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Hybrid molecularly imprinted membranes for targeted bisphenol derivatives

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Abstract

Bisphenol A (BPA) imprinted polymer, which was prepared with BPA methacrylate and divinyl benzene (DVB), was hybridized in porous membrane scaffolding of polystyrene (PS), cellulose acetate (CA), nylon 66 (Ny) and polysulfone (PSf) by phase inversion process. Resultant hybrid imprinted membranes showed high capture ability to the BPA having 148, 142 and 158 μmol/g for the hybrid CA, Ny and PSf scaffolds, respectively. Relative to corresponding scaffold polymers in the absence of BPA imprinted polymer, the hybrid PSf membrane had excellent recognition to the BPA. Scatchard analysis to the hybrid PSf scaffold membrane showed equilibrium binding constants of 20,700, 19,100 and 17,300 M^{-1} for BPA, bisphenol E and bisphenol F, respectively. The permselective separation of 2-(4-hydroxyphenyl)ethyl alcohol (HPA) and the bisphenol derivatives was accomplished by using the hybrid membranes for the mixture solution. Evidence of the separation of the mixture indicated that separation factor of BPA and HPA was estimated as 11.5, 8.1 and 10.8 for the hybrid CA, Ny and PSf, respectively. Effect of hybrid imprinted membrane on the enhanced separation ability was also discussed.

Keywords: Molecular imprinted membrane; Molecular recognition; Hybrid membrane; Adsorption; Endocrine disruptor

1. Introduction

Bisphenol A (BPA), which is known as endocrine disruptor, affects the reproduction and development of animal organism in extra-diluted concentration. In living organism, BPA acts by estrogen receptor as female sex hormone [1]. 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 [2–4]. In order to develop a novel type of highly selective adsorbing materials with artificial host sites of both specificity and high capacity, we believe that molecular imprinting is one of extensive research approach. So far, the BPA imprinted polymers showed selective and high adsorption nature to BPA [5–7]. In general, most technologies of molecular imprint polymer (MIP) are based on template polymerization using functional monomers and cross-linked monomer in the presence of template molecules [2,4–8]. In their BPA imprinted polymers, the cross-linked polymers retained the template volumetric spaces for the guest binding. However, these techniques have contained problems in fabrication of the MIPs for both membrane and film applications due to its powder shape. We have studied molecularly imprinted membranes, which display selective adsorption to target molecule [9–11]. The technique has been expanding to other research projects, which focus on separation interests on medical [12] and food fields [13]. The MIP membranes by using phase inversion process showed recognition and binding of the target molecule in continuous permeation operation to treat large amount of solute solution. Therefore, it can be believed that this kind of membrane promises a challenging technology for the selective binding to the environmental disruptor targets.

In the present work, we extend such advance of imprinting technique to develop novel imprinted membranes by hybridizing cross-linked MIP powder into membrane scaffolding. Herein, novel evidence is included for advantage in MIP membrane technique, which can extend to several fields in near future. We make use of phase inversion scaffold membranes involved BPA imprinted polymer, which was copolymerized with bisphenol A dimethacrylate (BADM) and divinyl benzene (DVB) (Scheme 1). As scaffold polymers, polystyrene (PS), cellulose acetate (CA), nylon 66 (Ny) and polysulfone (PSf) were used (Scheme 2). Binding nature of the hybrid membranes to BPA, BPA analogs and phenol derivatives were studied on basis of

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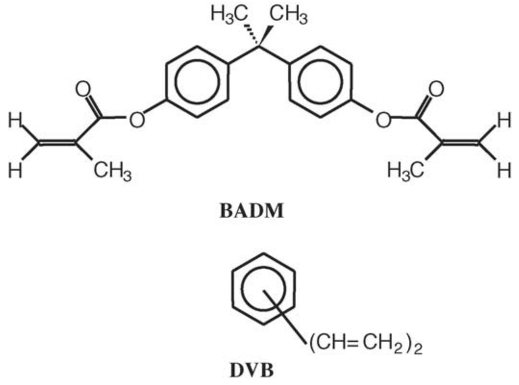


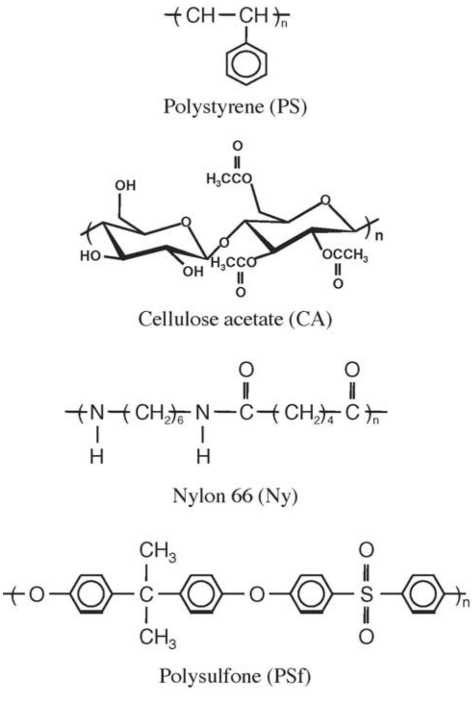
Scheme 1. Chemical structures of BADM and DVB.

selectivity and separation to their mixtures. We also focused and considered on the adsorbed abilities to BPA in view point of hybridization.

2. Experiments

2.1. Materials

BPA and DVB were purchased from Nacalai Tesque Inc. (Kyoto, Japan). BADM was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without purification. For phenol derivatives, which were products of Tokyo Kasei Industry Co. (Tokyo, Japan), 4,4′-ethylidenebisphenol (BPE), 4,4′-dihydroxydiphenylmetane (BPF), 2-(4-hydroxyphenyl)ethyl alcohol (HPA), resorcinol (RSO) and β-estradiol (EST) were used. PS, CA, Ny and PSf were purchased from Nacalai Tesque Inc. (Kyoto, Japan), Aldrich Chemical Co. (Milwaukee, WI), Asahi Kasei Co. (Tokyo, Japan) and PolyScience Inc. (Warrington, PA, USA), respectively.



Scheme 2. Chemical structures of PS, CA, Ny and PSf.

2.2. Procedures of copolymerization for BPA-MIP powder

In the presence of 0.5 wt.% of 2,2′-azobis(isobutyronitrile) under nitrogen atmosphere, the BPA imprinted powder was prepared with BADM and DVB (1:10 mol ratio) according to our previous report [7]. The resulting rigid copolymer was ground by pestle and mortar. Then, the BPA-MIP granule was sieved through 80-mesh sieve (177 μm aperture) and used for preparation of hybrid membranes.

2.3. Preparation of hybrid BPA-MIP (HMIP) membranes

Fig. 1 shows schematic procedure of preparation of the HMIP membrane. As scaffold membrane materials, PS, CA, Ny and PSf were used for hybridization with BPA-MIP powder. Phase inversion process of the polymer and the BPA-MIP powder was taken place as following. The BPA-MIP powder was mixed with 20 wt.% of each polymer solution by stirring overnight at 50 °C. Herein, THF was used as solvent for PS and CA, formic acid was used for Ny and *N*-methyl-2-pyrrolidone was used for PSf. In addition, the contents of the BPA-MIP powder in polymer solution were changed in the range of 20–56 wt.% to the scaffold polymer in the solvent solution. The resultant viscous solution was spread on glass plate (150 mm × 200 mm) with 100 μm thickness controlled by polyester film (Lumirror; Toray, Japan) used as spacer at 50 °C. Then, the spread polymer solution was immediately coagulated in 2 L of water at 25 °C and kept overnight in order to remove solvent. After solidification of each polymer, the resultant membrane (about 100 mm × 150 mm), which included the BPA-MIP powder, was washed with excess of water. We signified the hybrid molecular imprinted polymer as HMIP. As reference, PS, CA, Ny and PSf membranes without the BPA-MIP powder were prepared by similar phase inversion process. Scanning electron microscopy (SEM) images, FT-IR spectra and single-point BET surface areas of the HMIP membranes were measured by JSM-5310LVB (JOEL, Japan), IR Prestige-21 FTIR-

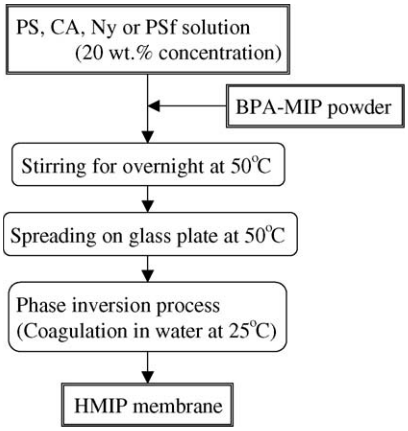
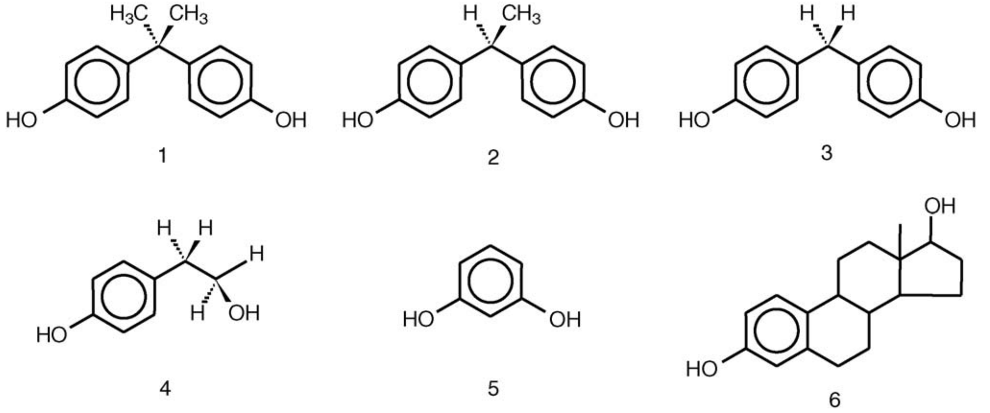


Fig. 1. Schematic produce of preparation of HMIP membrane.



Scheme 3. Chemical structures of BPA and BPA analogs. (1) Bisphenol A (BPA); (2) bisphenol E (BPE); (3) bisphenol F (BPF); (4) 2-(4-hydroxyphenyl)ethyl alcohol (HPA); (5) resorcinol (RSO); (6) β-estradiol (EST).

8400s (Shimadzu, Japan) and flowsorb 2300 (Shimazu, Japan), respectively.

2.4. Batch binding of substrate to HMIP membranes

Heterogeneous batch binding experiment was carried out in the presence of HMIP membrane (15 mm × 15 mm) in 40 mL volume of aqueous solution containing BPA, BPE, BPF, HPA, RSO or EST (Scheme 3). The substrate concentration was ranged from 10 to 400 μM. The solution contained the membrane was shook at 30 °C for 24 h in glass holder with 50 cm^3 volume. We confirmed that the binding was saturated within 24 h for each system. Then, substrate concentration in the solution was analyzed using absorption spectrophotometer (V570; JEOL) at 277 nm for phenyl band of the substrates. When the reduced absorbance of substrate was measured for the BPA-MIP powder system, 0.05 g of the powder was dispersed in substrate solution. The obtained absorbance of substrate was converted to mole concentration and to saturated binding amount [S] (μmol/g) of substrate by the following equation [9]:

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

where C_0 and C_t represent molar concentrations of substrates measured at an initial time and saturated binding time (24 h). V and W represent volume of substrate solution and weight of imprinted polymer, respectively.

2.5. Permselective binding of substrate for HMIP membranes

A 50-mL capacity ultrafiltration (UF) cell (UF-8050; Amicon Inc.) was used to permeate aqueous solution containing each 20 μM of BPA, BPE, BPF and HPA through the imprinted membrane. The imprinted membrane with 43 mm diameter was mounted in the UF cell and 40 mL of the substrates aqueous solution was fed into the cell. The solution was permeated through the membrane about 1 h under 5.9 N/cm^2 (0.6 kgf/cm^2). The concentration of substrates in permeated solution was determined by monitoring UV absorbance at 215 nm by HPLC (CCPS; Tosoh Corp.) equipped with UV detector (UV8000; System Instruments Co. Ltd.) and TSKgel ODS-80Ts QA column (4.5 mm i.d., 7.5 cm length; Tosoh Corp.) with an eluent of water/acetonitrile = 1/1 vol.% at a flow rate of 0.5 mL/min. The bound amounts of substrates were calculated by concentration changes resulted by the HPLC measurements. In addition, we estimated separation factor (α_s) of substrate on the basis of HPA as the following equation [14]:

$$\alpha_\mathrm{s} = \frac{C_\mathrm{sp}/C_\mathrm{HPAp}}{C_\mathrm{sf}/C_\mathrm{HPAf}},$$

where C_sp and C_HPAp are the binding concentrations of a substrate and HPA in the permeate solution and C_sf and C_HPAf are the concentrations of substrate and HPA in the feed solution. When $\alpha_\mathrm{s} > 1$, it was meant that the bisphenol derivatives bound to imprinted polymer was recognized.

2.6. Scatchard analysis

It is known that binding equilibrium constants (K_a) give quantitative and effective information about the substrate binding to the imprinted polymer. Thus, the value of K_a for the HMIP membranes was determined according to Scatchard equation [15]

$$\frac{[\mathrm{S}]}{C_\mathrm{e}} = -[\mathrm{S}]K_\mathrm{a} + nK_\mathrm{a},$$

where C_e and n represent free concentration of substrate in equilibrium condition and binding capacity of substrate to imprinted polymer, respectively. Here, when plot of [S]/C_e on the vertical axis and [S] on the horizontal one was performed, the values of K_a and n were determined by the slope and intersection with horizontal axis, respectively.

3. Results and discussion

3.1. Characteristics of HMIP membranes

Each imprinted membrane was prepared under phase inversion process, in which water was selected as coagulation medium for each system. This was because water showing high solubility

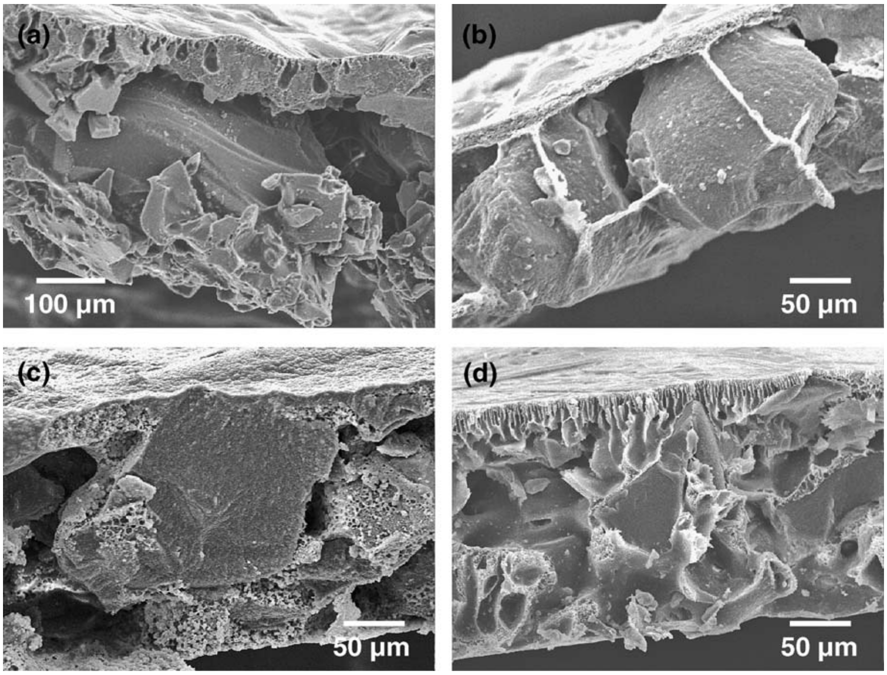


Fig. 2. SEM images of cross-section of (a) PS-HMIP, (b) CA-HMIP, (c) Ny-HMIP and (d) PSf-HMIP membranes.

for each solvent such as THF, formic acid and *N*-methyl-2-pyrrolidone, but not for PS, CA, Ny, PSf and the BPA-MIP powder. Therefore, the polymer phase inversion process formed the solidified membrane, which involved the BPA-MIP powder inside. The resultant membranes were opaque in appearance and satisfactory strong for experiments. Fig. 2 shows SEM images of cross-section of the HMIP membranes made of (a) PS, (b) CA, (c) Ny or (d) PSf. The SEM images showed that hybridization was successfully performed in each scaffold polymer. The thickness of the PS-HMIP membrane was about 300 μm and others were about 180 μm. We observed at ×7500 magnitude that the polymer layer was porous with less than 0.5 μm diameter of fine pores. In the SEM data, we noted that the BPA-MIP powders were embedded in the scaffold polymer layer. The pictures suggested that the scaffold PSf and the BPA-MIP powder were highly hybridized, because void space between the powder and the scaffold was absent in the cross-section of the resultant PSf-HMIP membrane. However, it was clear that the PS, CA and Ny-HMIP membranes contained void space at surrounding the BPA-MIP powders.

In order to confirm interaction between BPA-MIP powder and scaffold polymer membrane in the HMIP membrane, IR spectra of the BPA-MIP powder and the PSf membranes were measured (Fig. 3). In (a and b) spectrum for BPA-MIP powder and PSf membrane, IR bands of 1749 and 1236 cm^{-1} were assigned to >C=O stretching and $>\mathrm{S(=O)_2}$ stretching, respectively. In (c) for the PSf-HMIP membrane, it was found that the >C=O and $>\mathrm{S(=O)_2}$ stretching bands were shifted toward side of longer wavenumber of 1751 cm^{-1} from 1749 cm^{-1} and also 1244 cm^{-1} from 1236 cm^{-1}, respectively. It was also clear that the $>\mathrm{S(=O)_2}$ band near 1919 cm^{-1} for PSf membrane was disappeared in the PSf-HMIP membrane. These IR data suggested that there were interaction between the BPA-MIP powder and the membrane scaffold in the PSf-HMIP membrane. On the other hand, in PS, CA and Ny-HMIP membranes, the IR bands of BPA-MIP powder and each of scaffold polymer membrane were observed little shift of the IR band after the hybridization. As a result, the evidence of strong interaction between BPA-MIP powder and scaffold PSf membrane resulted in good hybridization of PSf-HMIP membrane. This also suggested by the SEM picture for the PSf-HMIP membrane which had no void.

3.2. Binding of BPA and various substrates to HMIP membranes

Studying binding ability of the HMIP membranes was performed in heterogeneous batch binding experiments. Fig. 4

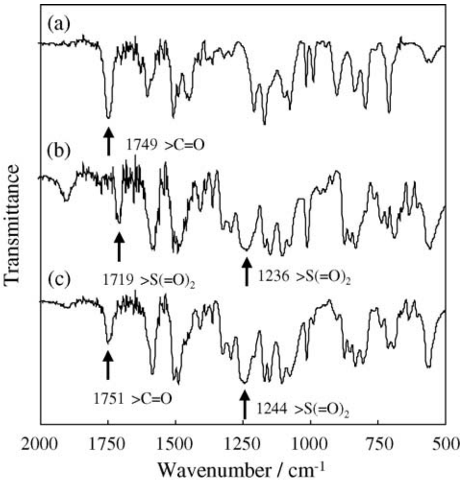


Fig. 3. FT-IR spectra of (a) BPA-MIP powder, (b) PSf membrane and (c) PSf-HMIP membrane.

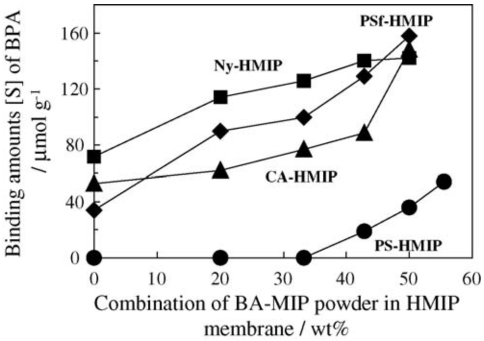


Fig. 4. Binding amounts of BPA for various compositions of BPA-MIP powder in HMIP membranes. For BPA binding experiments, concentration of BPA was 100 µM. The BPA binding amounts were on equilibrium condition for 24 h at 30 °C.

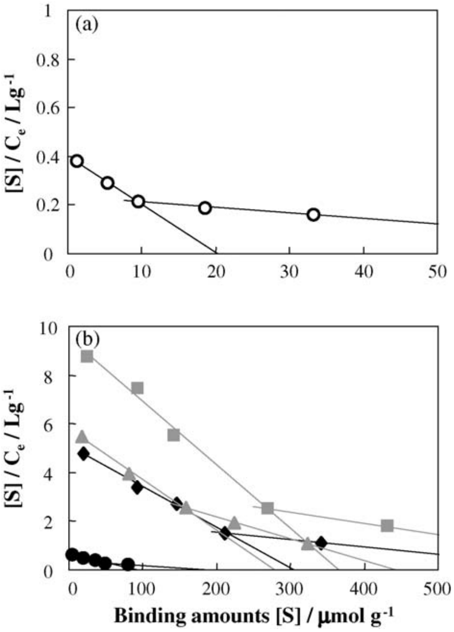


Fig. 5. Scatchard plots for BPA in (a) BPA-MIP (○) and (b) HMIP membranes, PS-HMIP (●), CA-HMIP (▲), Ny-HMIP (■) and PSf-HMIP (◆).

shows plots of [S] for BPA versus various contents of BPA-MIP powder in HMIP membranes. The weight percents of BPA-MIP powder changed were in 20, 33, 43, 50 and 56 wt.% in each polymer solution, which was used for phase inversion process. In cases of PS, the limitation of loading the BPA-MIP powder into the membrane was 56 wt.% and other polymers were for 50 wt.%. Herein, the membranes of PS, CA, Ny and PSf without BPA-MIP had binding ability to BPA, these binding amounts of BPA were 0, 53, 72 and 34 µmol/g, respectively. Among them, the PS membrane had no binding to BPA. Also, when the content of the BPA-MIP powder was changed between 0 and 33 wt.%, the PS-HMIP membranes showed no binding to BPA. For other membranes, there were tendency to gradually increase the binding amounts of BPA as the loading amounts of the powder increased. When the loading was 50 wt.%, the value of [S] was 38, 148, 142 and 158 µmol/g for PS, CA, Ny and PSf-HMIP membranes, respectively.

In order to investigate the binding ability for BPA in the resultant HMIP membranes, we carried out the Scatchard analysis for BPA-MIP powder and the membranes. Fig. 5 presents Scatchard plots obtained by heterogeneous batch experiments for BPA-HMIP membrane systems. The loading amounts of BPA-MIP powder for each HMIP membrane used were 50 wt.%. In the resultant plots, two straight line regions were obtained, except for those of non-hybridized CA, Ny and PSf membranes. This means that there were sites of specific and non-specific binding for the BPA molecule in BPA-MIP powder and HMIP membranes. From the straight area in the range of 1–150 µmol/g of binding amounts, binding equilibrium constants (K_a) was estimated (Table 1). In the slope data of 1–150 µM region, the obtained value of K_a for the PSf-HMIP membrane was almost similar to that of the BPA-MIP powder, while the binding capacity for PSf-HMIP membrane was about 14 times higher than that of the BPA-MIP powder. Therefore, it was clear that the PSf-HMIP membrane exhibited effective binding ability to BPA relative to the BPA-MIP powder. The resultant values of K_a for the CA-HMIP and Ny-HMIP membranes displayed similar tendency to the BPA-MIP powder. However, the value of K_a for the PS-HMIP membrane was somewhat lower than that of the BPA-MIP powder. Therefore, it was considered that no hybrid effect was caused in PS-HMIP membrane, because the PS scaffold had no binding ability to the BPA substrate. The

Table 1
BPA binding abilities in BPA-MIP powder, polymer scaffold membranes and HMIP membranes contained 50 wt.% of BPA-MIP powder

	Binding equilibrium constants (K_a)[a] (M^{-1})	Binding capacity (n)[a] (µmol g^{-1})	Binding equilibrium constants (K_{ah})[b] (M^{-1})
BPA-MIP powder	19700	20	2290
PS membrane	–	–	–
PS-HMIP membrane	7230	91	1960
CA membrane	780	1020	780
CA-HMIP membrane	16800	304	3040
Ny membrane	600	2140	600
Ny-HMIP membrane	22600	365	4610
PSf membrane	480	310	480
PSf-HMIP membrane	20700	279	8970

[a] The values in specific binding region were shown.

[b] As non-specific parameter, the values of equilibrium constant (K_{ah}) were estimated from high concentration region in Fig. 5.

Table 2
Binding amounts of BPA and BPA analogs for BPA-MIP powder, polymer scaffold membranes and HMIP membranes contained 50 wt.% of BPA-MIP powder

	Binding amounts [S] (μmol/g)					
	BPA	BPE	BPF	HPA	RSO	EST[a]
BPA-MIP powder	10	8	6	0.1	0	0
PS membrane	0	0	0	0	0	0
PS-HMIP membrane	38	30	28	3	0	0
CA membrane	53	55	56	2	0	0
CA-HMIP membrane	148	138	108	7	0	0
Ny membrane	72	60	54	2	0	0
Ny-HMIP membrane	142	135	120	6	0	0
PSf membrane	34	31	35	3	0	0
PSf-HMIP membrane	158	127	105	8	0	0

Initial concentration was 100 μM.

[a] EST was measured in ethanol solution.

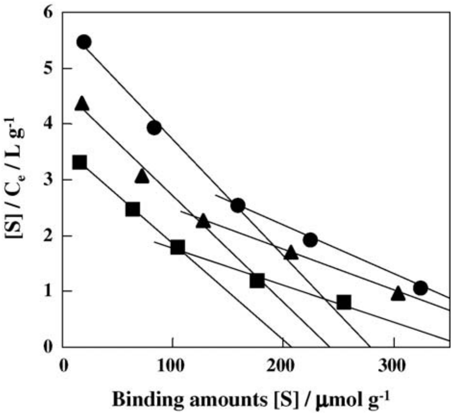


Fig. 6. Scatchard plots for BPA (●), BPE (▲) and BPF (■) in the PSf-HMIP membrane. The HMIP membrane was contained 50 wt.% of BPA-MIP powder.

table also contained the values of K_{ah} estimated from straight region of higher binding amount of BPA. For example, the value of $K_{ah} = 2290\,M^{-1}$ for BPA-MIP powder was from [S] = 10 to 30 μmol/g and that of $K_{ah} = 8970\,M^{-1}$ for PSf-HMIP membrane was from [S] = 220 to 340 μmol/g. The resulting K_{ah} was smaller than that obtained from lower binding amount region. This is due to the non-specific binding with physically adsorbed behavior of the BPA molecules. Namely, we noted that the enhanced binding capacities were caused by the hybridization of the polymer scaffolds with the BPA-MIP powder, especially for the CA, Ny and PSf-HMIP membranes.

3.3. Selective binding ability to BPA by HMIP membranes

Table 2 shows saturated binding amounts of each substrate for HMIP membranes for BPA and other BPA analogs. Herein, the HMIP membrane used was 50 wt.% of the BPA-MIP powder for the loading. It was observed that the BPA-MIP powder had binding amounts of 10, 8, 6, 0.1, 0 and 0 μmol/g for BPA, BPE, BPF, HPA, RSO and EST, respectively. The BPA-MIP powder had high binding ability to BPA and BPE and somewhat low binding to other phenol derivatives and estrogen. This tendency was also confirmed in each HMIP membrane. As shown in the Scatchard plots of BPA, BPE and BPF for the PSf-HMIP membrane (Fig. 6), the obtained plots were similar with those observed in Fig. 5, which showed non-straight line. The K_a and binding capacity for BPA indicated that their data were higher than those of BPE or BPF. The resultant values of K_a were 20,700, 19,100 and 17,300 M^{-1} for BPA, BPE and BPF, respectively. Therefore, it was confirmed that the PSf-HMIP membrane mostly recognized BPA and also similarly to BPE and BPF.

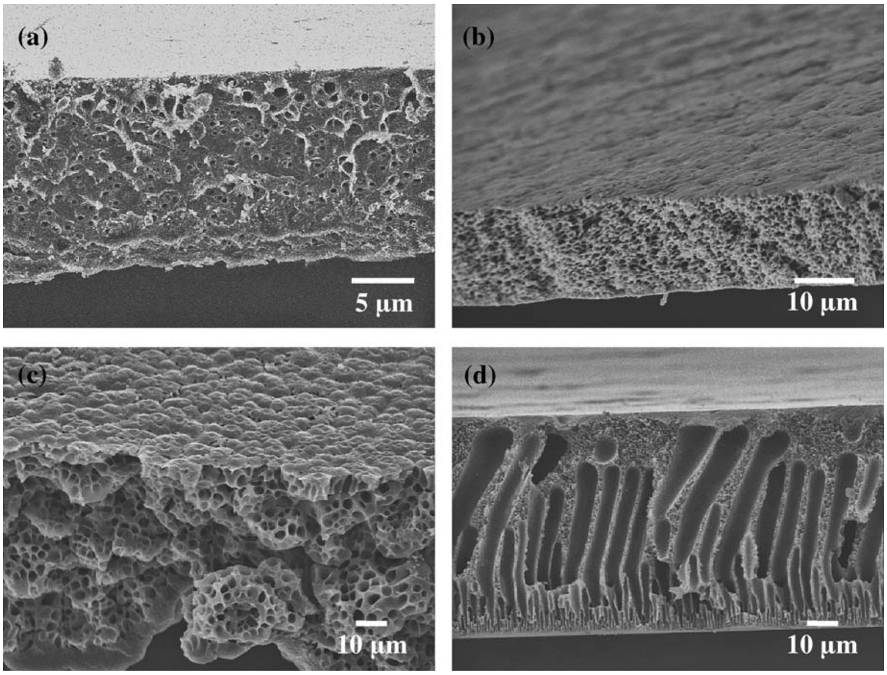


Fig. 7. SEM images of cross-section of (a) PS, (b) CA, (c) Ny and (d) PSf membranes.

Table 3
Separation factor (α_s) of various substrates for HMIP membranes in permeation experiments

	Surface area (m^2/g)	Pressure (kgf/cm^2)	Volume flux ($\times 10^{-6}$ $m^3/(m^2$ s))	Separation factor (α_s)			
				HPA	BPF	BPE	BPA
CA membrane	3.9	0	6.2	1.0	3.9	2.1	1.5
CA-HMIP membrane	66.7	0	5.7	1.0	10.0	10.6	11.5
Ny membrane	2.4	0.03	7.5	1.0	2.7	2.6	2.9
Ny-HMIP membrane	38.4	0.02	6.2	1.0	7.7	7.8	8.1
PSf membrane	20.0	0.1	7.2	1.0	0.4	0.4	0.4
PSf-HMIP membrane	66.4	0.6	7.0	1.0	9.6	10.0	10.8

3.4. Permselectively binding abilities to BPA by HMIP membranes

It is known that imprinted membranes are convenience for transport of substrate and for the selective binding into the imprinted sites [9–13]. Therefore, such polymer membrane can concentrate the target molecule and then separate the molecule from the mixture solution. In this section, we mention about permselective properties of the HMIP membranes. Because the resultant PS-HMIP membrane was fragile, it was impossible to use the PS-HMIP membrane for permeation experiments. Also, the PS membrane without the BPA-MIP powder was no perme-

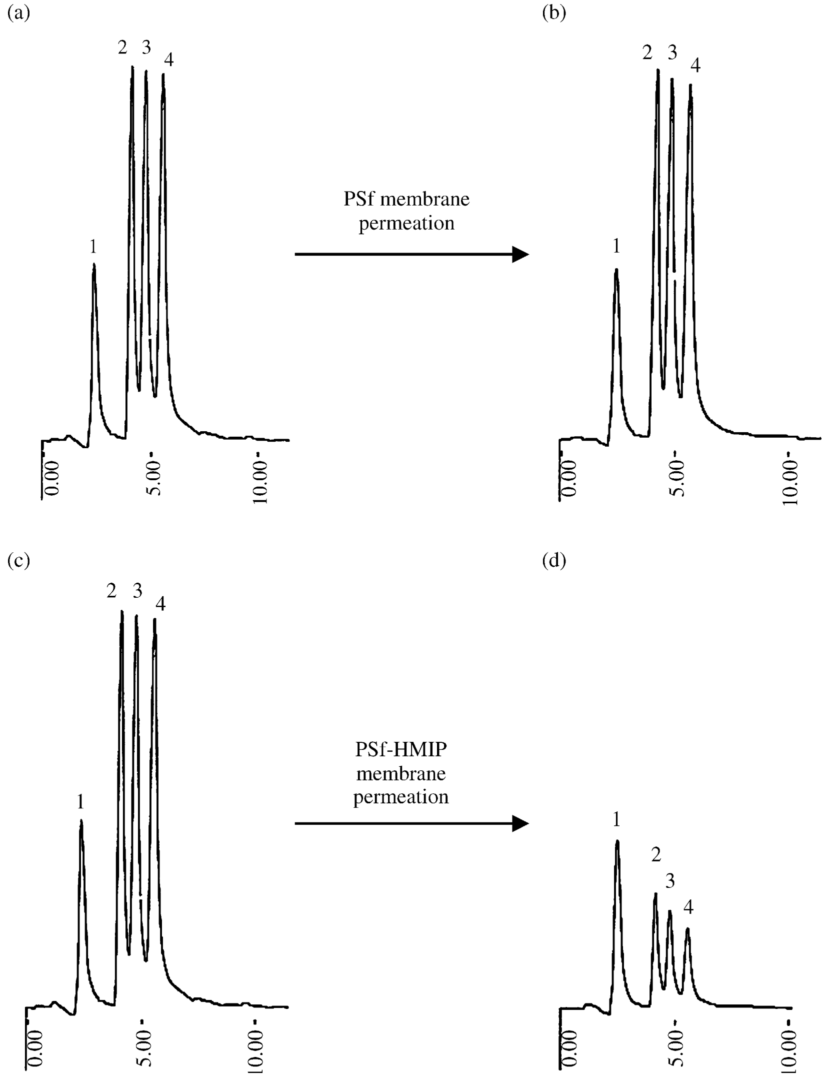


Fig. 8. HPLC charts of bisphenols and HPA mixture for separation experiment before and after permeation through PSf and PSf-HMIP membranes. Each 20 μM of HPA (peak 1), BPF (peak 2), BPE (peak 3) and BPA (peak 4) was mixed in the solution before (a and c) and after (b and d) permeation through the PSf and PSf-HMIP membranes. The PSf-HMIP membrane used contained 50 wt.% of BPA-MIP powder.

ation under high applied pressure of 5.9 N/cm^2 (0.6 kgf/cm^2). As shown in Fig. 7a, this was because of dense morphology without many micro-voids for the PS membrane. In the cases of CA and Ny membranes, many small pores with 1 μm size were observed in the cross-section. In PSf membrane prepared from 20 wt.% PSf solution in the absence of BPA-MIP powder, (d) shows that there were macrovoids in the cross-section. For solute permeation the PSf membrane had only permeation of water over 5.9 N/cm^2 (0.6 kgf/cm^2). Therefore, in order to prepare porous permeable membrane, 4 wt.% of LiCl was added to the PSf solution as reported by Shibata et al. [16]. On the other hand, it was observable that CA and Ny membranes had sufficient porous morphology in order to permeate water solution.

Fig. 8 compares HPLC chromatogram charts of the mixed substrate solution containing BPA, BPE, BPF and HPA. In (a and b) for the PSf membrane and (c and d) for the PSf-HMIP membrane, each peak area of substrates was observed before and after permeation through the membrane. For the permeation data of PSf membrane (a and b), significant changes of each peak area was not found for four substrate peaks obtained before and after the permeation. On the other hand, in the PSf-HMIP membrane (c and d), the peak intensity of HPA (indicated as peak 1) was almost kept constant before and after the permeation. It was noted that the peak intensities of bisphenol derivatives remarkably decreased by the permeation. Especially, the decrease of the BPA peak was larger than those of other BPE and BPF. The resultant HPLC data of Fig. 8 were used to convert to separation factor (α_s) (Fig. 9 and Table 3). As summarized in Table 3, the values of α_s of BPA (α_{BPA}) were 1.5, 2.9 and 0.4 for CA, Ny and PSf membranes, respectively. Therefore, it was confirmed for the non-imprinted membrane that non-selective binding was observed in bisphenols and HPA. On the contrary, the HMIP membranes had larger value of α_s for bisphenol derivatives. Accordingly, the HMIP membranes effectively separated the mixture of bisphenols and HPA by permeation experiments.

In order to consider the separation data, we determined surface area (SA) of membranes by BET technique. Table 3 also lists the value of SA of the resultant membranes. The HMIP membranes had high value of SA relative to the membranes without BPA-MIP powder. This was due to the hybridization of the BPA-MIP powder with the SA value of 133 m^2/g. The Ny-HMIP membrane showed 38.4 m^2/g, which was rather lower than 66.7 m^2/g for CA-HMIP and 66.4 m^2/g for the PSf-HMIP membrane. As a result, the hybridization of the imprinted powder caused high SA of the resultant HMIP membrane, which was suitable for substrate binding. On the other hand, the value of α_{BPA} was changed as 11.5, 8.1 and 10.8 for CA, Ny and PSf-HMIP membranes, respectively. Apparently, small numbers of BPA molecules were adsorbed by passing through the Ny-HMIP membrane. This was due to the low surface area of the Ny-HMIP membrane. It was noted that the capture effect of bisphenol substrates of the CA and PSf-HMIP membranes was clear. Among them, BPA was retained especially with high α. In addition, as listed in the table, the values of volume flux were observed to be 5.7×10^{-6} and 6.2×10^{-6} m^3/(m^2 s) for the CA and Ny-HMIP membrane under zero applied pressure. However, the value was 7.0×10^{-6} m^3/(m^2 s) for PSf-HMIP membrane under 5.9 N/cm^2 (0.6 kgf/cm^2) applied pressure. This was reasonable for considering the porous morphology of the resultant membranes as shown in SEM data (Fig. 2). In the present cases, the SEM observation suggested that the Ny and CA-HMIP membranes contained void space between the BPA-MIP powder and the Ny or CA scaffold. Therefore, such morphological structure was influenced on the permeation experiments.

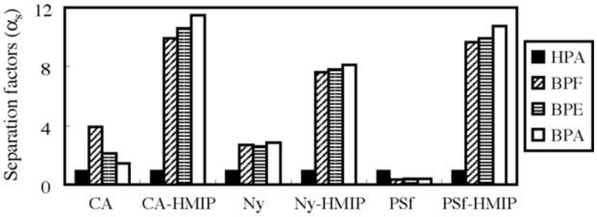


Fig. 9. Separation factors (α_s) of HMIP membranes for the mixed solution. Each BPA, BPE, BPF and HPA was contained in the solution with 20 μM content ration.

4. Conclusion

We firstly developed the hybridized membranes made of PS, CA, Ny and PSf with BPA imprinted polymer powder for bisphenol adsorbent and separation. It was showed that high binding ability of bisphenol derivatives was observed in batch and permeation binding experiments. Such substrate binding was dependent on the morphology and porous structure of the resultant membranes. We concluded that such porous imprinted membranes were very useful for separation of mixture of bisphenol and phenol derivatives. This would be research subject of subsequent our challenging work for future application of imprinted membranes.

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