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Selective Recognition and Permeation of Bisphenol A with Molecularly Imprinted Polyamide Membranes#

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BPA imprinted polyamide membranes as well as control membranes recognized BPA in preference to its analogue DPP and selectively permeated BPA from BPA/DPP mixtures. The imprinted membranes showed higher adsorption selectivity and permselectivity than the control membrane. The adsorption selectivity of the imprinted membranes reached 135 and permeated BPA 3.7 times faster than the control membrane.

Key words: polyamide／AMODEL／membrane／molecular imprinting／molecular recognition／bisphenol A

1. Introduction

Polymeric materials such as oligopeptide derivatives[1] and derivatives of natural[2] and synthetic[3-5] polymers were easily converted into molecular recognition materials by applying an alternative molecular imprinting technique[6] to the ones commonly used. 2,2-Bis(4-hydroxyphenyl)propane, known as bisphenol A (BPA), is a widely used monomer in the synthesis of polymers such as polycarbonates, epoxy resins, polysulfones, and other thermoplastics. The separation of BPA is relevant in the study of molecularly imprinted polymers in connection not only with BPA purification in chemical industry[7] but also with environmental protection[8]. For this purpose we adopted a commercial semi-crystalline polyamide AMODEL A-1000 as a material capable of the formation of a molecular recognition site as well as a membrane matrix. Since AMODEL A-1000 shows excellent mechanical properties, outstanding dimensional stability, and exceptional elevated thermal performance, it is expected that AMODEL A-1000 polyamide gives a stable self-standing membrane. In the present study, we report the preliminary investigation of the recognition and separation of BPA through the molecularly imprinted AMODEL membranes.

2. Experimental

2.1. Materials

AMODEL A-1000 polyamide polymer (produced and kindly provided by Amoco Performance Products) was used as a membrane material without further purification. AMODEL is a random co-polyamide consisting of terephthalic acid, isophthalic acid, adipic acid and hexamethylenediamine. The chemical composition of the polyamide was determined by ^{1}H-NMR analysis using 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 (HFIP-d_2) as the solvent (average molecular weight of constitutional repeating unit of AMODEL, 243.98). Bisphenol A (BPA), 2,2-diphenylpropane (DPP), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, a solvent for AMODEL), methanol, and 1-octanol were used without purification.

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Table Adsorption selectivity of BPA from BPA/DPP mixtures in the molecularly imprinted polymeric membranes

Membrane	Substrate	$(Substrate)_M$ / mol (g-mem.)$^{-1}$	$(Substrate)_M$ / (AMODEL)[a]	$S_{A(BPA/DPP)}$
Imprinted mem.[b]	BPA	8.7×10^{-5}	2.1×10^{-2}	135
	DPP	7.1×10^{-7}	1.7×10^{-4}	
Control mem.	BPA	6.7×10^{-5}	1.6×10^{-2}	39
	DPP	1.8×10^{-6}	4.5×10^{-4}	

[a] The average molecular weight of constitutional repeating unit of AMODEL was determined to be 243.98 by ^{1}H-NMR analysis.

[b] (BPA) / (AMODEL) = 0.15.

3. Results and Discussion

The adsorption selectivities toward BPA from the BPA/DPP mixtures for both BPA-imprinted and control membranes are summarized in the Table. The amounts of substrates are given not only in absolute amounts but also in relative amounts, by converted to those of average constitutional repeating unit. Both membranes showed an adsorption selectivity toward BPA in preference to DPP, but the imprinted membrane showed a much higher selectivity than the control one. The difference in chemical structure between BPA and DPP is that BPA has two hydroxyl groups at the 4-positions of phenyl moieties. Against expectation, a significant amount of BPA was incorporated into the control membrane. This might be partly due to an interaction between hydroxyl groups in BPA and the amide moieties in the membrane. DPP, which has no hydroxyl groups, was not easily incorporated into the cavity in the imprinted membrane, which was formed by the presence of BPA during the membrane preparation process, even though DPP has the same carbon skeleton as BPA. This suggests that the interaction between the target molecule and the membrane is also an important factor in the design of molecular recognition membranes, at least in the present study.

It is relevant to separate BPA from the BPA/DPP mixtures. For this separation, dialysis experiments of the BPA/DPP mixtures through membranes were studied. The time-transport curves of BPA and DPP through the imprinted and the control membranes are shown in the Figure. As shown in the Figure, both membranes preferentially permeated BPA, as expected from the adsorption selectivity results. Almost no permeation of DPP was observed. Following the

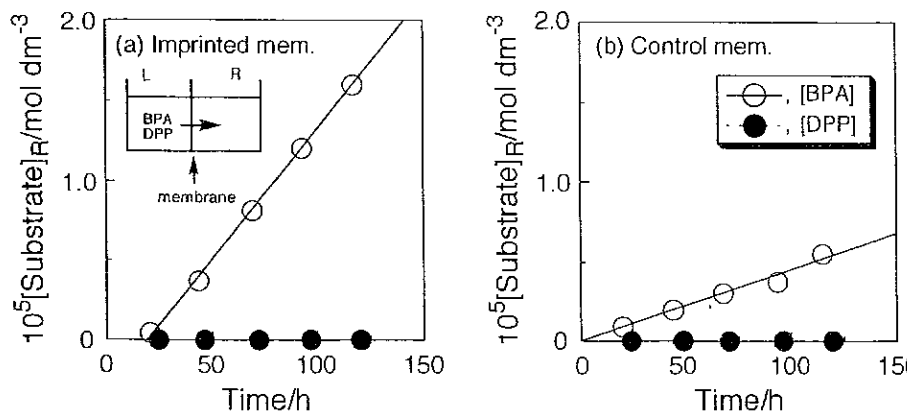
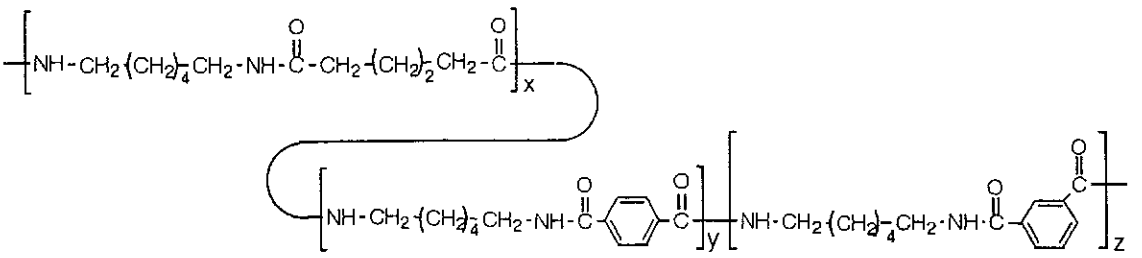


Figure Time-transport curves of BPA and DPP through (a) BPA inprinted and (b) control membranes. ((BPA)/(AMODEL) = 0.15 ; $[BPA]_{L,0} = [DPP]_{L,0} = 0.2$ mmol dm^{-3}.)



x = 0.88 , y+z = 0.12

2.2 Membrane Preparation

The polymeric membranes investigated in the present study were prepared from HFIP solution. The mole ratio of print molecule BPA to the average constitutional repeating unit of polyamide was fixed at 0.15. AMODEL A-1000 (500 mg) and BPA (70.2 mg) were dissolved in HFIP solvent (5 cm^3). The resulting solution was cast onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at ambient temperature for 24 h. Subsequently the membrane was dried at 50 ℃ for 2 h. After drying, the print molecule was extracted from the membrane by a known large volume of methanol until only traces of the print molecule BPA could be observed by UV analysis. In the present study, 72.6 % of the added print molecule was recovered from the membrane. The control membrane was prepared in a similar manner, but without the print molecule. The thickness of the imprinted membrane thus obtained was around 21 μ m and that of the control membrane 17 μ m.

2.3 Adsorption Selectivity

The two kinds of membranes were immersed in a BPA/DPP solution, which was the same one used for the dialysis experiment. The solution volume was 10 cm^3 and a 0.2 mmol dm^{-3} concentration of BPA and DPP in 1-octanol equilibrated at 40 ℃ was used. Quantitative measurements of aliquots of the solution at the initial stage and after equilibrium were made using a high performance liquid chromatography (HPLC) instrument (JASCO PU 980) equipped with a UV detector (JASCO UV 970) and a CrestPak C18S column (150 x 4.6 (i.d.) mm) (JASCO) and aqueous methanol solution as the eluent.

Adsorption selectivity $S_{A(BPA/DPP)}$ is defined as

$$S_{A(BPA/DPP)} = ((BPA) / (DPP)) / ([BPA] / [DPP])$$

where (BPA) and (DPP) are the amounts of BPA and DPP adsorbed in the membrane and [BPA] and [DPP] are the concentrations of BPA and DPP in the solution after equilibrium was reached, respectively.

2.4 Dialysis

The membrane having an effective area of 3.0 cm^2 was fixed tightly with Parafilm between the two chambers of a permeation cell. The volume of each chamber was 40 cm^3. The BPA/DPP solution in 1-octanol was placed in the left-hand side chamber (L-side) and pure 1-octanol in the right-hand side chamber (R-side). The concentrations of BPA and DPP were fixed at 0.2 mmol dm^{-3}, as with the adsorption experiment. The dialysis experiment was conducted at 40℃ with stirring. Aliquots were withdrawn from the permeate side at each sampling time. The amounts of BPA and DPP that permeated through the membrane (J_{BPA}, J_{DPP}) were determined on an HPLC instrument described above.

The separation factor $\alpha_{BPA/DPP}$ is defined as the ratio J_{BPA} / J_{DPP} divided by the concentration ratio.

$$\alpha_{BPA/DPP} = (J_{BPA} / J_{DPP}) / ([BPA] / [DPP])$$

solution-diffusion mechanism[9], it can be said that not only solubility selectivity but also diffusivity selectivity for both membranes showed BPA selectivity. As a result, permeation of DPP through both membranes was hardly observed. The flux value for BPA through the BPA imprinted membrane was determined to be 2.2 x 10^{-8} mol cm^{-2} h^{-1}, while that through the control membrane was 6.0 x 10^{-9} mol cm^{-2} h^{-1}. The flux of BPA through the imprinted membrane was 3.7 times higher than that through the control one. The time-transport curve of BPA through the control membrane did not give the time-lag, while the time-lag was observed in that of the imprinted one. This suggests that there might be a relatively strong interaction between BPA and the imprinted membrane and the diffusivity of BPA in the imprinted membrane was reduced compared with that in the control membrane.

4. Conclusions

Thc BPA imprinted polyamide as well as the control membranes recognized BPA in preference to its analogue of DPP. Both membranes selectively permeated BPA from BPA/DPP mixtures in dialysis experiments. The imprinted membranes showed higher adsorption selectivity and permselectivity than the control membrane.

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