilibrium content was calculated from high concentration region in Figure 7.

ing with physically adsorbed behavior of the BPA molecules, such as hydrophobic interaction.

Interaction between PES and template

FTIR spectrum is a useful method for characterizing the intermolecular hydrogen bonding.^{16,17} The difference in FTIR spectra of (a) PES, (b) PES with 5% BPA, and (c) PES with 5% BPhe before template extraction is shown in Figure 9. In these cases, IR bands for (a) PES at 1322.95 and 1152.19 cm^{-1} attributed to the asymmetric and the symmetric stretching for $\text{S}(=\text{O})_2$. IR band at 1295.97 cm^{-1} was for the $\text{S}=\text{O}$ stretching vibration.³³ In the (b) spectrum for PES with 5%BPA, the IR band around 3433.97 cm^{-1} was assigned to stretching of $-\text{OH}$ and 2964.81 cm^{-1} was corresponding to the stretching of $-\text{CH}$. In the (c) spectrum of PES with 5% BPhe, the bands of 3402.02 and 3355.50 cm^{-1} resulted from the stretching of $-\text{OH}$ of BPhe.

Comparing these spectrum, it was noted that for the PES-BPA [Fig. 9(b)], the bands at 1322.95 and 1152.19 cm^{-1} for the $\text{S}(=\text{O})_2$ stretching in Figure 9(a) shifted to 1318.95 and 1147.01 cm^{-1} , respectively. The difference of $\text{S}(=\text{O})_2$ stretching vibration was possibly corresponding to the intermolecular hydrogen bonding between BPA and PES. The $-\text{OH}$ in the BPA molecules and the oxygen atoms in the PES apparently were influenced with each other. Moreover, it was noted that the $\text{S}(=\text{O})_2$ stretching also changed for the PES-BPhe, as shown in Figure 9(c), but the shift was smaller. The results suggested that BPA offered more efficient intermolecular hydrogen-bonding interaction than BPhe with PES.

Further comparison was carried out by ^1H NMR spectrum for the PES-template in $\text{DMSO}-d_6$ solution. As shown in Figure 10 (a), the resonance peak at 1.526 ppm comes from the methyl proton of the BPA. The CH proton signal of the BPA phenyl ring appears near 6.621–6.698 ppm region. The peak at

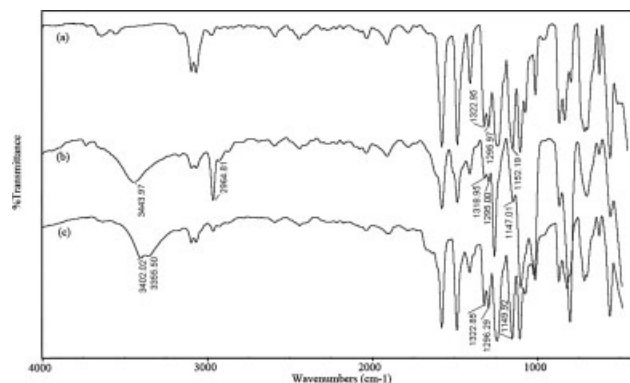


Figure 9 FTIR spectra of the BPA imprinted and non-imprinted BPA: (a) PES without imprinting (b) with 5 wt % BPA template (c) with 5 wt % BPhe template.

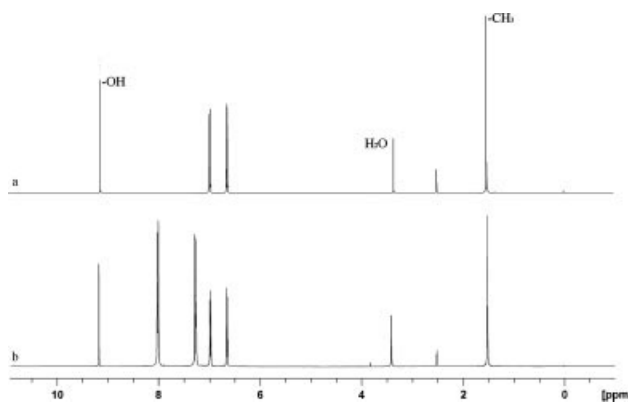


Figure 10 ^1H NMR spectra (400 MHz) of the PES membrane and BPA in $\text{DMSO}-d_6$ measured at 25°C: (a) BPA without the PES; (b) PES- $\text{DMSO}-d_6$ casting solution with 5% BPA template.

9.130 ppm is assigned to the H on the Ar-OH of BPA. As shown in Figure 10(b), the CH proton signal of the PES backbone appears about 7.263–8.01ppm. The resonance peak at 3.4–3.5 was assigned for the water. It was noted that the peak for the H on the Ar-OH of BPA shifted from 9.130 ppm toward the low magnetic field side of 9.170 ppm. The slightly downfield shift is due to the shielding effect of nearby group of the PES on the Ar-OH proton of BPA.

CONCLUSIONS

Template-imprinted PES particles were prepared by means of a phase inversion technique. The BPA analogue 4,4'-Biphenol could be used as template molecules to prepare molecular imprinted PES particles for BPA binding and recognition; while phenol could not be used due to the larger solubility in water. The non-solvent additives such as toluene, chloroform and ethanol, could not affect the binding and recognition properties of the imprinted PES particles. PES is inherently stable and the preparation of the particles is simple and inexpensive; these PES porous particles are readily available and have the potential to be used in environmental applications and chromatography.

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