

Molecularly Imprinted Polyethersulfone Microfibers for the Binding and Recognition of Bisphenol A

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Received 7 April 2009; accepted 23 June 2009

DOI 10.1002/app.31028

Published online 19 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Bisphenol A (BPA)-imprinted polyethersulfone (PES) microfibers for the recognition of BPA were prepared by means of wet-spinning method based on the liquid-liquid phase separation technique. Two kinds of the BPA-imprinted microfibers were fabricated with the diameters of about 85 μm and 265 μm , respectively. Extraction of BPA from the microfibers was carried out by immersing the imprinted microfibers into ethanol. In the recognition experiments, the binding amounts were about 24.0, 43.0, and 70.0 $\mu\text{mol/g}$ for the nonimprinted microfibers, whereas those were about 50.0, 87.0, 120.0 $\mu\text{mol/g}$ for the imprinted

PES microfibers with the diameter of about 85 μm in 100, 200, and 400 μM BPA solution, respectively. Both of the binding amounts and the adsorption rate for the imprinted microfibers with smaller diameter were higher than that for the microfibers with larger diameters. The selectivity results indicated that the BPA-imprinted microfibers showed higher recognition coefficient (α) for BPA than phenol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 4036–4041, 2009

Key words: microfiber; molecularly imprinting; bisphenol A; polyethersulfone

INTRODUCTION

Polymer microfibers, wet- or electro-spun, have been investigated from both fundamental and technological aspects,^{1,2} such as conductive microfibers^{3,4} and elastic microfibers.⁵ Microfiber is a fairly new technology, with many applications in industrial fields. Cleaning with microfiber products is fast, easy, and environmentally friendly. Microfiber cleaning fabrics are sometimes described as having a magnetic attraction to dirt and dust. Recently, microfibers were used for juice analysis by solid-phase microextraction.⁶ Our interest is focused on molecular-imprinted microfibers, which might be used for solid-phase extraction, since the molecular-imprinted microfibers could be used directly compared with nanofibers.⁷

Molecular imprinting is a technology in which specific recognition sites are formed in a polymer matrix by synthesis in the presence of the template molecule, or "imprinting" molecule which results in the formation of specific recognition cavities complementary to the template in shape and chemical functionality.⁸

Besides the good physical and chemical stability, the molecular imprinting polymers (MIPs) possess several advantages over their biological counterparts including low cost and easy for preparation. MIPs have been widely studied in many fields, such as chiral separation,^{9,10} protein adsorption,¹¹ solid-phase separation,¹² environmental applications,¹³ sensor design,¹⁴ membrane separation,¹⁵ and reaction catalysis.¹⁶

The MIPs would be extremely useful as adsorbents to environmental unfriendly compounds in terms of environmental pollution and impact. Since people have faced severe endocrine disruptor problems, some methods to treat endocrine disruptor polluted waters and wastewater are essential. In 2000, the concentration of the contaminants found in the polluted water ranges from 1.56 to 7.97 $\mu\text{mol/L}$, and the concentration range of BPA had a sublethal effect to the early life.¹⁷ It is necessary for the adsorbents with selectivity and high efficiency to environmental unfriendly compounds. To develop a novel type of high-selectivity adsorbing materials for the target molecules, a molecular-imprinted polymer is one of the extensive research approaches for preparing host cavities of specific selective binding.

In this article, bisphenol A (BPA)-imprinted polyethersulfone (PES) microfibers were prepared by using a wet-spinning technique, the recognition and binding properties for two kinds of microfibers were studied. Compared with the particles, which has been reported in our earlier publication,^{8,18} the binding sites located on the microfibers surface or near the surface are more accessible due to the small diameter.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50673064.

Contract grant sponsor: State Education Ministry of China (Doctoral Program for High Education); contract grant number: JS20061116506327.

EXPERIMENTAL

Materials

Polyethersulfone (PES, Ultrason E 6020P, CAS No.25608-63-3) was purchased from BASF chemical company (Germany) and was used to prepare the porous microfibers. Bisphenol A (BPA) was purchased from Shanghai Chemical Reagent Co. (China) and was used as the template. Dimethyl acetamide (DMAc) and ethanol were obtained from Chengdu Chemical Reagent Co. (China). All the chemicals are of analytical grade and are used without further purification unless otherwise described. Distilled water passed through ion-exchange columns was used throughout the study.

Preparation of the imprinted microfibers

Molecularly imprinted microfibers were prepared by wet-spinning technique based on a modified procedure of the phase inversion method. Polyethersulfone (PES) and bisphenol A (BPA) solution were prepared with a concentration of 21 wt % and 5 wt % in dimethylacetamide (DMAC), respectively. The mixed polymer solution was extruded into distilled water by using syringe needles at room temperature to prepare porous microfibers, the injection rate was about 60 cm/min and the microfibers were continuous long fiber. By using different syringe needles (0.4 mm or 0.6 mm), two kinds of microfibers with different diameters were prepared. The microfibers were incubated in water for over 3 days to elute the DMAc from the microfibers. Then, extraction of the template molecules from the solidified matrix was carried out by washing them with ethanol for several days at room temperature. After the extraction, the recognition sites were preserved in the PES matrix. Using an UV-vis spectrophotometer U-200A (Shanghai Spectrum Instruments Co., Shanghai, China), extraction was confirmed with the disappearance of 276 nm BPA adsorption in the extracted solutions. Furthermore, the FTIR spectra of the nonimprinted PES microfibers and imprinted microfibers could confirm the template's absence in imprinted microfibers based on the disappearance of the BPA peaks. Simultaneously, PES solution with a concentration of 21 wt % was used to prepare nonimprinted PES microfibers in the same manner, and by controlling the pressure of the force pump to preserve the diameter of the microfibers.

Scanning electron micrograph

For the scanning electron micrograph (SEM) observation, the BPA-imprinted microfiber samples were dried at room temperature. Then, the microfibers

were quenched by liquid nitrogenous gas, 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 microfiber cross section.

Calculations of the microfibers' diameter and porosity

The diameter and porosity of the microfibers can be calculated from the density of the polymer and the sample weight change before and after drying by using the equation¹⁹:

$$\text{Diameter} = 2\sqrt{\frac{[(W_B/\rho_P) + (W_A - W_B)/\rho_W]}{L \times \pi}} \quad (1)$$

$$\text{Porosity} = \frac{(W_A - W_B)/\rho_W}{W_B/\rho_P + (W_A - W_B)/\rho_W} \times 100\% \quad (2)$$

where W_A is the weight of the sample before drying; W_B is the weight of the sample after drying; L is the length of the fibers; $\pi = 3.14$; $\rho_W = 1.0 \text{ g/cm}^3$ is the density of water; and $\rho_P = 1.43 \text{ g/cm}^3$ is the density of the polyethersulfone.

Recognition experiments

Template recognition was studied by binding experiments at room temperature and immersing the microfibers in BPA aqueous solution. For the experiments, the microfibers were cut with the average length of about 7 cm, then 30 mg of the microfibers with smaller diameters were added into 25 mL solutions containing various concentration of BPA (the concentrations were 100, 200, and 400 μM , respectively). Then, the concentration of BPA at different time intervals was monitored by the UV-vis spectrophotometer for 276 nm BPA adsorption. The recognition of the microfibers with different diameters and the particles (prepared as our earlier study⁸) were also investigated using the same method. Binding amounts of the template to the microfibers, $[S]_b$ ($\mu\text{mol/g}$), were calculated by the following equation⁸:

$$[S]_b = (C_0 - C_t) \frac{V}{W} \quad (3)$$

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

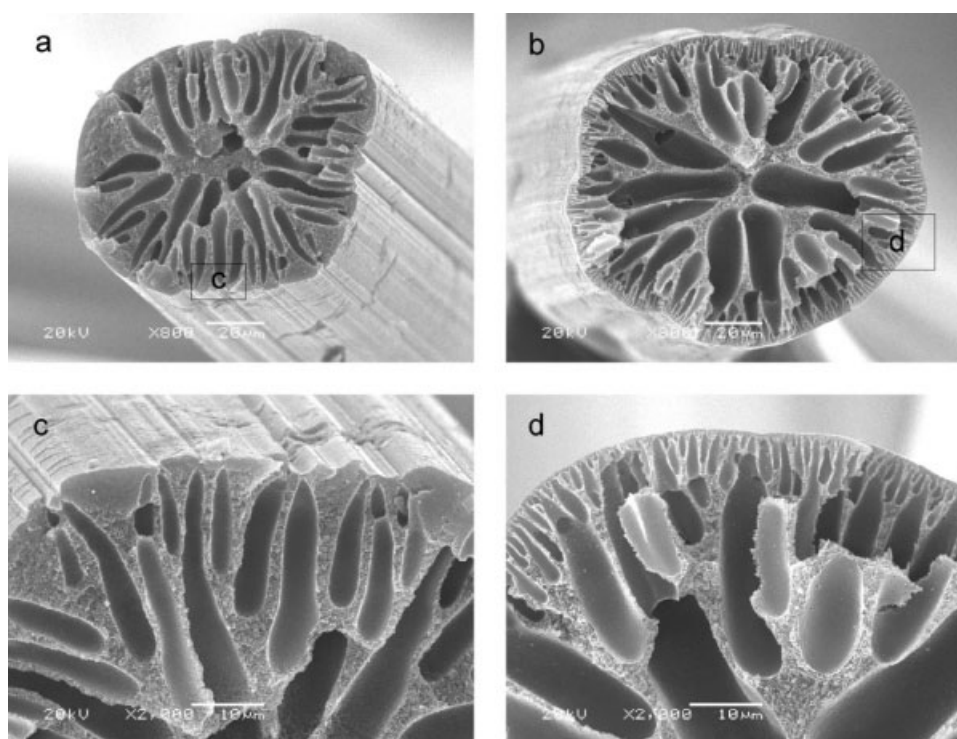


Figure 1 SEM photographs of the cross sections of the microfibers. The imprinted microfiber: a and c; the nonimprinted microfiber: b and d. Voltage: 20 kV; magnification: (a) and (b) $\times 800$; (c) and (d) $\times 2000$.

Recognition coefficient (α) was used to evaluate the recognition ability and can be defined as following⁸:

$$\alpha = \frac{[S]_{\text{imprinted}}}{[S]_{\text{nonimprinted}}} \quad (4)$$

where $[S]_{\text{imprinted}}$ is the BPA binding amount to imprinted microfibers ($\mu\text{mol/g}$), and $[S]_{\text{nonimprinted}}$ is the binding amount to nonimprinted microfibers ($\mu\text{mol/g}$).

Selectivity of the imprinted microfibers

The selectivity of the imprinted microfibers was studied by immersing the microfibers into aqueous solutions including BPA, phenol, hydroquinone (HDQ), or dibenzofuran (DBF) at room temperature, respectively. Then, the concentration of these compounds at different time intervals was monitored by a UV-vis spectrophotometer at 276 nm for BPA, 270 nm for phenol, 288 nm for HDQ, and 280 nm for DBF. All of the selectivity adsorption tests for the BPA, phenol, HDQ, and DBF were carried in single environment. Recognition coefficient (α) was used to evaluate the selectivity and can be calculated according to the eq. (4).

RESULTS AND DISCUSSION

Characterization of the MIPs microfibers

A wet-spinning method was employed to fabricate the BPA-imprinted PES microfibers from PES-DMAc-BPA solution. In the imprinting process, non-solvent water was selected as the coagulation medium, which was commonly used to prepare PES membrane. Here, water showed high solubility for DMAc but not for PES and BPA. Therefore, when the PES-BPA-DMAc solution was extruded into water, liquid-liquid phase separation that was caused by the rapid exchange of the solvent DMAc and water occurred. Simultaneously, imprinting occurred immediately during PES solidification, and the BPA template was retained in the solidified microfibers. With the completion of the exchange between the solvent and the nonsolvent, the microfibers were prepared. After extraction of the template molecules, imprinted microfibers were prepared. According to eq. (1), the diameters of the imprinted microfibers were 262.4 ± 15.2 and $81.2 \pm 9.3 \mu\text{m}$, which had no significant difference with the measured diameters (about $270 \mu\text{m}$ and $90 \mu\text{m}$, respectively) by micrometer. For the controlling, two kinds of nonimprinted microfibers with the diameters of about $265 \mu\text{m}$ and $85 \mu\text{m}$ were prepared.

The prepared PES microfibers were opaque in appearance due to the porous structure. Figure 1 shows the SEM photographs of the BPA-imprinted

microfibers (a) and the nonimprinted microfibers (b) which were magnified 800 \times , both the imprinted microfibers and the nonimprinted microfibers had the porous structure. Figure 1 also shows the SEM photographs of the BPA-imprinted microfibers (c) and the nonimprinted microfibers (d) which were magnified 2000 \times . As shown in the figure, skin layers were found both in the imprinted and nonimprinted microfibers, followed by which were finger-like structure, which was regarded as a typical structure for fibers prepared using the liquid–liquid phase separation technique. There was no significant difference between the imprinted and nonimprinted microfibers.

A little difference was found for the imprinted and nonimprinted microfibers. For the nonimprinted fiber, the thickness of the skin layer was small, followed by was small size finger-like structure, and then the big size finger-like structure; whereas for the imprinted fiber, the thickness of the skin layer was larger, and no small size finger-like structure was found. These might be caused by the hydrophobic BPA, which decreased the mass transfer in the phase separation and cumbered the forming of the cavities. The porosities of the imprinted and nonimprinted microfibers were about 63.3% and 66.9%, which were calculated according to the eq. (1).

Binding of BPA in various concentration solutions

To study the recognition ability of the BPA-imprinted microfibers, binding experiments of the thin microfibers with the diameters of about 85 μm were carried out firstly in various BPA concentrations (100, 200, and 400 μM BPA aqueous solutions) at room temperature. Figure 2 shows the kinetic curve of BPA to the imprinted [Fig. 2(a)] and nonimprinted [Fig. 2(b)] PES microfibers in BPA aqueous solutions. The binding amounts ($\mu\text{mol/g}$) increased with time and the saturated binding amounts were observed after about 10 h for all the solutions. It was noted that the amounts of BPA binding to the imprinted PES microfibers was higher than that to the nonimprinted ones in all the solutions. The saturated binding amounts of BPA were about 50.0, 87.0, 120.0 $\mu\text{mol/g}$ for the imprinted PES microfibers in 100, 200, and 400 μM BPA solutions, respectively; whereas those were 24.0, 43.0, and 70.0 $\mu\text{mol/g}$ for the nonimprinted PES microfibers, respectively. The recognition coefficients, which were calculated from eq. (4), ranged from 1.7 to 2.1.

With the increase of BPA concentration in the aqueous solutions, the binding amounts increased both for the imprinted and nonimprinted microfibers. These can be explained by the adsorption theory.²⁰ Langmuir sorption isotherm could be used

for the adsorption. The Langmuir equation was as follows:

$$\frac{[C_e]}{[Q]} = \frac{1}{k[Q]_{\max}} + \frac{[C_e]}{[Q]_{\max}} \quad (5)$$

where $[C_e]$ and $[Q]$ are the equilibrium concentration of BPA and the amount of adsorbed-BPA on per gram weight of PES; and k is the adsorption–desorption equilibrium constant related to the binding energy; $[Q]_{\max}$ is the maximum amount of adsorbed-BPA on per gram weight of PES.

The data were fitted to the linear form of Langmuir equation.

For the imprinted microfibers,

$$\frac{[C_e]}{[Q]} = 0.4723 + 0.0062[C_e] \quad k = 0.013,$$

$$[Q]_{\max} = 161.3, \quad r^2 = 1$$

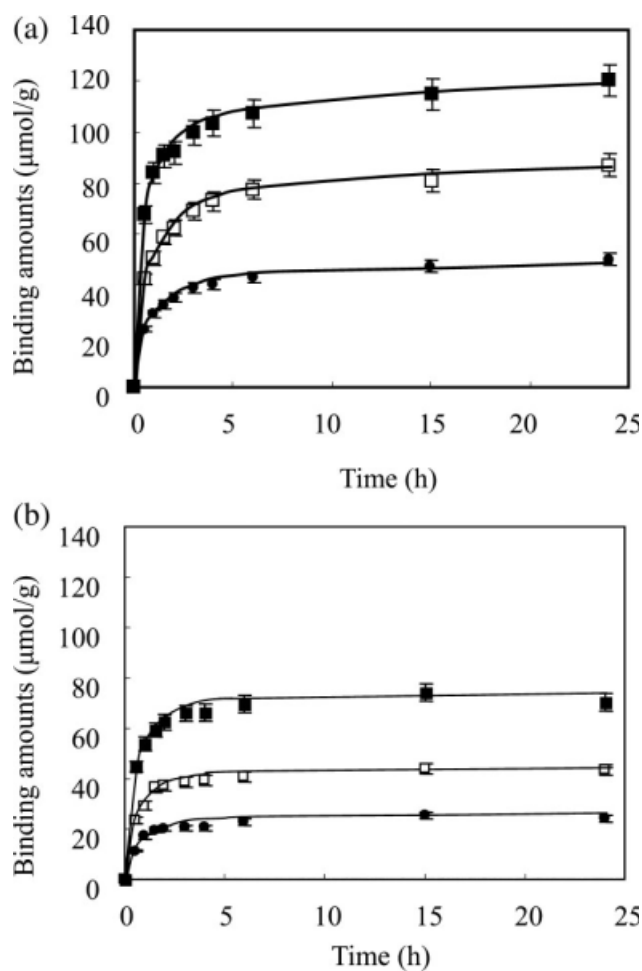


Figure 2 Time course of binding to the imprinted (a) and nonimprinted (b) microfibers with the diameter of about 85 μm in BPA aqueous solution, including 100 μM (\bullet), 200 μM (\square) and 400 μM (\blacksquare). Duplicate experiments gave the similar results.

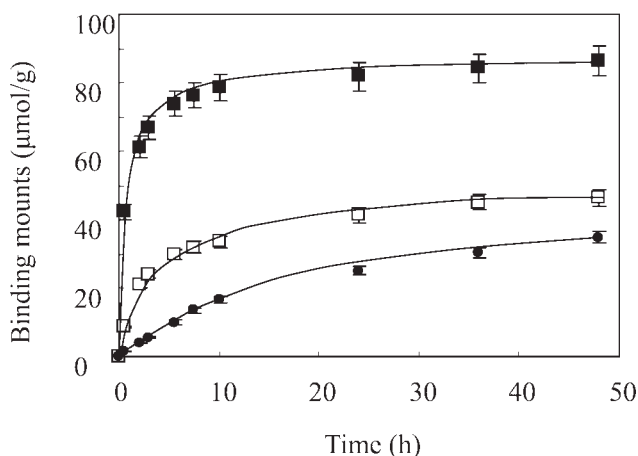


Figure 3 Time course of binding amounts in 200 μM BPA aqueous solutions. For the particles (\bullet), the microfibers with the diameter of about 265 μm (\square) and about 85 μm (\blacksquare).

For the nonimprinted microfibers,

$$\frac{[C_e]}{[Q]} = 2.3407 + 0.0069[C_e] \quad k = 0.003,$$

$$[Q]_{\max} = 144.9, \quad r^2 = 0.9989$$

With the increase of BPA concentration in the aqueous solutions, the equilibrium concentration increased; thus, the binding amounts increased both for the imprinted and nonimprinted microfibers.

The BPA binding amounts to the imprinted microfibers were higher than that to the nonimprinted ones. The nonimprinted microfibers bound BPA due to the hydrophobic interaction between the BPA and the PES and the porosity of the microfibers.²¹ For the imprinted microfibers, specific recognition sites formed by the template molecule played an important role in the BPA binding amounts, besides the hydrophobic interaction^{21,22} and the porosity. Furthermore, the hydrophobic and porosity effects acted as nonselective binding force in the BPA uptake to the imprinted PES microfibers.

Binding of BPA to PES fibers

In this study, two kinds of BPA-imprinted microfibers with different diameters were fabricated. Figure 3 shows the binding kinetics of BPA to the two kinds of BPA-imprinted PES microfibers and the BPA-imprinted PES particles (with the diameter of about 2300 μm). The saturated binding for the imprinted particles was observed after 60 h, whereas that was observed after about 35 h for the imprinted microfibers with the diameter of about 265 μm and was observed after about 10 h for the imprinted microfibers with the diameter of about 85 μm . The saturated binding amounts of BPA were about 32.0, 44.0, and

87.0 $\mu\text{mol/g}$ for the imprinted particles, imprinted microfibers with large and small diameters, respectively.

Clearly, the adsorption rates of the microfibers with different diameters are different. To analyze the BPA binding kinetics, the following equation was used.²³

$$A = B \times e^{K/t} \quad (6)$$

where A is the binding amounts; t is the time; B and K are the adsorption coefficients. Table I shows the calculated coefficients B and K for the particles, the microfibers with different diameters, respectively. It can be noticed that both of the B and K were higher for the microfibers with smaller diameter than those for the particles and the microfibers with larger diameter.

The adsorption rate can be deduced from the derivation of the binding amounts, thus from eq. (6), the adsorption rate can be written as follows:

$$v = \frac{dA}{dt} = -\frac{B \times K}{t^2} \times e^{\frac{K}{t}} \quad (7)$$

where v is the adsorption rate. According to this equation, the adsorption rate at any time t can be calculated and compared. The largest coefficients B and K for the microfibers with small diameter indicated that the adsorption capacity and adsorption rate were the largest.

Selectivity of the imprinted microfibers

To examine the selectivity, BPA-imprinted and non-imprinted microfibers with the diameter of about 85 μm were applied in BPA, phenol, HDQ, or DBF aqueous solutions, respectively. All of their concentrations were 200 μM . Figure 4 shows the binding amounts for BPA, phenol, HDQ, and DBF to the imprinted and nonimprinted microfibers, respectively. The binding amounts of BPA, phenol, HDQ, and DBF were about 88.0, 63.0, 75.0, and 65.0 $\mu\text{mol/g}$ for the imprinted microfibers, respectively; whereas those were about 42.0, 54.0, 59.0, and 45.0 $\mu\text{mol/g}$ for the nonimprinted microfibers,

TABLE I
Coefficients B and K for the Imprinted Microspheres and Microfibers with Different Diameters

	Particles ($d = 2300 \mu\text{m}$)	Microfibers ($d = 265 \mu\text{m}$)	Microfibers ($d = 85 \mu\text{m}$)
B	29.37	43.38	84.77
K	-4.51	-1.62	-0.69
Binding amounts	$A = 29.37$ $\times e^{-4.51/t}$	$A = 43.38$ $\times e^{-1.62/t}$	$A = 84.77$ $\times e^{-0.69/t}$

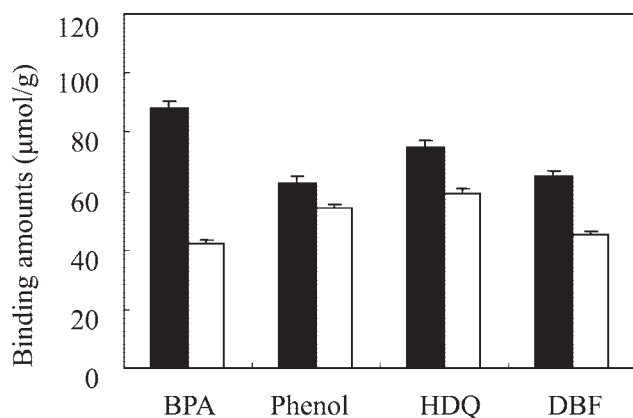


Figure 4 Binding amounts of BPA, phenol, HDQ, and DBF for the imprinted (■) and nonimprinted (□) microfibers with the diameter of about 85 μm.

respectively. The recognition coefficient (α) of BPA, phenol, HDQ, and DBF were 2.09, 1.17, 1.27, and 1.44, respectively, according to the eq. (4). Clearly, the recognition coefficient for BPA was much higher than that for the others. It can be deduced that special recognition sites for the BPA were formed in the imprinted microfibers so that they show selectivity for the BPA molecules.

CONCLUSIONS

BPA-imprinted polyethersulfone (PES) microfibers were prepared by using wet-spinning technique for the binding and recognition of bisphenol A (BPA). The binding amounts increased with the increase of the BPA concentration in solutions. The adsorption rate was higher for the microfibers with smaller diameter, since the binding sites located on the microfibers surface or near the surface are more accessible. The imprinted microfibers showed selectivity for BPA. Moreover, it is easy to prepare the imprinted microfibers by using this method, and the microfibers can be used directly for the binding and recogni-

tion. Because of the excellent adsorption capability, the microfibers can be used in environmental applications and chromatography.

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