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Molecularly Imprinted Membrane Applied for Selective Separation

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Abstract: Molecular Imprinting Polymer (MIP) technique is well known for creating polymer materials with molecule selectivity in adsorption and separation. MIPs have mostly been prepared by bulk polymerization and grinding the resulting brittle polymer to prepare particles of the desired dimensions. However, this technique also suffered some backdrops such as limitation in its application due to powder shape and limitation in binding ability. To circumvent these problems, we had extended such technique on formation of membrane adsorbents using phase inversion imprinting technique. Namely, copolymerization of a template-containing monomers with commercial scaffold monomer was achieved such membranes in order to selectively separate the target molecules. One main feature of this system is the imprinted polymer forming film which is possible to be use as filtration materials for selective separation. In the present study, we prepared the imprinted membranes by copolymerization of covalently linked tocopherol methacrylate (α-TMA) monomer and acrylonitrile (AN) followed by phase inversion in water non-solvent for membrane formation. Herein, the evidence included advantage in phase inversion covalently imprinting technique in their binding natures to tocopherol (Toc) and phenol derivatives and was studied on basis of selectivity of the imprinted membrane. Scatchard analysis indicated that the imprinted membranes exhibited high affinity and good selective binding of α-Toc relative to its analogs, δ-Toc and 4-chromanol (4-Chr). Results of permeation of Tocs and phenol mixture showed that the imprinted membranes were achieved higher separation factor of α-Toc and 4-Chr as compared to the non-imprinted membrane. This indicated that the covalent imprinting of α-Toc in AN segment scaffold was able to recognize both chemical structures with or without methyl group in the Toc derivatives.

Key words: Molecular imprinting membrane, phase inversion, adsorption, selectivity, α-tocopherol

INTRODUCTION

Synthetic receptor materials having selective guest recognition abilities have been well documented and might be a promising tool for separation and analytical methods due to its high efficiency and easy operation. Recently, an imprinting technique has been expanded to uses in the analytical fields of chemicals and drugs, since molecular imprinting technique is an effective method for preparation of advantageous functional polymers which selectively recognize and separate a target molecule from mixture solution (Bartsch and Maeda, 1998; Wulff, 1995; Yan and Ramstrom, 2005). We have reported that the membrane technique of hybrid-molecular imprinting is very useful, because the hybridization is successfully performed by only mixing imprinted polymer powders with scaffold polymer which is available for membrane preparation. Such advantage results in effective applications to waste water treatment containing endocrine disruptor, bisphenol derivatives (Takeda and Kobayashi, 2006) and medical field, targeted to indole derivatives (Takeda *et al*., 2007). For instance, Bisphenol A (BPA) which is known as endocrine disruptor, affects the reproduction and development of animal organism in extra-diluted concentration (Takeda and Kobayashi, 2005). 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 was applied as alternative methods (Ikegami *et al*., 2004). We have studied that preparation and characterization of molecularly imprinted polymer (MIP) which selectively and effectively adsorb to BPA (Metzler, 2001). We also have extended such technique on uses of crosslinking polymer imprinted for indole (Takeda *et al*., 2007) and tocopherol derivatives (Faizal and Kobayashi, 2008).

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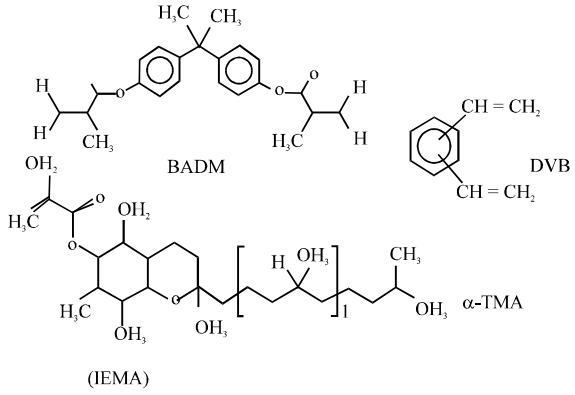
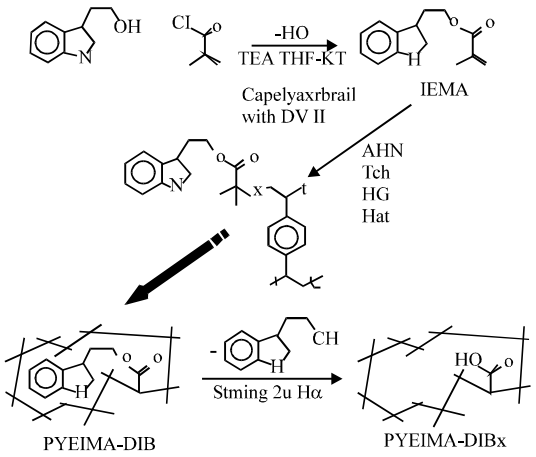
Herein, methacrylate containing Indole Ethanol (IE) and Tocopherol was selected as target molecule. For their targeted molecules the evidence included for advantage in HMIP membrane technique in their binding on basis of selectivity of the HMIP membrane. Through these works, it will be focused and considered on view point of hybridized imprinting technique which contained fabrication characteristics on the MIP for membrane applications due to its powder shape. Accordingly, in order to fabricate selectively permeable membrane, we would propose hybrid of MIP powder in porous membrane scaffolding as a new separation materials. Results of our recent topics for imprinted behavior of BPA, indole and tocopherol by using crossrinked copolymer with divinylbenzene and each functional monomer are presented.

MATERIALS AND METHODS

In the presence of 0.5 wt.% of 2,2-azobis(isobutyronitrile) under nitrogen atmosphere, the BPA imprinted powder was prepared with Bisphenol A dimethacrylate (BADM) and divinylbenzene (DVB) (1:10 mol ratio) according to our previous report (Takeda and Kobayashi, 2006). 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.



Indole-3-ethyl methacrylate (IEMA) was used as functional monomer for imprinting Indole-3-Ethanol (IE) and synthesized by H3C esterification of IE and methacrylic acid chloride (Takeda *et al*., 2007). In the presence of AIBN, the resultant IEMA monomer was copolymerized with divinylbenzene (DVB) (1:10 mol ratio). In order to synthesize IE imprinted polymer, IE segments from the P(IEMA-co-DVB) (Scheme 1) were extracted as followed. The P(IEMA-co-DVB) was hydrolyzed in 2 M HCl aqueous solution with stirring for 12 h at 60°C. In order to prepare HMIP membrane, the resultant IE imprinted polymer was hybridized with polysulfone (PSf) membrane by phase inversion process (Takeda and



Scheme 1: Synthesis of functional monomer (IEMA) and illustration of preparation of IE imprint

Kobayashi, 2006; Takeda *et al*., 2007). The imprinted polymer (1.5 g) powder was mixed in PSf (1.5 g) N-methyl-2-pyrrolidone solution. The mixture solution was spread on glass plate at 50°C and then coagulated in water. As a reference, PSf membrane without MIP powder was also prepared. Functional monomer, α-tocopherol methacrylate (α-TMA), was copolymerized in covalent networks of divinyl benzene (DVB). For α-tocopherol (α-Toc) imprinting, esterification of α-Toc with metacryloyl chloride was carried out. The resulting TMA monomer was copolymerized with DVB (1:20 mol ratios) in the presence of AIBN. The copolymer was hydrolyzed in 2M H_2SO_4 for 24 h to remove the template from the copolymer. The resulting MIP was hybridized in range of 50 wt.% toward scaffold membranes PSf. The scaffold membrane solution contained the MIP powder was similarly prepared by phase inversion process. As the reference, each scaffold membrane without MIP powder also was prepared in the same manner. Uptake experiments of substrate for resultant HMIP were carried out in ethanol or hexane solvent (20 mL) containing each 100 μM of α-Toc, δ-Toc, pentamethyl-6-chromanol (PMC) and 4-chromanol by shaken at 30°C for 24 h. The binding amounts of each substrate to HMIP membranes were calculated by concentration changes before and after the uptake experiments.

RESULTS AND DISCUSSION

Membrane characterization of HMIP: Each imprinted membrane was prepared under phase inversion process, in which water was selected as coagulation medium for each system (Takeda *et al*., 2007; Takeda and Kobayashi, 2006; Faizal and Kobayashi, 2008). This was because water showing high solubility for each solvent such as N-methyl-2 pyrrolidone.

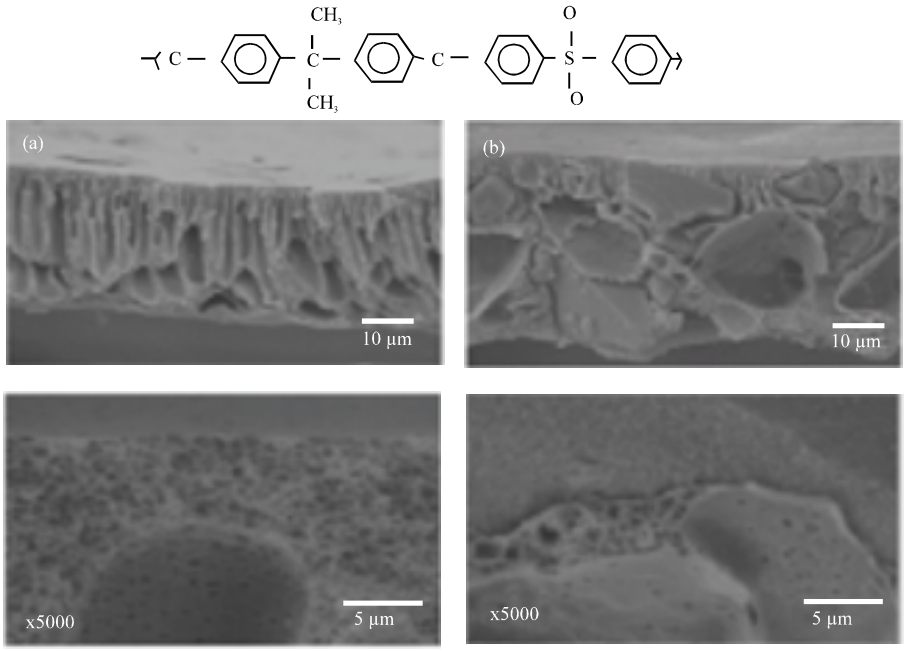


Fig. 1: SEM pictures of cross-section of (a) Psf and b) HMIP membranes embedded for BPA imprinted polymer powders

Table 1: BPA binding abilities in BPA-MIP powder, scaffod PSF membranes and HMIP membranes contained 50 wt% of BPA-MIP powder for BPA binding by scatchard analysis

	Binding constants (Ka)[a] (M^{-1})	Binding capacity (n^a) (moL g^{-1})	Binding constants (Kah)[b] (M^{-1})
BPA-MIP powder	19700	20	2290
PSF membranes	480	310	480
PSF-HMIP membranes	20700	279	8970

[a]The values in specific binding region were shown. [b]As non-specific parameter, the values of equilibriun constant (Kah) were estimated from high concentration region

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.

Figure 1a and b show SEM images of cross-section of PSf and HMIP membranes, respectively. These pictures were for hybridization successfully performed in PSf scaffold polymer. This was because that void space between the imprinted polymer powder and the scaffold was absent in the cross-section of the resultant HMIP membrane. The BPA-MIP powders were embedded in the scaffold polymer layer. 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. In spectrum for BPA-MIP powder and PSf membrane, IR bands of 1749 and 1236 cm^{-1} were assigned to C = O stretching and S(= O)2 stretching, respectively. In PSf-HMIP membrane, it was found that the C = O and S(= O)2 stretching bands were shifted toward side of longer wave number of 1751 from 1749 cm^{-1} and also 1244 from 1236 cm^{-1}, respectively. It was also clear that the 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.

Binding experiments by Scatchard analysis: 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. In the resultant plots, two straight line regions were obtained except for those of non-hybridized PSf membrane. 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 1-50 µ moL g^{-1} g of bindingamounts, binding equilibrium constants (K_a) was estimated (Table 1). In the slope data of 1-150 µM region, the obtained value of Ka 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.

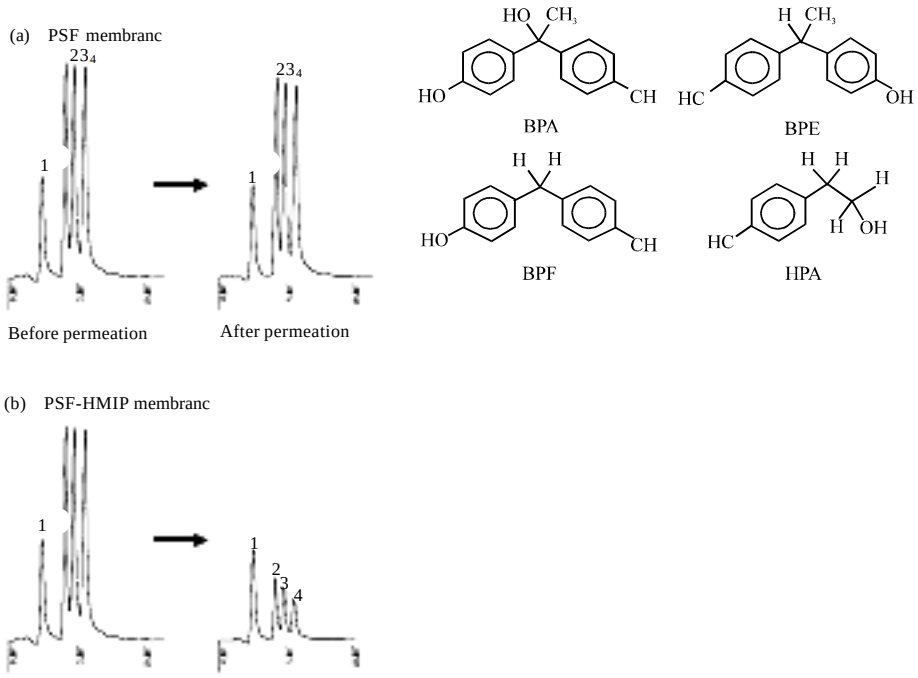


Fig. 2: HPLC charts of aqueous solution containing HPA (1), BPF (2), BPE (3), BPA (4) before and after permeation by the (a) PFS and (b) PSF-HMIP membrane

Table 2: Binding amounts, μmoL g^{-1}, of substances and imprint efficient (αi) of substances

Sorbents	α-Toc	δ-Toc	PMC	4-Chromanol
α-TMA-MIP	11.8 (1)	5.8 (0.49)	3.7 (0.31)	0.5 (0.04)
PSF	20.5 (1)	16.6 (0.89)	18.3 (0.89)	10.3 (0.50)
PSF-HMIP	42.7 (1)	25.8 (0.60)	21.6 (0.51)	21.1 (0.49)

Permselective Separation of mixture by HMIP membranes: Figure 2a and b compare HPLC chromatogram charts of the mixed substrate solution containing BPA, BPE, BPF and HPA in the PSf membrane and the PSf-HMIP membrane, respectively. Each peak area of substrates was observed before and after permeation through the membrane. For the PSf membrane, insignificant changes of each peak intensity were determined in four substrates as obtained before and after the permeation. On the other hand, in the PSf-HMIP membrane, the peak intensity of HPA (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. Accordingly, the HMIP membranes effectively separated the mixture of bisphenols and HPA by permeation experiments. Table 2 lists the obtained values of binding amounts and imprint efficient, α_i, each sorbent retained by the each HMIP membrane. Almost similarity to that of the α-TMA-MIP powder was observed in HMIP, while the binding capacity for HMIP membrane was about 2~4 folds higher than that of the α-TMA-MIP. Therefore, it was clear that the HMIP membrane exhibited effective binding ability to α-Toc relative to that of the α-TMA-MIP. This indicated that the covalent imprinting of α-Toc was able to recognize both chemical structures of tocopherol derivatives with or without methyl group in their chemical structures. Furthermore, the reason of high recognition ability for α-Toc in the HMIP membrane was considered that surrounding environment of the scaffold polymer changed the binding ability of the MIP powder.

Figure 3 shows HPLC chromatogram charts of the mixture solution containing pyrrole, HQ, IE and indole before and after the solution was permeated through the membranes. For the PSf membrane, insignificant changes in each peak intensity were found for four substrate peaks obtained before and after the permeation (Fig. 3a). On the other hand, for the HMIP membrane, the peak

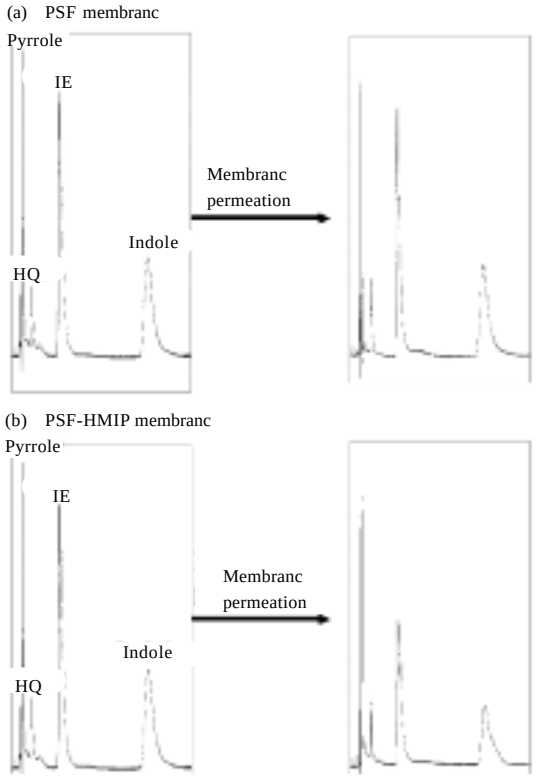


Fig. 3: HPLC charts of each 25 μM of pyrrole, HQ, IE and indole in mixture aqueous solution before and after permeation by (a) PSF and (b) HMIP membrane

intensities of pyrrole and HQ were almost kept constant before and after the permeation and the peak intensities of IE and indole remarkably decreased by the permeation. (Fig. 3b).

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