

# PREPARATION OF CYCLODEXTRIN MEMBRANE AND ITS SELECTIVE PERMEATION

H. Hirai, M. Komiyama, H. Yamamoto  
Department of Industrial Chemistry, Faculty of Engineering,  
The University of Tokyo,  
Hongo, Bunkyo-ku, Tokyo 113  
Japan

**ABSTRACT.** Smooth and stable cyclodextrin membranes are successfully prepared from the oriented-cyclodextrin-polymers, by drying layers of the polymers. The polymers are obtained by the reaction of the crystal of  $\beta$ -cyclodextrin-water inclusion complex with hexamethylene diisocyanate as cross-linking agent in anisole. The cyclodextrin membranes exhibit selective permeation of various materials in water.

## 1. INTRODUCTION

Cyclodextrins (CyDs) show specific complex formation with various guest compounds in aqueous solutions (1). Resins containing CyDs were used for separation in column chromatography (2-4).

A membrane containing CyD was prepared by dispersing CyD in a modified cellulose (5). The CyD in the membrane, however, should be dissolved out on standing the membrane in water for a long period. There has been no report on the preparation of membranes from CyD polymers, which can be successfully used in water without gradual loss of CyDs.

This paper describes the preparation of CyD membranes from polymers of CyD. The polymers are obtained by the reaction of the crystals of CyD-water inclusion complex with hexamethylene diisocyanate (HMDI). The use of this condensation polymer (the oriented-CyD-polymer) is essential for the preparation of smoothly plane membrane.

## 2. MATERIALS AND METHODS

### 2.1. Synthesis of Fixed CyD Crystal

Crystals (20 g) of inclusion complexes of CyD with various guest compounds were reacted with HMDI (25 g) in anisole (100 ml) at 154°C for 5 h, after being dried in vacuo at 150°C for 12 h. The resulting solid was filtered, washed with petroleum ether, and then dried in vacuo at 100°C for 12 h.

## 2.2. Synthesis of Oriented-CyD-Polymer

The fixed CyD crystals, prepared by the above method, were treated with boiling water for 1 h. Oriented-CyD-polymers were obtained as the insoluble parts.

## 2.3. Synthesis of Random-CyD-Polymer

CyD (5 g) and HMDI (2 g) were reacted in dimethyl sulfoxide (50 ml) at 140°C for 8 h in the presence of molecular sieve 4A.

## 2.4. Selective Permeation through CyD Membranes

CyD membranes were prepared from the CyD-copolymers on various supports in an ultrafiltration apparatus (Toyo Kagaku Sangyo Co., model USP-25). Permeation of materials in water was carried out at 35°C under 5 atm nitrogen.

# 3. RESULTS AND DISCUSSION

## 3.1. Oriented-CyD-Polymer

Crystals of inclusion complexes of  $\alpha$ - and  $\beta$ -CyDs with methyl orange, 4-nitroacetanilide, 2-propanol, and water were successfully fixed with the use of hexamethylene diisocyanate (HMDI) as cross-linking agent.

As shown in Fig. 1, the powder X-ray diffraction pattern of the fixed crystal of  $\alpha$ -CyD-water inclusion complex is virtually identical with that of the original crystal prior to the reaction with HMDI. This result indicates that mutual conformations of CyD molecules in the crystals of the inclusion complexes are kept virtually intact during the fixation.

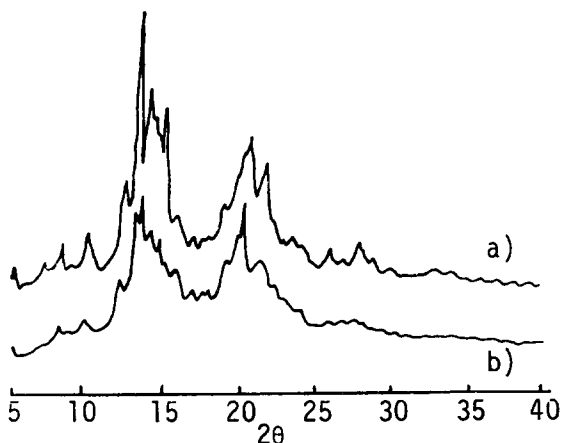


Figure 1. Powder X-ray diffraction patterns of  $\alpha$ -CyD-water complex crystal

a) original crystal

b) fixed crystal

Oriented-CyD-polymer was obtained in around 5 % yield by treating the fixed crystal with boiling water. In the oriented-CyD-polymer, CyDs and hexamethylene groups were linked three-dimensionally with urethane bonds, as confirmed by infrared stretching bands at 1680 and 1530  $\text{cm}^{-1}$ . No bands at 1620 and 1580  $\text{cm}^{-1}$ , assignable to urea bonds, were observed at all. The molar ratio of  $\beta$ -CyD to HMDI in the polymer, estimated by elemental analysis, was 1.0 : 1.5. In the powder X-ray diffraction pattern, main peaks are located at the same  $2\theta$  values as those in the pattern of the original crystal (Fig. 2).

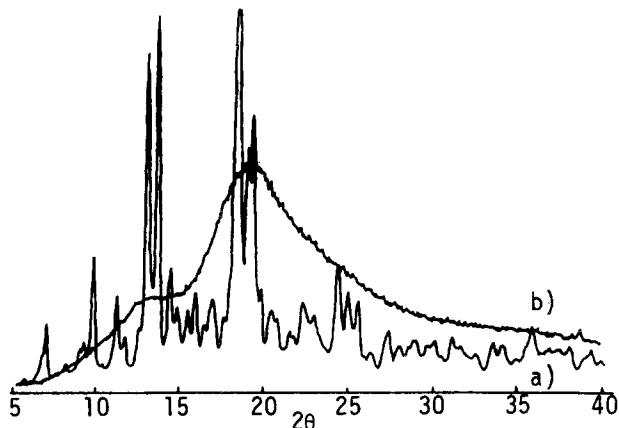


Figure 2. Powder X-ray diffraction patterns of a) original  $\beta$ -CyD-water complex crystal and b) oriented-CyD-polymer

### 3.2. Preparation of CyD Membranes

Smooth and stable CyD membranes were successfully prepared by drying the layers of the oriented-CyD-polymer, synthesized from the crystal of  $\beta$ -CyD-water inclusion complex. The layers were obtained by filtrating suspension of the polymer (20 mg) in water (20 ml) with various filters such as common filter papers, glass filters, membrane filters, and ultrafiltration membranes. Alternatively, the layers were prepared on the plates of glass, graphite, metallic copper, and metallic aluminium by coating their surfaces with the aqueous suspension of the oriented-CyD-polymer.

As the drying of the layers of the oriented-CyD-polymer proceeded, the surfaces of the layers gradually became velvety, and smoothly plane membranes were formed. The resulting CyD membranes prepared were stable in water, and no effusion of the polymer out of the membrane was detected at all after contact of the membrane with water for 1 day.

Fig. 3(a) depicts the SEM photograph of the surface of the membrane formed from the oriented-CyD-polymer. In a side view (Fig. 4), a thin membrane with a thickness of around 3  $\mu\text{m}$  is seen on the surface of the filter paper used as the support. Here, fiber-like materials, formed from the CyD polymer, are also observed, indicating that the oriented-CyD-polymer has a rather crystalline structure.

Preparation of a smooth and dry membrane using the random-CyD-polymer in place of the oriented-CyD-polymer has not been successful as

yet. Fine cracking of the layer of the random-CyD-polymer takes place as shown in Fig. 3(b), as drying of the layer proceeds.

The hydroxyl group in the oriented-CyD-polymer is quite important for the formation of smooth membrane. When the oriented-CyD-polymer is first reacted with n-butyl isocyanate and then is subjected to membrane preparation, the layer of the polymer finely cracks on drying (Fig.3(c)).

Coating of the surfaces of plates of glass, graphite, and metals with thin CyD membranes was also successfully achieved by drying the layer of the oriented-CyD-polymer, prepared from the aqueous suspension of the polymer.

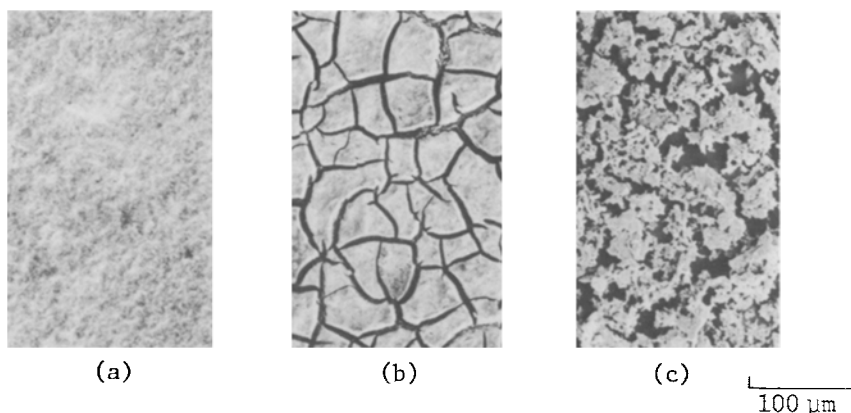


Figure 3. SEM photographs of the surfaces of CyD membranes ( $\times 300$ )  
 a) oriented-CyD-copolymer b) random-CyD-copolymer c) oriented-CyD-copolymer reacted with butyl isocyanate

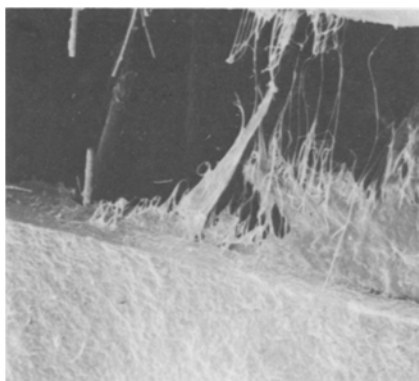


Figure 4. SEM photograph of cross-section of the membrane prepared from the oriented-CyD-polymer on a filter paper as a support ( $\times 1200$ ).

### 3.3. Selective Permeation through CyD Membranes

TABLE I lists relative permeation rates of various amino acids through the membranes prepared from the oriented- and the random-CyD-polymers. The permeation is carried out at  $35^{\circ}\text{C}$  under 5 atm nitrogen pressure. The membrane of the oriented-CyD-polymer satisfactorily exhibits

specificity. In the case of the membrane of the random-CyD-copolymer, however, no specificity is observed. Here, drying of the layer of the oriented- or random-CyD-polymer for the preparation of membrane was maintained to a low degree so that the formation of fine cracking, as shown in Fig. 3(b), of the layer of the random-CyD-polymer could be avoided.

TABLE I. Relative Permeation Rates of Amino Acids through Membranes Prepared from Oriented- and Random-CyD-Polymer<sup>a, b</sup>

Amino Acids	CyD Polymer	
	Oriented	Random
His	1.0 (0.56)	1.0 (0.73)
Val	1.3 (0.75)	1.0 (0.76)
Thr	1.4 (0.79)	1.0 (0.75)
Phe	1.3 (0.71)	0.9 (0.69)
Trp	1.2 (0.69)	1.0 (0.70)

a. The value for His is taken as unity.

b. The numbers in parentheses show the ratios of the concentrations of amino acids after permeation through the membrane to the values before that.

The relative permeation rates for various materials through the membrane prepared from the oriented-CyD-polymer are as follows:

$$\begin{array}{cccccc}
 \text{creatinine} & \approx & \text{urea} & \approx & \text{vitamin B}_{12} & > & \text{amino acids} & > & \text{sucrose} \\
 102 & & 102 & & 100 & & 95 - 67 & & 80 \\
 (0.85) & & (0.85) & & (0.84) & & (0.80 - 0.56) & & (0.67) \\
 \\ 
 & \approx & \text{m,p-nitrophenols} & > & \text{o-nitrophenol} & \\
 & & 80 - 75 & & 40 & \\
 & & (0.67 - 0.63) & & (0.34) & 
 \end{array}$$

Here the numbers in parentheses refer to the ratios of the concentrations of solutes after permeation with respect to the values prior to that. The order has no clear relationship with the molecular size of the solutes. For example, a large molecule such as vitamin B<sub>12</sub> permeates more rapidly through the membrane than smaller molecules such as amino acids, sucrose and nitrophenols. m- and p-Nitrophenols permeate at about two fold larger rates than the corresponding ortho-isomer. Thus, the CyD membranes exhibit specific permeation for various materials in water.

The binding properties of o-, m-, and p-nitrophenols to the oriented-CyD-polymer in water were estimated by incubating 1 mg of nitrophenols and 20 mg of the polymer in 20 ml of water at 25°C for 25 h. Absorption spectroscopy on the liquid phase, obtained after the separation of the polymer-nitrophenol complex by centrifugation, showed that the amounts of o-, m-, and p-nitrophenols bound to 20 mg of the polymer were 0.03, 0.09, and 0.36 mg, respectively. Thus, the difference in the permeation rates of nitrophenols ( m ≈ p > o ) can not

be attributed to the difference in the binding strength of the phenols to the polymer alone. Probably, the specificity in the permeation through the membrane prepared from the oriented-CyD-polymer is associated with the interaction between the solutes and the aggregates of CyD molecules, which have mutually ordered orientation, in the membrane.

#### 4. CONCLUSION

CyD membranes are prepared from the polymers obtained by the reaction of the crystals of CyD inclusion complexes with hexamethylene diisocyanate. The membranes exhibit specific permeation for various materials in water.

#### REFERENCES

- 1) M. L. Bender, M. Komiyama, 'Cyclodextrin Chemistry', Springer-Verlag, 1978, Berlin.
- 2) N. Wiedenhof, J. N. J. J. Lammers, C. L. van Panthaleon van Eck, *Staerke*, 21, 119 (1969).
- 3) J. L. Hoffman, *J. Macromol. Sci.-Chem.*, A7, 1147 (1973).
- 4) Y. Mizobuchi, M. Tanaka, T. Shono, *J. Chromatogr.*, 194, 153 (1980).
- 5) C. H. Lee, *J. Appl. Polym. Sci.*, 26, 489 (1981).