Functionalization of polysulfone hollow fiber membranes with amphiphilic \( \beta \)-cyclodextrin and their applications for the removal of endocrine disrupting plasticizer

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**A B S T R A C T**

For the removal of endocrine disrupting chemicals (EDCs), such as di-(2-ethylhexyl) phthalate (DEHP), from drinking water, we prepared \( \beta \)-cyclodextrin included polysulfone (PSf/CD) hollow fiber membranes. \( \beta \)-Cyclodextrin (\( \beta \)-CD) was modified with fatty acid chlorides to produce amphiphilic \( \beta \)-CDs. PSf/CD hollow fiber membrane was prepared from polysulfone (PSf) dope solution with those amphiphilic \( \beta \)-CDs by phase inversion process. In the membrane formation process, the amphiphilic \( \beta \)-CDs migrated to the membrane surfaces via hydrophilic- and hydrophobic-mediated self-assembly. The performances of PSf/CD hollow fiber membranes were measured and the results showed that PSf/CD hollow fiber membranes can effectively remove DEHP from aqueous solutions and provided good water permeability.

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1. **Introduction**

Since the 1990s, researchers have found that endocrine disrupting chemicals (EDCs) are present as pollutants in many water resources worldwide, and they pose serious risks to human health [1–5]. Regulatory agencies have warned of the dangers of EDC exposure, which include detrimental effects on human and wildlife reproduction. Di-(2-ethylhexyl) phthalate (DEHP), which is used as a plasticizer in the manufacture of flexible plastics, is the most common EDC contaminant detected in water resources [6]. Recent studies have shown that DEHP concentrations in rivers and sediment deposits in many countries are on the order of several micrograms per liter or kg, even after wastewater treatment [6–9]. Therefore, the removal of EDCs, including DEHP, from waste streams that discharge into the environment becomes an important issue.

Several methods, such as nanofiltration (NF) and reverse osmosis (RO), have been suggested for the removal of organic contaminants from drinking water [10–13]. A hybrid system that combines NF with homogeneous catalytic oxidation and surface modification of NF membranes has been investigated for the effective degradation of EDCs [12,13]. These processes, however, have not been adopted in industrial commercial processes for EDC removal due to high energy costs and the low flux. Microfiltration (MF)/ultrafiltration (UF) membranes permit a relatively high flux and remove bacteria, viruses, and small particles so that they are used for water and wastewater treatment [14–16]. But, they have larger pore size than NF or RO so they could not remove EDCs effectively.

Recently, polysulfone (PSf) has been widely studied as a base material for modification in order to give some special functions to MF/UF membranes through a variety of modifying methods – hydrophilic polymer coatings [17,18], graft-copolymerization with hydrophilic monomers [19], and phase inversion with an amphiphilic block copolymer [20,21]. Among those methods, the phase inversion presents a promising approach to membrane modification because it avoids extra processing steps to enable economical and low-cost manufacturing processes.

Cyclodextrins (CDs) are cage-shaped molecules consisting of a hydrophilic cavity that can host a variety of guest molecules to form inclusion complexes, depending on the size and polarity of the CD [22]. CDs have been studied for use in the removal of heavy metals and organic pollutants from water via inclusion complexes [23,24]. In these studies, CDs were used as a form of nanosponges and a modifying agent for ceramic membranes. Among the three common forms of CDs, \( \alpha \)-, \( \beta \)-, \( \gamma \)-, which possess

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six, seven, or eight glucose units, respectively, β-CD yielded the best organic pollutant removal performance [23]. Recently, polymer membranes chemically modified with CDs have been prepared for the chiral separation of racemic amino acids and the pervaporation of liquid–liquid mixtures [25,26]. To the best of our knowledge, however, no in-depth studies of membrane with β-CD have been performed for use in water treatment applications.

Herein, we prepared β-cyclodextrin included polysulfone (PSf/CD) MF/UF membranes for water treatment applications to yield a high flux and remove EDCs effectively. For this aim, we modified β-CD with various fatty acid chlorides to produce amphiphilic β-CDs. The amphiphilic β-CDs were introduced into the membrane to produce the PSf/CD membranes via phase inversion method, especially, hydrophilic- and hydrophobic-mediated self-assembly. PSf/CD membranes were prepared in two types – flat sheet and hollow fiber membrane and the performances of these membranes were evaluated. The effects of amphiphilic β-CD on the membrane structure and the removal of DEHP from aqueous solution also are discussed.

2. Experimental

2.1. Materials

β-Cyclodextrin (β-CD) was purchased from Tokyo Chemical Industry Co., Ltd., Japan, dried in a vacuum oven at 50 °C for 24 h before use, and then kept in a desiccator. Capryloyl chloride (99%), lauroyl chloride (98%), and palmitoyl chloride (98%) were purchased from Sigma–Aldrich and used to modify β-CD. Anhydrous pyridine, N,N-dimethylacetamide (DMAC), and n-hexane were supplied by Tokyo Chemical Ind. Co. and were used without further purification. PSf (Ultrason® S6010) and polypivalylpyrrolidone (PVP, Luvitec® K30) were obtained from BASF and dried in a vacuum oven at 80 °C for 24 h before use. DEHP was provided by LG Chem. Ltd., Korea.

2.2. Preparation of amphiphilic β-CDs

To introduce β-CD into the membrane, β-CD was modified with fatty acid chlorides to produce amphiphilic β-CDs. Three fatty acid chlorides with different aliphatic chain lengths were used as listed in Table S1 and the molar ratios of fatty acid chlorides were selected to prepare a variety of amphiphilic β-CDs. The modification was conducted in accordance with the procedures described in the literature [27]. Dried β-CD (11.35 g) was dissolved in 200 mL anhydrous pyridine to give a 10 mmol solution, to which was added the desired amount of fatty acid chloride (see Table 1). The mixed solution was stirred at room temperature for 65 h, followed by concentration by evaporation under reduced pressure at 50 °C. The solution was dripped into 1 L n-hexane with stirring to precipitate and filtered out to produce the crude product. The crude product was slowly resuspended in cold n-hexane and filtered several times to remove excess solvent and unreacted monomer. Finally, the resulting materials were dried in a vacuum oven at 30 °C.

2.3. Preparation of PSf/CD membrane

Flat sheet and hollow fiber membranes were prepared by a phase inversion process. The PSf polymer was dried in a vacuum oven at 120 °C for 24 h. A dope solution was prepared in the formulation PSf/PVP/DMAC = 15/10/75 wt% with an additional 4–8 wt% amphiphilic β-CDs, as well as with unmodified β-CD. The solution was stirred vigorously at room temperature for 6 h, and then was settled overnight for degassing. To form a flat sheet membrane, the dope solution was cast on a glass plate using a 200 μm applicator followed immediately by immersion in deionized water. After coagulation, the membrane was rinsed with deionized water at 80 °C for 10 h to remove the solvent, followed by drying at 50 °C in a convection oven.

For preparing hollow fiber membranes, a bore fluid of 80/20 (w/w) DEG/DMAC solution and dope solution were fed into the inner tube and annulus, respectively, of a spinneret. After the dope and bore fluids were delivered from the spinneret, they passed through an air gap before entering a coagulation bath. The as-spun hollow fibers were wound on a bobbin, rinsed with hot water to remove residual solvent, and dried. A schematic diagram of the spinning process is described in Fig. 1. The spinning and post-treatment conditions for the PSf hollow fiber membranes are listed in Table S2.

2.4. Characterization

2.4.1. Instrumentation

Preparation of amphiphilic β-CD and the presence of β-CD moieties in the membranes were verified by Fourier transform infrared (FT-IR) and attenuated total reflection (ATR) infrared spectroscopy in the range 4000–600 cm⁻¹ using a Perkin Elmer GX spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed using a Voyager-DETM STR (Applied Biosystems Inc.) operated in the molecular weight range 1000–5000 using a UV pulsed laser (Nitrogen, 337 nm, 3 ns pulse) with 2,5-dihydroxybenzoic acid (DHBA) as the matrix and methanol as the solvent. 1H nuclear magnetic resonance (¹H NMR) spectroscopy was performed at 400 MHz using a JEOL spectrometer FX400 in DMF-d7. To investigate the degree of substitution (DS) of β-CD and the presence of residual β-CD in the membrane, Field-emission scanning electron microscopy (FE-SEM) was performed to observe the morphology of the surface and cross-section of the membrane using JEOL-JSM-6700F.

2.4.2. Permeability with pure water and DEHP removal performance

The permeability and DEHP removal performance of the hollow fiber membranes were measured using a lab-scale filtration unit (see Fig. S1). For the filtration tests, a mini module was prepared, consisting of 10 cm long hollow fiber membranes, one end of which was sealed with a polyurethane adhesive and the other end of which was potted in a plastic tube 20 cm in length. The pure water permeability (PWP) was measured using deionized water at a constant pressure (1 bar) and was calculated using the equation

\[ PWP = \frac{Q}{A \cdot \Delta P} \]  

(1)

where Q is the volume of the permeate (mL), t is the filtration time (min), A is the effective area of the membrane (cm²), and ΔP is the transmembrane pressure (bar).

DEHP removal experiments were performed using a 50 mg/L DEHP solution (in an ethanol/water = 100/123.77 (v/v) solution), which was filtered at the constant flow rate of 10 mL/min and collected at the 1, 5, 10, 20 min time points. To determine the DEHP concentration of the filtrates, the absorbance at 270 nm was measured using a Perkin Elmer Lambda 25 UV–vis spectrometer. The absorbance values of standard DEHP solutions (10–100 mg/L) were plotted as a function of the DEHP concentration, and the unknown concentration of each filtrate was determined by linear regression with the standard values [28]. The reduction in DEHP was calculated according to the equation

\[ R(\%) = \left(1 - \frac{C_f}{C_i}\right) \times 100 \]  

(2)
Table 1
Recipe and degree of substitution (DS) of the amphiphilic β-CD, determined by 1H NMR and MALDI-TOF MS.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Recipe for amphiphilic β-CD</th>
<th>Fatty acid chloride (g)</th>
<th>Degree of substitution by 1H NMR</th>
<th>Degree of substitution by MALDI-TOF MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCD</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Capryloyl chloride 11.40 (70 mmmol, 7 equiv.)</td>
<td>5.50</td>
<td>4.48</td>
</tr>
<tr>
<td>LC1</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Lauroyl chloride 4.38 (20 mmmol, 2 equiv.)</td>
<td>1.48</td>
<td>1.36</td>
</tr>
<tr>
<td>LC2</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Lauroyl chloride 8.76 (40 mmmol, 4 equiv.)</td>
<td>2.62</td>
<td>2.67</td>
</tr>
<tr>
<td>LC3 (LCD)</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Lauroyl chloride 15.32 (70 mmmol, 7 equiv.)</td>
<td>5.10</td>
<td>4.83</td>
</tr>
<tr>
<td>LC4</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Lauroyl chloride 21.88 (100 mmmol, 10 equiv.)</td>
<td>9.17</td>
<td>8.63</td>
</tr>
<tr>
<td>PCD</td>
<td>β-CD 11.36 g (10 mmol)</td>
<td>Palmitoyl chloride 19.24 (70 mmmol, 7 equiv.)</td>
<td>6.23</td>
<td>5.08</td>
</tr>
</tbody>
</table>

where $R$ is the reduction in DEHP, $C_p$ is the concentration in the permeate, and $C_f$ is the concentration in the feed solution.

3. Results and discussion

3.1. Characterization of the amphiphilic β-CD

The amphiphilic β-CDs were denoted CCD, LCD, PCD, according to the fatty acid chloride with various chain length, and LC1–LC4 according to the fatty acid chloride molar ratio (see Table 1). Fig. S2 shows the FT-IR spectra of β-CD, capryloyl chloride (CaCl), and CCD, in which the broad O–H (3300 cm⁻¹) of β-CD and the C=O stretching (1734 cm⁻¹) and C–H stretching (2800 cm⁻¹) peaks are visible after modification [29]. The shift of C=O stretching peak indicates the successful change of acyl group in the fatty acid chloride to ester group with β-CD. The other amphiphilic β-CDs yielded results identical to those of CCD, suggesting that the modification reactions were successful (see Figs. S3 and S4). 1H NMR analysis provided additional evidence for the successful modification of β-CD with fatty acid chlorides. As shown in Fig. S5, the chemical shifts of the primary (δ = 4.42 ppm, 6-OH) and secondary (δ = 5.68, 5.64 ppm, 2,3-OH) alcohols of β-CD disappeared, and the signal for the first alkyl group (δ = 3.12 ppm, α position) of CaCl shifted to δ = 2.40 ppm in CCD [30]. These results indicated the successful esterification of β-CD and CaCl, and similar results were observed for the other fatty acid chlorides, as shown in Figs. S6 and S7.

The number of substituents on each β-CD molecule, that is, the degree of substitution (DS), could be calculated from the 1H NMR and MALDI-TOF MS spectra [30,31]. In 1H NMR spectra, DS could be calculated from the ratio between the integral areas under the H-1 peak and δ peak – the terminating methyl group of the aliphatic chain (see Figs. S5–S7). Figs. S8 and S9 show the MALDI-TOF MS spectra of amphiphilic β-CDs. These MS spectra permit estimation of the DS, as

$$DS = \frac{\sum I_i D S_i}{\sum I_i}$$

where $I_i$ denotes the intensity of the i-th peak and DS$_i$ denotes the degree of substitution corresponding to the i-th peak [31]. The DS results are listed in Table 1 and indicate DS values of 1.4–9.2, obtained from NMR. These results suggest that the DS of the amphiphilic β-CDs could be controlled according to the initial molar ratio of the reagents.

Previous studies revealed that the primary hydroxyl groups (6-OH) of β-CD are more nucleophilic than their secondary hydroxyl groups (2,3-OH), and strong electrophiles, such as fatty acid chloride, could prefer to attack the 6-OH [32]. The NMR spectra showed that a peak at 4.5–4.6 ppm corresponding to the 6-OH of

Fig. 1. Schematic diagram of the preparation of PSf/CD hollow fiber membranes.
β-CD disappeared, and the diastereotopic 6-H at δ = 4.09 ppm and δ = 4.34 ppm appeared after esterification. Fig. S9 shows that the molecular weight distribution of LC4 displayed two maximum intensities corresponding to the number substitution of 5 and 8, in contrast with the results of LC1–LC3. The number of -OH in β-CD was seven. Although the primary positions were not fully substituted, the secondary positions may be preferred due to steric hindrance. These results suggested that esterification mainly occurred at the primary position first, and the excess reaction occurred at the secondary position.

3.2. Characterization of PSf/CD flat sheet membranes

It was important to determine the maximum loading of amphiphilic β-CD achievable on the membrane surfaces, and the optimal conditions for preparing such membranes. Flat sheet membranes with various levels of amphiphilic β-CD loading were prepared by varying the β-CD concentration in the dope solution. The fabricated flat sheet membranes were denoted like C-4, L3-4, and P-8 according to the initial letter and composition of amphiphilic β-CD in the dope solution. Residual β-CD content in the PSf membrane was measured by 1H NMR spectroscopy, as shown in Fig. S10. A peak at 4.9 ppm indicates the protons at the 1-position of β-CD, whereas the peak at 7.3 ppm arose from protons at the α-position of PSf. The weight ratio of β-CD to PSf could be calculated from the areas under the 1 and α peaks. The calculated residual β-CD contents are described in Fig. 2, along with the substituted aliphatic chain length and the degree of substitution. Residual β-CD was not observed in the membrane prepared with the original β-CD, and the amount of β-CD increased with the length of the aliphatic chain in the amphiphilic β-CD. These results suggest that the original β-CD was lost during the membrane formation process and that the aliphatic chain of amphiphilic β-CD was anchored more strongly to the PSf membrane as the chain length increased. The solubility of amphiphilic β-CD in the dope solution increased with increasing degree of substitution so that 8% of β-CD contents could be achieved with the LC3 and LC4. In addition to the solubility, the residual β-CD content in the PSf membrane also increased as the degree of substitution increased. The maximum rate of substitution of the fatty acid chain in β-CD to form LC4 yielded a water-soluble modified β-CD that dissolved during the phase inversion process. The residual β-CD was, therefore, very small. The maximum residual β-CD

![Fig. 2. Optimization of preparation of PSf/CD membrane; residual β-CD contents to, (a) chain length of amphiphilic β-CD; (b) degree of substitution of amphiphilic β-CD (by 1H NMR).](image)

![Fig. 3. (a) ATR-IR spectra of both surfaces of PSf/CD flat sheet membranes modified with LC3; (b) schematic diagram of hydrophilic- and hydrophobic-mediated self-assembly in the PSf/CD membrane formation.](image)
content in the membranes was 15.0% for the L3-8, which indicates 8% LC3 in the dope solution.

The surface chemistry of the modified PSf/CD flat sheet membranes was investigated by ATR-IR to demonstrate surface segregation of the β-CD moieties. Fig. 3a shows the IR spectra of both sides of the membrane, where the front side corresponds to the water contact side of the membrane and the back side corresponds to the inside of the membrane in contact with glass. The IR spectra of the front sides displayed specific peaks due to β-CD that were not found in the back side IR spectra. During the phase inversion process, the front side of the membrane contacted the water and coagulated at first, and the other surface contacted the glass at a later time. The time difference induced the hydrophilic part of amphiphilic β-CD to shift toward the front surface of the membrane (see Fig. 3b). The asymmetric membrane surface chemistry provided evidence for hydrophilic- and hydrophobic-mediated self-assembly during phase inversion process.

### 3.3. PSf/CD hollow fiber membrane characteristics

Hollow fiber membranes were prepared from the optimum formulations used to prepare flat sheet membranes, L3-8, in which the optimum aliphatic chain length was lauroyl and the maximum amphiphilic β-CD content was 8%. We prepared the hollow fiber membranes with dope solution containing PSf/PVP/DMAC = 15/10/75 wt% with 4, 6, and 8 wt% of LC3, denoted H-L3-4, H-L3-6, and H-L3-8, respectively, as well as neat hollow fiber membrane without LC3. The morphologies of hollow fiber membranes were observed by FE-SEM and are shown in Fig. 4. The neat PSf hollow fiber membrane had a fiber-like structure with lots of macrovoids in the cross-section. The macrovoids in membranes decreased with increasing LC3 contents in dope solution from H-L3-4 to H-L3-8. The thermodynamic instability is a key factor on the formation of macrovoid. The delay of demixing is suppressed when the thermodynamic instability of the dope solution increases by addition of nonsolvent into the dope solution. This results in the formation of sponge-like structure, the enlargement of pore size in the surface and the flux increment [33]. LC3 made the dope solution instable thermodynamically because of its high concentration and developed the sponge-like structure from neat to H-L3-8 as shown in Fig. 4.

Fig. 5 shows the pure water permeabilities of the PSf/CD hollow fiber membranes. The pure water permeability increased dramatically as LC3 contents in dope solution increase so that those of H-L3-6 and H-L3-8 were about 5000 LMH/bar. These results were also because the thermodynamic instability of the dope solution...
increased with the addition of LC3 and help the formation of more porous sponge-like structure. Such porous structures can minimize the transport resistance during water permeation so as to increase the water flux.

The residual β-CD content in the hollow fiber membranes was measured according to the method used to analyze the flat sheet membranes. The trends and values were similar to the flat sheet membranes as described in Fig. S11 and the H-L3-8 had the largest residual CD content in the membrane.

3.4. DEHP removal using the PSf/CD hollow fiber membrane

DEHP removal tests using both neat PSf and PSf/CD hollow fiber membranes were conducted with 50 mg/L DEHP in an EtOH/H2O solution over a time interval of 1-20 min. As shown in Fig. 6, the DEHP removal efficiency decreased in the order H-L3-8 > H-L3-6 > H-L3-4 > neat, that is, the DEHP removal efficiency increased considerably with the amount of β-CD added in the dope solution, and the maximum reduction efficiency was 70% higher than that of the neat PSf membrane. This trend was consistent with the residual β-CD measured by NMR spectroscopy. High β-CD concentrations in the dope solution increased the residual β-CD amount in the PSf/CD hollow fiber membranes and results in increasing the quantity of DEHP removed by the membranes.

In the previous studies, the concentrations of DEHP in the source solutions were from 20 μg/L to 10 mg/L in the DEHP removal tests – much lower than the concentration used in this study [23,24]. For low concentrations of DEHP in source water, the removal performances of neat PSf and PSf/CD hollow fiber membranes were indistinguishable due to adsorption of DEHP onto the PSf material itself. This was the result from the affinity of DEHP toward the phenyl groups of the PSf [34]. Therefore, in this study, DEHP removal tests were conducted at very high concentrations of DEHP, much higher than could be observed in the environment.

These results showed that DEHP in the source solution could be removed effectively at high flux using PSf/CD hollow fiber membranes and the removal rate increased with the residual β-CD content. PSf/CD hollow fiber membranes are, therefore, appropriate for removing DEHP from source water and available for an eco-protective water treatment system.

4. Conclusion

In this work, β-cyclodextrin included polysulfone (PSf/CD) membranes were successfully prepared via one-pot phase inversion process using PSf and amphiphilic β-CD. Amphiphilic β-CD was synthesized by modifying β-CD with fatty acid chlorides. The modification of β-CD and the presence of β-CD moieties in the PSf/CD membranes were verified by FT-IR, MALDI-TOF, 1H NMR spectroscopy and in particular, ATR-IR spectroscopy showed that β-CD was present on the surface of the membrane, indicating the successful hydrophilic- and hydrophobic-mediated self-assembly. The β-CD amount in the PSf/CD membranes was highest as about 15 wt%, when the lauroyl chloride was used in β-CD modification and the amphiphilic β-CD was added at 8 wt% into dope solution. The DEHP removal efficiency of PSf/CD membrane increased considerably with the amount of β-CD, and the maximum reduction efficiency was up to 70%. These results open up the possibility that PSf/CD membranes can be used as the commercially available and eco-protective water treatment system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2012.03.037.

References


