

Molecularly Imprinted Polysulfone Membranes Having Acceptor Sites for Donor Dibenzofuran as Novel Membrane Adsorbents: Charge Transfer Interaction as Recognition Origin

Takaomi Kobayashi,* P. Sreenivasulu Reddy, Michiyoshi Ohta, Masanori Abe, and Nobuyuki Fujii

Department of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka 940-2188, Japan

Received October 2, 2001. Revised Manuscript Received February 14, 2002

Novel molecularly imprinted membranes having dibenzofuran (DBF) recognition were developed and binding properties of DBF were studied using the polysulfone membrane prepared by phase inversion imprinting. Polysulfone (PSf) having a phenyl-sulfone group and DBF template was solublized in dimethyl acetamide (DMAc) and the polymer solution was coagulated in water to prepare porous membranes. After template molecules were extracted from the membranes by washing with methanol, recognition experiments with DBF-imprinted membranes were carried out in methanol solution, water/methanol solution, and water solution for DBF and DBF analogues, dibenzodioxin (DBD), diphenyl ether (DPE), and benzodioxin (BDO). In water, high binding amounts of DBF and DBD were observed in the range of 28–39 $\mu\text{mol/g}$ capacity, but the recognition was very low. Methanol/water media showed high recognition of the imprinted membrane with a low binding capacity of DBF (4.5 $\mu\text{mol/g}$). These results indicated that nonselective binding occurred in the water media due to a hydrophobic effect. Evidence revealed that membrane recognition in methanol and methanol/water was effective for DBF because of charge transfer (CT) complexation between the donor DBF and acceptor phenyl-sulfone group of PSf. This kind of interaction was very useful for high retention and recognition of DBF as an efficient membrane adsorbent via donor–acceptor CT interaction.

Introduction

Molecular imprinting plays an important role in constructing molecule recognition sites in some polymers in tailor-made fashion.^{1,2} Related to recognition materials, separation and concentration by the imprinting polymer are important processes in chromatography,³ solid-phase extraction,⁴ and membrane.⁵ Such recognition processes would be extremely useful as adsorbents to environmental estrogens⁶ for dibenzo-*p*-dioxins (DBD) and dibenzofurans (DBF) analogous, which are toxic compounds in terms of environmental

pollution and impact.⁷ Since people in advanced countries have faced severe dioxin problems, some methods to treat dioxin-polluted waters and wastewater is essential. Actually, the activated carbon adsorption method is widely used for dioxin removal from municipal and other waste incinerators.⁸ However, highly effective adsorbents with selectivity should be necessary for environmental toxic compounds. To develop a novel type of high selectivity adsorbing materials for such target molecules, a molecular-imprinted polymer (MIP) is one extensively researched approach for preparing host cavities of specific selective binding. In general, a molecularly imprinted cross-linked polymer retains template volumetric spaces for guest binding and is used as a selective recognition material in several fields.⁹ For their molecular-imprinting methods, two main approaches such as covalent and noncovalent imprinting were developed by Wulff¹ and Mosbach and co-workers,² respectively. In fact, MIP materials were applied to environmental estrogen and displayed selective adsorption using these methods. For example, covalent binding

* To whom correspondence should be addressed.

(1) (a) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812. (b) Sellergren, B.; Lepisto, M.; Mosbach, K. *J. Am. Chem. Soc.* **1988**, *110*, 5850.

(2) (a) Bartsch, R. A.; Maeda, M. *Molecular and Ionic Recognition with Imprinted Polymers*; ACS Symposium Series 703, American Chemical Society: Washington, DC, 1998. (b) Allender, C. J.; Andersson, H. S.; Brain, K. R.; Ramstrom, O. Ed. *Anal. Chim. Acta* **2001**, *435*.

(3) (a) Kempe, M.; Mosbach, K. *J. Chromatogr. A* **1995**, *694*, 3. (b) Takeuchi, T.; Haginaka, J. *J. Chromatogr. B* **1999**, *728*, 1 and references therein.

(4) Daulis, K.; Klibanov, A. M. *Biotechnol. Bioeng.* **1992**, *39*, 176. Vlatakis, G.; Andersson, L. I.; Muller, R.; Mosbach, K. *Nature* **1993**, *361*, 645.

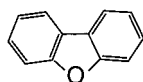
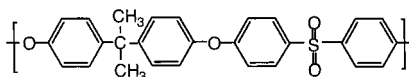
(5) (a) Kobayashi, T.; Wang, H. Y.; Fujii, N. *Chem. Lett.* **1995**, 927. (b) Yoshikawa, M.; Izumi, J.; Ooi, T.; Kitao, T.; Guiver, M. D.; Robertson, G. P. *Polym. Bull.* **1998**, *40*, 517. (c) Mathew-Krotz, J.; Shea, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 8154.

(6) Lubke, M.; Whitcombe, M. J.; Vulfson, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 13342.

(7) (a) Rawls, R. L. *Chem. Eng. News* **1979**, *12*, 23 (b) Kilbane, I. I.; John, J. U.S. Patent Appl. 5,750,065, 1998.

(8) Yang, R. T.; Long, R. Q.; Padin, J.; Takahashi, A.; Takahashi, T. *Ind. Eng. Chem. Res.* **1999**, *38*, 2726.

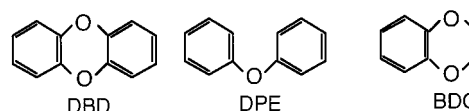
(9) (a) Shea, K. J.; Sasaki, D. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4109. (b) Matsui, J.; Nicholls, I. A.; Takeuchi, T.; Mosbach, K.; Karube, I. *Anal. Chim. Acta* **1996**, *336*, 71. (c) Kriz, D.; Ramsrom, O.; Mosbach, K. *Anal. Chem.* **1997**, *69*, 345A.

Scheme 1. Dibenzofuran (DBF)**Scheme 2. Chemical Structure of Polysulfone (PSf)**

of tetrachlorodibenzodioxin (TCDD) was performed in cross-linked polymers with pmol/g capacity for the capture.⁶ There were also reports of MIP adsorbents with uniform-size polymer for phenolic estrogenic compounds.¹⁰ Therefore, selective adsorption of such toxic compounds by MIP materials is considered increasingly useful for toxic removal from waste solution. However, still little was known about MIP uses for environmental estrogen compounds functionalized with a noncovalent imprinting method. In addition, little research has been done for application work to environmental estrogenic compounds in the MIP field.

We have developed a noncovalent imprinting method for MIP preparation, which makes use of the phase inversion process.¹¹ The resultant imprinting membranes showed permselective recognition of the target molecules and were very useful for selective binding and continuous operation to treat for large amounts of solute solution. Because of these advantages, it is very convenient to concentrate environmental pollutant compounds, which are present in extreme dilute concentration in wastewater. More recently, with use of phase inversion imprinting for an environmental estrogenic compound, dibenzofuran (DBF) (Scheme 1), poly(vinyl chloride) (PVC) and other polymers were used as imprinted materials.¹² However, the recognition characteristic as a membrane adsorbent for DBF was limited to selective binding with DBF structural analogies. In the present work, research effort was undertaken, aiming at using the DBF-imprinted polymer membrane made of polysulfone (PSf) (Scheme 2).

It is well-known that PSf has good mechanical stability and antisolvent properties¹³ and can produce a good-quality membrane with a common phase inversion procedure.¹⁴ To prepare the DBF-imprinted PSf membrane, thus, phase inversion imprinting was applied.^{15–18} We concentrated on recognition properties of DBF-imprinted membranes for DBF and its analogous. As DBF analogues, DPE, DBD, and BDO (Scheme 3) were used. We focused on how the imprinted PSf was functionalized in recognition for DBF by membrane

Scheme 3. Chemical Structure of DBF Analogues

adsorption. Additionally, the solvent effect on DBF recognition was studied and the recognition origin was discussed.

Experimental Methods

Materials. Polysulfone (PSf), having Mw of 30,000, was received from Polysciences, Inc. (Warrington, PA). Dimethyl acetamide (DMAc) and methanol (MeOH) were purchased from Nakarai Tesque, Inc. (Japan). DBF and its analogues were purchased from Tokyo Kasai Kogyo Co., Ltd. (Japan) and DBD was from Ultrascientific Ltd. (RI). All 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 and Characterization of Molecularly Imprinted Polymer Membrane. MIPs were prepared by a modified procedure of the phase inversion method as reported previously.¹² PSf and template DBF concentration were prepared with a concentration of 25 and 5 wt % in DMAc, respectively. Resultant polymer solution was cast on a glass plate at 50 °C and coagulated in distilled water at 20 °C to prepare a porous membrane. Extraction of the template molecules from solidified polymers was carried out by washing them with methanol for several days at 40 °C. Using a UV-vis spectrophotometer (Shimadzu, UV-190), extraction was confirmed with the disappearance of 280-nm DBF absorption in the extracted methanol solutions. In addition, template extraction from polymers was also confirmed by FT-IR spectral analysis for a thin membrane with about 20-μm thickness. IR spectra of imprinted and unimprinted thin membranes were measured with FT-IR 8200 (Shimadzu, Japan). Fluorescence spectroscopy (Shimadzu 5300 spectrofluorometer) and UV-visible reflection absorption spectrometry (V-570 spectrophotometer with ISV-469 (Jasco Co. Japan)) were adopted for characterization of DBF-imprinted membranes. A scanning electron micrograph (SEM) (JSM-5310 LVB (JEOL)) was used for morphology observation of the membrane cross section and surface for the imprinted membrane. The sample preparation for SEM measurements was followed by a previous method.¹⁵

Recognition Experiments. Template and substrate recognition was studied by both binding experiments of heterogeneous batch and membrane permeation at 20 °C. For the batch experiments, 20-mg of imprinted membrane was added into 5 mL of methanol solution containing 100 μM concentration of DBF or its analogues. Then, the concentration at different time intervals was monitored by a UV-vis spectrophotometer for 280-nm DBF absorption. Permeation experiments were carried out by a pressure-driven setup at 1 kg/cm² using an Amicon-type 8050 cell with 50-mL volume. DBF or its analogues concentration in feed solution was 250 μM and the concentration in permeate solutions was analyzed by HPLC (CCPD, Toyo Soda Co.) with a TSKgel-ODS80 column (1.5 × 20 cm). The eluent solution was MeOH:H₂O = 7:3(v/v) and the eluent rate was operated at 0.5 mL/min. The absorbance of the permeate solution was monitored at 280 nm by a UV-vis detector (UV8000) connected to the HPLC apparatus. Binding amounts, [S]_b (μmol/g of polymer) of template or analogues to the membrane were calculated by the following equation,

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

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

(10) Haginaka, J.; Sanbe, H. *Chem. Lett.* **1999**, 757.

(11) Kobayashi, T.; Wang, H. Y.; Fukaya, T.; Fujii, N. Molecular Imprinted Membranes Prepared by Phase Inversion of Polyacrylonitrile Copolymers Containing Carboxylic Acid Groups. In *Molecular and Ionic Recognition with Imprinted Polymers*; Bartsch, R. A., Maeda, M., Eds.; ACS Symposium Series 703; American Chemical Society: Washington, DC, 1998; p 188.

(12) Reddy, P. S.; Kobayashi, T.; Fujii, N. *Eur. Polym. J.* **2002**, 38, 779.

(13) Staude, E.; Breitbach, L. *J. Appl. Polym. Sci.* **1991**, 43, 559.

(14) Pinnau, I.; Koros, W. J. *J. Appl. Polym. Sci.* **1991**, 43, 1491.

(15) Wang, H. Y.; Kobayashi, T.; Fujii, N. *Langmuir* **1996**, 12, 4850.

(16) Reference 2a in Chapter 13, p 188.

(17) Wang, H. Y.; Kobayashi, T.; Fujii, N. *Langmuir* **1997**, 13, 5396.

(18) Reddy, P. S.; Kobayashi, T.; Fujii, N. *Chem. Lett.* **1999**, 293.

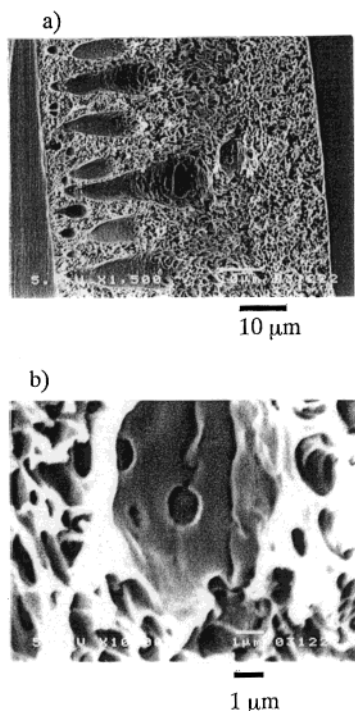


Figure 1. SEM photographs of the (a) cross section and (b) surface of DBF-imprinted membranes.

Results and Discussion

Characteristics of MIP Membranes. Imprinted polymers made of PSf were prepared by the phase inversion method from PSf–DBF–DMAc solution. In the imprinting process, nonsolvent water was selected as the coagulation medium, which was commonly used.¹⁹ Here, water shows high solubility for DMAc but not for PSf and DBF. Thus, imprinting occurred immediately during PSf solidification in water; DBF template was retained in the solidified membrane. The preparing PSf polymer membranes were opaque in appearance and satisfactorily strong for a thin membrane. As shown in Figure 1, scanning electron micrograph (SEM) photographs were measured for the cross section and surface of the PSf membranes. In the total cross section of about 80-μm thickness, many macrovoids on the left side of the picture (a) were observed. The macrovoids distributed in porous PSf networks contained pores of $\approx 1\text{-}\mu\text{m}$ diameter as shown in part b, which was magnified 10000 \times . In this case, the pores were observed on the membrane surface, which faced the water medium during solidification. The SEM morphology suggests that the PSf transformation from cast solution to the solid state occurred quickly in poor water solvent and followed by instantaneous demixing of PSf precipitation.¹⁹ This also suggests that the solvent exchange between DMAc and water proceeded in the presence of the template molecules. Thus, imprinting sites of the template were forming during the coagulation process in water.

Binding of Various Substrates to Imprinted Membranes. To study the recognition ability of the DBF-imprinted membranes, binding experiments were

carried out in methanol with 100 μM substrate concentration at 20 $^{\circ}\text{C}$. Here, DBF analogue compounds of DBD, DPE, and BDO were used as a binding substrate. In methanol, it is known that PSf undergoes no swelling because methanol is a nonsolvent for the polymer.¹³ In batch experiments, the imprinted membrane was soaked in respective substrate methanol solutions and the template concentration of the bulk solution was estimated at various times. Figure 2 shows the amounts of substrate bound to (a) DBF-imprinted PSf and (b) nonimprinted PSf. Values of binding amounts ($\mu\text{mol/g}$) of each substrate increased with time and saturated binding was observed in 9–24 h. It is noted that DBF binding to the imprinted PSf was higher than that of the nonimprinted one. The saturation binding amounts of DBF were 4.5 and 1.4 $\mu\text{mol/g}$ for the imprinted and nonimprinted PSf, respectively. In addition, the DBF-imprinted PSf showed high binding for DBD, although another analogues of DPE and BDO showed less binding to the imprinted PSf. In Figure 2b for DBD, high binding was observed in the nonimprinted PSf. This implies that DBD is taken to PSf with nonselective binding.

To obtain further information about uptake behavior of the imprinted PSf for their molecules, we examined the binding in methanol/water and water solutions. Figure 3 shows binding amounts of various substrates to DBF-imprinted membranes in (a) methanol/water and (b) water. Data of the dashed lines were observed in nonimprinted PSf. The time profiles of DBF binding presented similar saturation binding in both solutions. Table 1 lists the values of $[S]_b$, which are binding amounts at saturated binding in various solution systems. In addition, the ratio of the saturation binding amounts obtained between the DBF-imprinted and nonimprinted membranes is also compared. Here, the value of ratio $\alpha_{(\text{imprint factor})}$ for each substrate is defined in the following equation:

$$\alpha_{(\text{imprint factor})} = [S]_{(\text{imprint})}/[S]_{(\text{unimprint})} \quad (2)$$

The saturated binding amounts of DBF in methanol/water were 21.5 and 13 $\mu\text{mol/g}$ for the imprinted and nonimprinted PSfs, respectively. In water, the binding amount of DBF to the imprinted membrane was 39 $\mu\text{mol/g}$ and the nonimprinted one was 32 $\mu\text{mol/g}$. Apparently, the binding of both DBF and its analogues was enhanced in water. However, the obtained value of α means less selectivity in water because the α values were in the range of 0.98–1.1 for the water system. The high α value of DPE in water is due to less binding of DPE in nonimprinted PSf. It is interesting to note that the α value observed in methanol was 3.3 and in methanol/water 1.8 for DBF. This indicates that the binding of DBF occurred with high selectivity in methanol. Thus, the water effect on the DBF binding means that the higher binding in water is due to a hydrophobic interaction between the substrate and PSf. The addition of methanol disrupted ice-like structured water molecules around DBF in a PSf environment. Also, data show that the hydrophobic effect acts as a nonselective binding force in the solute uptake to the imprinted PSf.

Membrane Adsorbents in Permeation of DBF Solution for Imprinted PSf. Because imprinted membranes have properties of specific binding and perm-

(19) (a) Radovanovic, P.; Thel, S. W.; Hwang, S. T. *J. Membr. Sci.* **1991**, *65*, 213. (b) Radovanovic, P.; Thel, S. W.; Hwang, S. T. *J. Membr. Sci.* **1992**, *65*, 231.

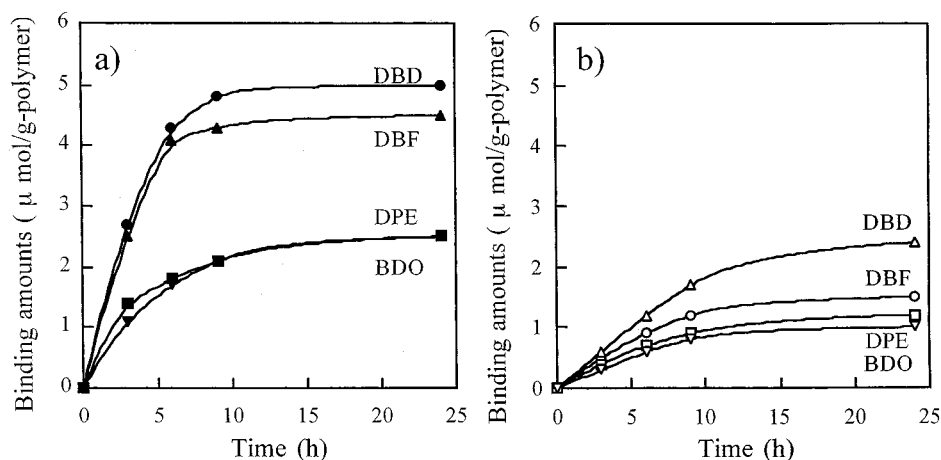


Figure 2. Time course of binding to (a) DBF-imprinted membranes and (b) nonimprinted membranes in methanol. (●,○) DBF, (▲, △) DBD, (■, □) DPE, and (▼, ▽) BDO. Binding experiments were carried out in 100 μ M solute concentration at 25 $^{\circ}$ C.

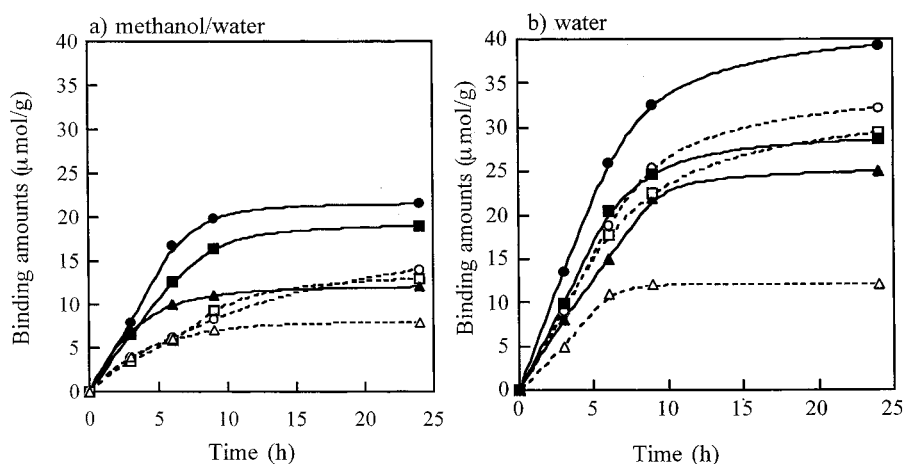


Figure 3. Time course of solute binding observed in batch experiments of (a) methanol/water and (b) water media. Solid line and dashed line were for imprinted and nonimprinted membranes, respectively. Symbols of solute were the same as those shown in Figure 2.

Table 1. Summarized Values of Binding Amounts and Imprinted Factor in Various Solutions

	DBF		DBD		DPE	
	[S] _b (μ mol/g)	α	[S] _b (μ mol/g)	α	[S] _b (μ mol/g)	α
methanol	5	3.3	4.5	1.8	2.5	2.0
methanol/water	21.5	1.8	19	1.4	10	1.2
water	39.3	1.1	28.6	0.98	25	2.1

selectivity for the target molecule, they were applied in various chemical and biological fields.^{5,20,21} We mentioned that imprinted membranes prepared by the phase inversion method exhibit the excellent property of selective absorption for theophylline^{5a} and amino acid molecules.²² In the PSf imprint membrane for DBF, we confirmed the morphology of the DBF-imprinted membrane (Figure 1) by SEM and the imprinted membranes had a porous structure, which is suitable for the permeation membrane.²³ Thus, such a porous membrane was successfully applied as membrane material

for low-pressure permeation of solute solution for membrane absorbents.

In permeation experiments of DBF solution or its analogue solution, both volume flux and solute concentration were determined at different time intervals. Permeation of the methanol solution or methanol/water solution with 250 μ M solute concentration was carried out with 1 kg/m² applied pressure. The volume flux of 3×10^{-7} and 3.3×10^{-7} m³/(m² s) for methanol and methanol/water solutions was obtained during the permeation experiments. It could be seen that the volume flux in methanol/water was slightly reduced to 3×10^{-7} m³/(m² s) with an increase of permeation time at 24 h. Figure 4 shows binding amounts of DBF and its analogues by the DBF-imprinted membrane in methanol and methanol/water. The binding amounts of the solute to the membrane were increased with an increase of the time and almost became constant at 24 h. The saturation behavior of the binding amounts suggests solute binding to the volumetric space of the imprint sites. The values of the binding amounts are listed as [S]_p in Table 2. The saturated value of DBF binding amounts was 102 μ mol/g for methanol/water solution and 8 μ mol/g for methanol solution. To compare the binding amounts of the substrate between batch and permeation experiments, the values of [S]_b for batch

(20) Hong, J.; Anderson, P. E.; Qian, J.; Martin, C. R. *Chem. Mater.* **1998**, *10*, 1029.

(21) Piletsky, S. A.; Panasyuk, T. L.; Piletskaya, E. V.; Nicholls, I. A.; Ulbricht, M. *J. Membr. Sci.* **1999**, *157*, 263.

(22) Reddy, P. S.; Kobayashi, T.; Fujii, N. *Eur. Polym. J.* **2002**, *38*, 521.

(23) Reference 11, p 58.

Table 2. Saturated Binding Amounts $[S]_p$ of DBF and Its Analogues and Volume Flux of Methanol and Methanol/Water Solution for Permeation Experiments^a

	DBF			DBD			DPE		
	$[S]_p$ ($\mu\text{mol/g}$)	flux ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	$[S]_b$ ($\mu\text{mol/g}$)	$[S]_p$ ($\mu\text{mol/g}$)	flux ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	$[S]_b$ ($\mu\text{mol/g}$)	$[S]_p$ ($\mu\text{mol/g}$)	flux ($\text{m}^3/\text{m}^2 \cdot \text{s}$)	$[S]_b$ ($\mu\text{mol/g}$)
methanol/water	102	3.3×10^{-7}	170	59	3.3×10^{-7}	120	17	3.3×10^{-7}	70
methanol	8	3×10^{-7}	27	7	3×10^{-7}	25	3	3×10^{-7}	12

^a Permeation of the solute solution was carried out under N_2 feed pressure with $1 \text{ kg}/\text{cm}^2$. Concentration of solute in permeated solution with a small quantity was evaluated by HPLC. $[S]_p$ and $[S]_b$ were saturation binding amounts of substrate for permeation and batch experiments, when the substrate concentration was $250 \mu\text{M}$.

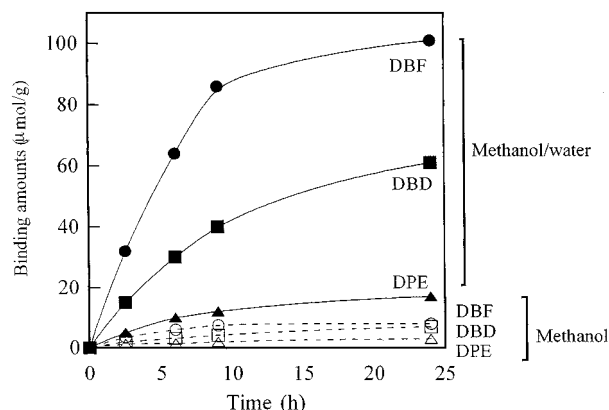


Figure 4. Time course of solute binding to DBF-imprinted membranes in permeation under $1 \text{ kg}/\text{cm}^2$ pressure. Solid lines were for methanol/water solution and dashed lines for methanol solution. Binding experiments were carried out in $250 \mu\text{M}$ solute concentration at 25°C .

experiments were measured in $250 \mu\text{M}$ concentration and were listed in Table 2. The obtained $[S]_b$ of DBF was 170 and $27 \mu\text{mol/g}$ for batch experiments performed in methanol/water and methanol, respectively. The binding was evidently decreased in the DBF permeation experiments. We observed similarly in amino acid-imprinted Nylon membrane²² that the saturation binding of permeation experiments was somewhat lower than that of batch experiments. Because the permeation was under pressure-driven experiments, the imprinted sites may change the complementary structure to the DBF. This may be due to the decrease of DBF binding to the imprinted sites under hydraulic flow condition operated with $1 \text{ kg}/\text{cm}^2$ pressure.

In permeation for DPE, the DBF-imprinted membrane bound 17 and $3 \mu\text{mol/g}$ capacity in methanol/water and methanol, respectively, but the binding amounts were lower than those for DBF. A similar tendency was also observed in batch experiments for DBF and DPE binding. As compared with their chemical structures of DBF and DPE, of which the molecular weights were 168 and 170, respectively, the difference may be due to free rotation of the phenyl ring on the ether bond of DPE. The rotation is completely restricted in DBF. Therefore, the restriction may provide a difference in the retention by the imprinted membrane. There is another interesting fact that DBD binding was higher than DPE. In methanol/water, DBD could be bound to the DBF-imprinted membrane with 59 and $120 \mu\text{mol/g}$ to the imprinted membrane for permeation and batch experiments, respectively. Therefore, the imprinting encoded the volumetric size of the flat shape template molecule in the PSf segments, although the data suggest somewhat loose recognition of the DBF-imprinted membrane.

Interaction between DBF and PSf. In our previous paper,¹² several polymers of PVC, polystyrene (PSt), polyacrylonitrile (PAN), and PSf were used for DBF imprinting. In these polymers, DBF showed high binding to DBF-imprinted PVC. IR data suggested that the DBF ring interacted with the chlorine of PVC. However, for PSt and PAN with phenyl and cyano groups DBF showed only little binding with low selectivity to the DBF-imprinted polymers. Therefore, it is necessary to involve scaffolding sites for molecular imprinting of DBF in the polymer segments. In the present work, the polymer of DBF imprinting is PSf with a sulfone group and ether linkage between phenyl rings (Scheme 2). To research PSf and DBF interaction, FT-IR analysis was carried out. The difference in FT-IR spectra of (a) DBF, (b) PSf, and (c) imprinted PSf obtained before the template DBF extraction is shown in Figure 5. In these cases, IR bands for (b) PSf at 1245 cm^{-1} corresponded to $\text{S}(=\text{O})_2$ asymmetric stretching and 1150 and 1050 cm^{-1} to symmetric stretching.¹⁶ Also, $\text{C}-\text{O}-\text{C}$ stretching of the main chain of PSf appeared near 1015 cm^{-1} . IR bands between 800 and 900 cm^{-1} were for $\text{S}-\text{O}-\text{C}$ stretching. Aromatic bending peaks at 715 , 691 , and 557 cm^{-1} were assigned to out-of-plane CH bending.²⁴ In the (a) spectrum for DBF, the IR band around 1200 cm^{-1} was assigned to asymmetric $\text{C}-\text{O}-\text{C}$ stretching and 970 – 1030 cm^{-1} to symmetric stretching.²⁵ The bands of 720 and 750 cm^{-1} resulted from out-of-plane aromatic $\text{C}-\text{H}$ bending of DBF. In the (c) spectrum of PSf membrane with DBF, both characteristic IR bands of PSf and DBF are present. However, a difference between spectrum (a) and (c) was apparently observed in DBF bands. The 750 and 720 cm^{-1} $\text{C}-\text{H}$ bending of the DBF peak slightly shifted to 755 and 725 cm^{-1} in the imprinted PSf. The strong 928-cm^{-1} band, arising from phenyl bending completely disappeared and the 1200-cm^{-1} stretching band appeared near 1185 cm^{-1} in spectrum (c). Thus, IR evidence indicates that the electronic state of the DBF aromatic ring is strongly influenced in the neighboring PSf environment.

Because IR data suggested the presence of interaction between DBF and PSf, we further examined absorption spectra of DBF in PSf. Here, transparent PSf films were prepared from 25 wt % PSf–DMAc solution with 5 and 10 wt % DBF under evacuation. Figure 6 shows reflection absorption spectra of the PSf without and with DBF. The absorption band for DBF in dimethylsulfoxide (DMSO) showed 283 nm of transmittance line, assigned to the phenyl ring B-band. When DBF was added to PSf

(24) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons Inc.: New York, 1991; p 183.

(25) Pohland, A. E.; Yang, G. C. *J. Agric. Food Chem.* **1972**, *20*, 1093.

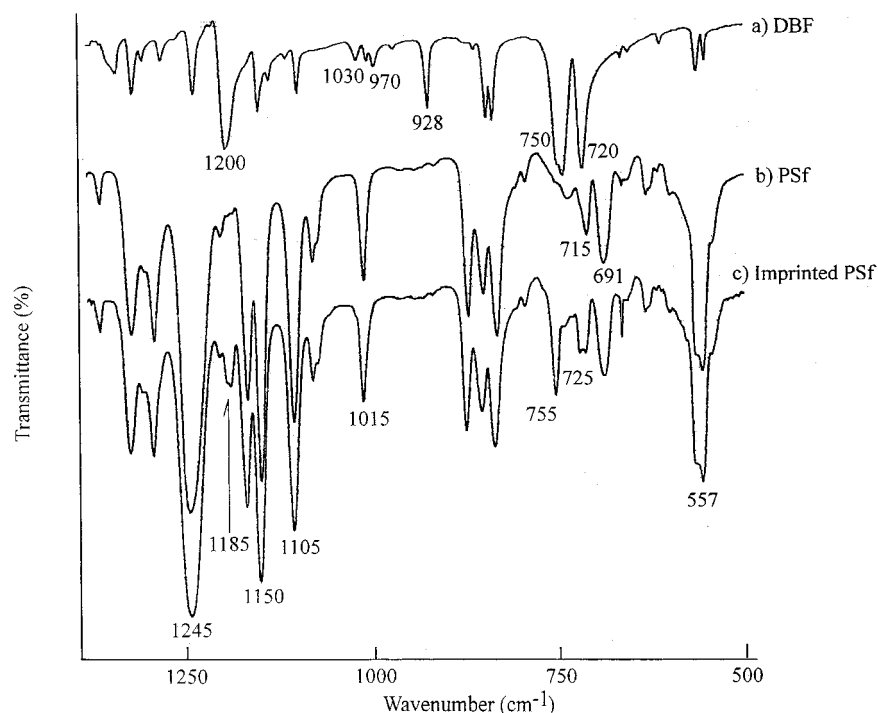


Figure 5. FT-IR spectra of the (a) DBF template and PSf membrane (b) before and after DBF extraction.

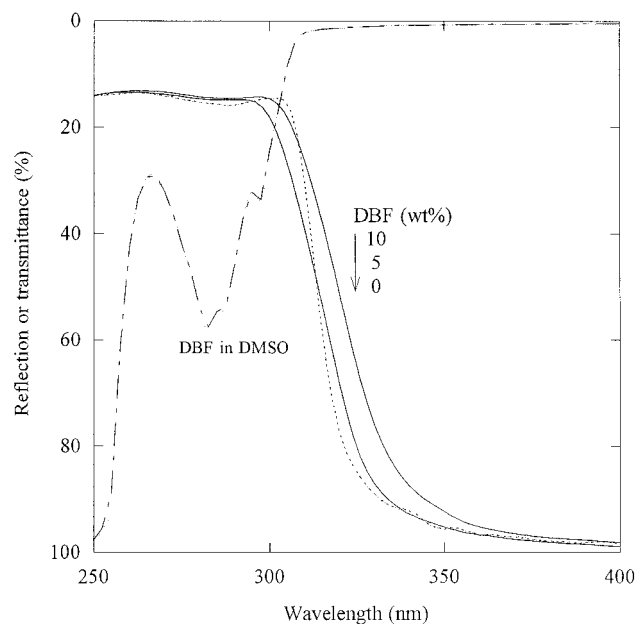


Figure 6. Reflection absorption spectra of PSf films with different contents of DBF. Absorption spectrum of DBF in DMSO was shown by a dashed line (---).

film, the absorption shoulder near 320–360 nm was shifted to the longer wavelength side. This is evidence that the electronic condition of the DBF ring was disturbed by interaction with PSf segments.

Figure 7 presents fluorescence spectra of the PSf films prepared from PSf solution with 5 and 10 wt % DBF concentration. The 280-nm excitation beam was irradiated. For comparison, we measured emission spectra of DBF in methanol and DMSO solution and pellet. DBF showed monomer emission in methanol and DMSO at 312 and 320 nm, respectively. It can be seen from Figure 7a that DBF pellet showed monomer emission near 334 nm and a weak excimer band near 430 nm. Also, PSf film without DBF showed a weak emission band near

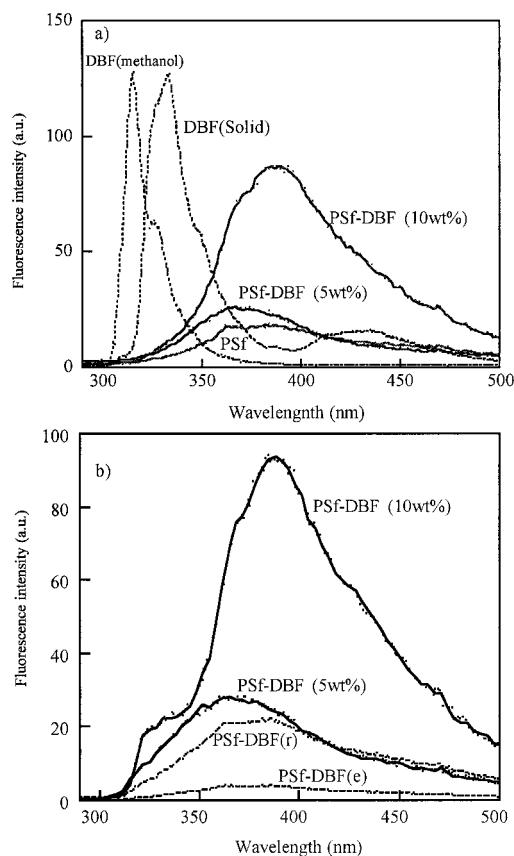
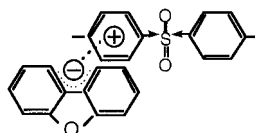


Figure 7. Fluorescence spectra of (a) PSf films and (b) membranes containing DBF. Excitation was carried out at 280 nm. DBF solid pellet with 1-cm diameter and 1-mm thickness was prepared by pressing DBF under 10 kg/cm² pressure. The dashed lines in Figure 7b were emission spectra of PSf-DBF (e) and PSf-DBF(r), which were measured before and after the saturation binding experiments in 100 μ M DBF concentration (Figure 3a), respectively.

360–400 nm. In contrast, the PSf-DBF films showed no monomer and excimer emission. The PSf-DBF film

Scheme 4. Charge Transfer Complexation between DBF and PSf Residue

emitted a structureless band near 360–450 nm. Also, fluorescence spectra of the DBF-imprinted membranes prepared by phase inversion imprinting are shown in Figure 7b. The DBF-imprinted membranes prepared from phase inversion of PSf solution containing 5 and 10 wt % of DBF concentration emit similarly the structureless band near 360–450 nm. It is noted that when the DBF content was increased from 5 to 10 wt % in the membrane, the emission maximum of 365 nm was shifted to 390 nm. Evidently, DBF addition enhanced emission intensity near 390 nm. We also confirmed that the structureless emission band near 360–450 nm was very weak after the DBF extraction (PSf-DBF(e)) and became high after rebinding experiments of DBF to the imprinted membrane (PSf-DBF(r)). Obviously, these mean that the emission species was formed in the imprinted membrane when DBF was taken into the membrane. The spectroscopic data strongly suggested that there is a charge transfer (CT) complex between DBF and PSf. In DMSO containing the S=O group, the emission was only with the monomer band near 320 nm. Hence, phenylsulfone segments of PSf may form a CT complex with DBF (Scheme 4). Under UV irradiation, the complex produced exciplex²⁶ and had an emission with a structureless broad band near 350–400 nm. Exciplex formation implies that donor–acceptor interaction is present in the PSf–DBF film. As il-

lustrated in Scheme 4, the S(=O)₂ group is capable of accepting electronic charge by the resonance effect.²⁷ Thus, it is stabilizing negative charge in the phenyl ring. In the PSf environment, the DBF molecule acts as a donor to the PSf acceptor segments. Accordingly, these spectral analyses of DBF–PSf mean that the imprinting materials would give a CT complex between DBF and PSF. In addition, high recognition in methanol suggests that such donor–acceptor interaction behave as recognition forces for DBF imprinting. The present work is the first example of a CT complex as an imprinting origin.

Conclusions

The present study suggested that DBF-imprinted PSf membranes could recognize DBF molecules well, which were used as a template for phase inversion imprinting. These results showed that DBF-imprinted membranes could be used for efficient adsorption of DBF. While good selectivity was observed in methanol solution, lower binding property occurred with imprinted membranes. It was found that an aqueous methanol medium provided successful binding with high recognition of DBF. Evidence of the imprinting PSf was the first report of imprinting uses as membrane absorbents. In addition, CT complexation was an important factor of recognition origin in DBF imprinting. Because PSf provides excellent mechanical, thermal, and chemical stability, further efforts for functional molecular imprinting are now in progress.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (entitled “The environmental risk of endocrine disruptor”; No. 13027227) and (C) (No. 12650764) from the Ministry of Education, Science, Sports, Culture and Technology, Japan.

CM0109692

(26) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley International: London, 1970; p 415.

(27) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 3th ed.; McGraw-Hill Ltd.: New York, 1970; p 807.