Ultrathin 2D-Layered Cyclodextrin Membranes for High-Performance Organic Solvent Nanofiltration

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Synthetic membranes with a high selectivity for demanding molecular separations and high permeance have a large potential for the reduction of energy consumption in separation processes. Herein, for the first time, the fabrication of an ultrathin layered macrocycle membrane for molecular separation in organic solvent nanofiltration using per-6-amino- β -cyclodextrin as a monomer for membrane manufacturing by interfacial polymerization is reported. Compared to a regular nonfunctionalized cyclodextrin, a higher reactivity is observed, enabling a very fast membrane formation under mild conditions. The formed membrane is composed of a layered structure of polymerized cyclodextrin, which shows high stability in different organic solvents. The membrane exhibits excellent separation performance for organic solvent nanofiltration, both with nonpolar and polar solvents. Most importantly, this new membrane type can discriminate between molecules with nearly identical molecular weights but different shapes. The unmatched high permeance and shape selectivity of the membranes can be attributed to the ultralow thickness, controlled microporosity, as well as the layered macrocycle structure, which makes the membranes promising for high-performance molecular separation in the chemical and biochemistry industry.

There are two straightforward and effective strategies for this purpose. One is to design composite membranes with ultrathin separation layers. However, subtle manipulation or multistage procedures are frequently needed for the preparation of ultrathin membranes, which makes the process complex and difficult.^[3–6] The other is to tailor the intrinsic polymer properties and to create an interconnected microporosity within the membrane at a molecular level. Numerous methods have been developed up to date to design membranes with such desired characteristics.^[7–13] For example, by the surface-initiated Sonogashira–Hagihara polymerization, all-rigid microporous membranes comprising conjugated polymers were prepared.^[9] The presence of abundant, interconnected, and permanent micropores in 3D networks leads to high permeance for a wide range of organic solvents with a molecular weight cutoff of about 560 g mol^{−1}. Polymers

1. Introduction

Among various membrane-based technologies, organic solvent nanofiltration (OSN) is an emerging attractive technique for molecular separations (200–2000 Da) in organic solvents.^[1,2] Because of the harsh working environment of OSN, the membranes should be robust enough in organic solvents, a requirement that could not be satisfied with many currently available polymers. Therefore, to extend the industrial applications, membranes with high permeability and selectively in organic solvents of different polarities are required.

of intrinsic microporosity (PIMs) constitute a novel class of ladder-like materials composed of contorted, rigid monomers and have also been used for membrane preparation. Due to the inefficient packing of polymer chains, the membranes are endowed with high free volume, leading to a good performance for nonpolar organic solvents.^[10] However, PIMs are soluble in various polar solvents, restricting their wide application in OSN. Efforts have also been made to improve the microporosity and interconnected void (i.e., cavities) by adding microporous organic materials into membranes, such as zeolites, metal–organic frameworks (MOFs),^[14–16] covalent organic frameworks (COFs),^[17,18] carbon materials,^[19–22] and clay.^[23,24] The compatibility between these fillers and the polymer matrix is not always satisfying, resulting in large voids or defects, decreasing the membrane selectivity.^[25] Therefore, using small organic molecules with intrinsic microporosity could be a better option. Recently, cyclodextrins (CDs), which are sustainable and non-toxic macrocycle molecules obtained from starch, have been used as main building blocks for membrane preparation.^[26] Due to the well-known hollow cavity structure, its intrinsic and well-defined microporosity can enhance permeability and selectivity of membranes. But because of the low reactivity of the cyclodextrin hydroxyl groups, a high monomer concentration, a highly basic (pH > 13) environment, and a long reaction time were demanded in the membrane formation.^[26] This complicates the manufacturing process. Furthermore, in such

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Figure 1. Interfacial polymerization of polyamide-CD films.

fabrication conditions, cyclodextrin is randomly crosslinked; both sides of the cavity react with crosslinkers. This may result in a high resistance for molecular transport through their cavities. In addition, the long reaction time leads to relatively thick membranes. The primary hydroxyl groups of the cone-shaped CD molecule are located on the narrow rim of the cone. These OH- groups are more reactive than the secondary OH- groups on the larger rim, and the amination happens here preferentially (refer to Scheme S1 in the Supporting Information). We postulated that CD with highly reactive and regioselective groups could be easily crosslinked via interfacial polymerization leading to ultrathin dense polymer network structures. In this way, CD is more favorable for molecules' access and transport compared to the random crosslinking on both sides of CD cavity.

Herein, we propose a novel type of ultrathin-layered CD membranes with unprecedented permeance based on per-6-amino-β-cyclodextrin (amino-CD). Due to the high reactivity of the amino groups of the modified CD for interfacial polymerization, the membrane can be quickly formed under mild conditions with low reactant concentration. Interestingly, the formed membrane is constructed in a 2D-layered structure, which is rarely observed in the interfacial polymerization process. The as-prepared polyamide-CD membrane exhibits excellent separation performance for organic solvent filtration, outperforming the commercial membranes to a large extent, and being comparable or better than recently reported OSN membranes. Most importantly, this new membrane type can discriminate between molecules with nearly identical molecular weights but different shapes. This work demonstrates that by suitable molecular engineering, novel macrocycle membrane with special microstructure can function as a promising candidate for high-performance precise molecular separation in both aqueous and organic solvents.

2. Results and Discussion

2.1. Synthesis of Polyamide-CD Membrane

Amino-CD was synthesized according to the literature.^[27] However, the amino-CD has very low solubility in water due to a strong

intramolecular or intermolecular hydrogen bonding. To prepare an aqueous phase of amino-CD with reasonable concentration, the pH of the aqueous phase was appropriately adjusted to fully dissolve the amino-CD in water (Figure S1, Supporting Information). As confirmed by electrospray ionization-mass spectrum (ESI-MS), most of the amino groups maintained a free state without of protonation (Figure S2, Supporting Information). **Figure 1** shows the fabrication of the polyamide-CD membranes by interfacial polymerization between an aqueous phase containing amino-CD and an organic phase containing terephthaloyl chloride (TPC). Because of the high reactivity of the amino groups with the acyl chloride group, a highly crosslinked polyamide network can be formed. Figure S3 (Supporting Information) shows scanning electron microscopy (SEM) images of the surface of the polyamide-CD membrane fabricated on polyacrylonitrile (PAN) substrate. Compared to the porous PAN support, a dense layer is formed without visible defects even with low amino-CD (down to 0.16 wt%) and TPC concentration (0.05% w/v) in just 1 min. We found that the use of supports with high surface hydrophobicity and pore heterogeneity resulted in destructive defects (refer to Figure S4 in the Supporting Information). The amino-CD concentration in the aqueous phase solution has a strong effect on the membrane surface morphology. At a low amino-CD concentration in the aqueous phase solution, the membrane surface is flat and smooth, while with the increase in concentration, the membrane surface becomes rougher and some protrusions can be observed.

2.2. Morphology and Chemical Structure Characterization

The boundary between the PAN supports and the ultrathin polyamide-CD films could be hardly identified (Figure S5, Supporting Information) by SEM to determine the film thickness. Therefore, we prepared a freestanding polyamide-CD membrane by the same procedure applied on the PAN support, which is shown in Figure S6 (Supporting Information). **Figure 2a,b** shows the freestanding membrane formed at the free interface between the organic and aqueous phases, which is then transferred to float on the water surface. The diameter of the membrane is about 3 cm; it has a defect-free appearance.

Figure 2. Freestanding film. A freestanding polyamide-CD film formed at the a) aqueous/organic interface, b) floating at the water surface, and c) captured by an anodic alumina oxide support. SEM image of the d) surface morphology and e) cross section of a freestanding polyamide-CD film on an anodic alumina oxide support. f-i) AFM images and the corresponding height profiles of the freestanding polyamide-CD film. j) Thickness increase of polyamide-CD film with the amino-CD concentration.

The freestanding film could be transferred onto anodic alumina oxide supports (Figure 2c). The cross-sectional SEM image clearly shows an ultrathin layer covered on the alumina support (Figure 2e). Interestingly, the SEM image of the membrane surface (Figure 2d) reflects the morphology of the support beneath the polymerized layer, as a result of the extremely low thickness of the polyamide-CD film. The freestanding films were also deposited onto a silica wafer to better quantify the thickness by atomic force microscopy (AFM) (Figure 2f–i). The topology of these membranes suggests that the thickness of the membranes increases with the increase of the amino-CD concentration (Figure 2j; Figure S7, Supporting Information). A monolayer of polyamide-CD (1 nm in thickness) could be formed when 0.16% of amino-CD was used. Recently, Moradi et al. studied the monolayer formation capability of a calixarene derivative, which has a similar structure as cyclodextrin, at the air–water interface by the Langmuir–Blodgett technique.^[28] A 2D supramolecular freestanding molecular thin layer was formed via the dipole–dipole interactions between building units. In comparison, the CD film in this study was constructed via covalent bonds leading to a more stable structure. The thickest membrane (10.6 nm) was obtained with the highest amino-CD concentration (1.3%), which is still significantly thinner than a common polyamide membrane. Karan et al. prepared an ultrathin polyamide membrane by the interfacial reaction of metaphenylene diamine (MPD) and trimesitylene

chloride (TMC).^[3] However, a sacrificial interlayer was needed to prepare such thin membranes.

To study the morphology and bulk properties of the polyamide-CD membrane, we continuously collected a large amount of the polymerized samples from the interfacial reaction zone (Figure S8, Supporting Information). The synthesized polyamide-CD has film-forming characteristics (Figure S9a, Supporting Information), whereas samples with the same chemical composition (Figure S10, Supporting Information), but obtained from a monophasic reaction, are powders with agglomerated particles (Figure S9b, Supporting Information). Their chemical structure as polyamide was verified by Fourier transform infrared spectroscopy (FTIR) (Figure 3a; Figure S10, Supporting Information) and X-ray photoelectron spectroscopy (XPS) (Figure 3b–d; Figures S11 and 12 and Table S1, Supporting Information). Since the amino-CD has only a narrow rim with amino groups, it can regioselectively react with TPC when these amino groups face to the organic phase during the interfacial polymerization process, resulting in a certain orientation of the CD in the formed film. Wide-angle X-ray diffraction (XRD) patterns show two big Bragg diffraction peaks emerging at $2\theta = 9.8^\circ$ and 18.8° , respectively (Figure 3e). They correspond to layer spacings of 0.89 and 0.47 nm, which can be well indexed as (001) and (002) reflections.^[29,30] This indicates an ordered layered structure of the film. Considering that the height of cyclodextrin is 0.8 nm, these XRD patterns

Figure 3. Chemical characterization of the polyamide-CD film. a) FTIR spectra of pristine CD and a polyamide-CD film synthesized by continuous collecting the polymer from the interfacial reaction zone. b) XPS survey of i) PAN support, ii) polyamide-CD/PAN membrane, and iii) polyamide-CD film. c) C 1s spectra and d) N 1s spectra of a polyamide-CD film. e) XRD pattern of the polyamide-CD film (red) and β -cyclodextrin (blue). f) TGA curves of pristine CD and a polyamide-CD film.

suggest a 2D-stacked structure of crosslinked cyclodextrin film, as illustrated in Figure 1. In contrast to the reversible reactions for the common 2D COF synthesis,^[31] the amidation between the amino-CD and TPC is irreversible. Though the regular in-plane structure was not observed, an ordered structure in the z-direction is still formed, implying the significance of rational molecule design and proper synthesis conditions. For pristine cyclodextrin membranes, no such XRD peaks are present, due to the random crosslinking of CDs during the membrane formation. Water contact angle (CA) measurements also confirmed the asymmetry of the polyamide-CD film. The contact angle is 29° on the film bottom, which is much more hydrophilic than the top surface without hydroxyl groups (72°; Figure S13, Supporting Information). Using data from C 1s and N 1s XPS

spectra, it is estimated that the CD content of the film is about 61.5 wt%, and each CD unit is covalently connected with four other CDs in the membrane by TPC as the crosslinker (refer to Supporting Information for details on the estimation). Due to such a high crosslinking degree, the polyamide-CD membrane has a highly dense structure and a high chemical and mechanical stability. Although the thickness of the membrane is only about 10 nm, it has good mechanical stability, and it maintains its integrity when covering a metal ring (Figure S14, Supporting Information). The polyamide-CD membrane also shows high resistance in a wide range of solvents (Figure S15, Supporting Information). Moreover, the thermogravimetric analysis (TGA) measurement demonstrates that it was thermally stable up to 250 °C in a nitrogen atmosphere (Figure 4e). The weight loss

Figure 4. Nanofiltration performance. a) The permeance of various solvents through the polyamide-CD membrane (0.64%). b) Water flux as a function of the applied pressure. c) Rejection of various dye molecules in methanol solution by the polyamide-CD membranes. d) UV absorption spectra and photos of the mixed dyes (methylene blue, safranin O) in methanol solution before (blue) and after (red) permeation through a polyamide-CD membrane (1.28%). e) GPC chromatogram of e) linear PEG 1000, f) α -cyclodextrin, and g) trimethylolpropane ethoxylate in methanol, respectively, before (red) and after (blue) filtration through polyamide-CD membrane (1.28%).

in the temperature range of 250–400 °C was attributed to the decomposition of the CD. From the curve, the CD content in the membrane was calculated to be about 57 wt%, which is well in accordance with the result from the XPS measurement.

2.3. OSN Performance

The OSN performance of polyamide–CD membrane/PAN composites was evaluated in detail. The polyamide–CD membrane (0.64%) is highly permeable for both polar and nonpolar solvents (Figure 4a). This could be attributed to both hydrophilic and hydrophobic passageways existing within the film. Among the investigated solvents, water shows the highest permeance because of its smallest molar volume. Acetone, though having a large molar volume, had the second highest permeance, due to the low viscosity (Table S2, Supporting Information). For alcohols, the membrane permeance decreases sharply with the increase of the solvent viscosities (Figure S16, Supporting Information). Besides polar solvents, nonpolar ones can also pass through the membrane at high rates, because of the favorable hydrophobic cavity of the CD unity. These results demonstrate that the solvent viscosity and the molar volume, as well as the film microstructure, all influence the performance.

The permeance for the polyamide–CD nanofilm membranes is plotted as a function of time in Figure S17 (Supporting Information). Even after 6 h continuous filtration operation, the permeance is maintained constant, indicating the good long-term durability. Furthermore, as shown in Figure 4b, the fluxes increase proportionally with the increasing applied pressure up to 8 bar. On decreasing the pressure to 0.5 bar, the flux was recovered, indicating that the membrane has excellent resistance and maintained its microstructure under high pressure.

The membrane selectivity has been evaluated using various dye molecules (Table S3, Supporting Information) as model solutes, and the rejection results are shown in Figure 4c and Figure S18 (Supporting Information). It is obvious that with the increase of the molecular weight of the dye molecules, the rejection increased. For the polyamide–CD membrane (0.64%), the low-molecular-weight dye, methyl red, has only a rejection of 81%, while the high-molecular-weight dye, brilliant blue, is totally rejected (>99%). The rejection of dyes is higher for thicker membranes. We believe that during the membrane formation process via interfacial polymerization, small defects or weak points might be present in the thinnest layer. The defects are covered or the layer is strengthened as the thickness increases, leading to an improved rejection capability, while the permeance decreased accordingly (Figure S19, Supporting Information). In addition, the hydrolyzed acyl chloride could impart a negative charge to the membrane surface, repelling negatively charged dye molecules, while small neutral and positive dyes molecules passed easily (Figure S20, Supporting Information). Because of the ultralow thickness of the membrane with intrinsic open porosity, the polyamide–CD membrane outperformed the commercial membranes to a large extent, and it is comparable or better than recently reported OSN membranes (Table S4, Supporting Information).

2.4. Shape Selectivity of the Membrane

The most interesting characteristics of the polyamide–CD membrane are their ability to discriminate molecules based on shape selectivity. Since β -CD has a rigid cavity in its structure, it can effectively reject molecules with the kinetic size larger than the cavity size (>0.61 nm). These molecules can only go through the membrane via the interstitial space between cyclodextrin molecules. For example, the rejection of two molecules, Safranin O (351 g mol⁻¹) and methylene blue (320 g mol⁻¹), is quite different, although their size is similar. Most of methylene blue molecules permeate (38% of rejection), while 72% of Safranin O has been retained. Considering the small difference in their molecular weight, this significant separation arises from their different molecular shape. Safranin O has a T-shape structure, which makes the molecule bulky in any direction, impeding its permeation through the membrane, while methylene blue, with a slim structure, can pass through the membrane with much lower resistance. However, because of the possible undesired molecules' transport via the interspace between the CD units, the shape selectivity is compromised inevitably. After the mixture solution separation, the permeate solution becomes almost blue, while the feed solution is purple (Figure 4d). Larger molecules have also been tested to verify the membrane shape selectivity. Poly(ethylene glycol) (PEG) (1000 g mol⁻¹), a molecule with the ability to go through the cyclodextrin cavity,^[32] has a rather low rejection by the membrane (Figure 4e). In contrast, molecules (trimethylolpropane ethoxylate, 1014 g mol⁻¹; α -cyclodextrin (α -CD), 973 g mol⁻¹) of similar molecular weight but having a shape too bulky for the cyclodextrin cavity were substantially retained (Figure 4f,g). We think that these findings with differently shaped molecules of similar molecular weights are a strong indication of a shape selectivity. But more insight would be desirable. Blocking the CD cavity pathway and calculation of an effective molecular diameter like proposed by Van der Bruggen et al.^[33] are possible instruments for future experiments.

3. Conclusion

In summary, the layered cyclodextrin membranes have been facilely fabricated via interfacial polymerization of amino-CD and TPC under mild condition. The amino-CD is regioselectively crosslinked to form a strong and dense polyamide network in the membrane, in which cyclodextrin molecules were crosslinked to form a layered structure. In spite of its ultrathin structure, the membrane has high stability in water and organic solvents, and shows outstanding performance for organic solvent nanofiltration. Due to the hydrophobic cavity and hydrophilic periphery of cyclodextrin, the membrane promotes a high transport for nonpolar and polar solvents. Most importantly, the membrane has a high shape selectivity. It can discriminate between molecules of similar size based on their shape. This work is the first study on an ordered layered macrocycle membrane. We expect that by rational monomer molecular design and controlled polymerization, our approach will inspire further studies of novel engineered macrocycle membranes with desired microstructures composed of

cyclodextrin as well as other cavitands for potential applications in demanding separations.

4. Experimental Section

Amino-Cyclodextrin Aqueous Solution: Per-6-amino- β -cyclodextrin was synthesized according to the literature,^[27] and the details are described in the Supporting Information. To a dispersion of per-6-amino- β -cyclodextrin (0.6 g, 0.53 mmol) in water (30 mL), HCl (0.1 M) was added drop wise until the pH = 7.8, and the concentration was about 1.28% w/w. To prepare lower concentrations (0.64%, 0.32%, and 0.16% w/w) of cyclodextrin aqueous solution, the above solution was diluted accordingly and pH was adjusted to 7.8.

Interfacial Polymerization: Polyamide-CD membranes were prepared by interfacial polymerization as follows, unless otherwise stated. Porous PAN ultrafiltration membrane (GMT GmbH, Rheinfelden, Germany) was used as the support and fixed in a polytetrafluoroethylene frame. After impregnation with cyclodextrin aqueous solution for 10 min, the PAN support was subjected to a rubber roller to remove the excess of the aqueous solution. Then, a solution of TPC in Isorpar G (0.05% w/v) was poured on the PAN surface for 1 min. Finally, after removing the excess TPC solution, the membrane surface was washed with hexane five times to remove unreacted TPC and then dried in air overnight and stored in Milli-Q water. All the interfacial polymerization was conducted at 25 °C and a relative humidity of about 60%.

Freestanding polyamide-CD films were prepared at the free interface between aqueous and organic solutions with the same concentration as that of polyamide-CD membrane using PAN support. After 1 min of reaction time, the formed films were then picked up by silica wafers or anodic alumina oxide supports as the procedure shown in Figure S6 (Supporting Information).

Membrane Performance: Nanofiltration experiments were conducted using Sterlitech stainless steel cells (model HP4750, an effective membrane area of 13.8 cm²) with pressure (0.5–10 bar). The performance of the membranes was analyzed in terms of the permeance of water or various organic solvents and the rejection of dye molecules. All experiments were done at room temperature, and the collected data were the average of repeated three parallel tests. The solute concentration used in the tested solutions was 10–20 ppm for dyes solution in methanol. The solute concentration was measured on a NanoDrop UV-vis spectrophotometer using quartz cuvettes.

The solvent flux (J) and permeance (P) were determined according to Equations (1) and (2), respectively

$$J = V/At \quad (1)$$

$$P = J/\Delta P \quad (2)$$

where V is the permeate volume, A is the effective filtration area (A), t is the operation time, and ΔP is the applied pressure for filtration.

The rejection was measured by the concentration ratio of permeate and feed solution according to Equation (3), where C_f and C_p represent concentration of feed solution and permeate, respectively

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (3)$$

The shape selectivity of the membrane was tested with two sets of molecules of the same charge, charge number, and similar molecular weight: methylene blue ($M_w = 320 \text{ g mol}^{-1}$) and Safranin O ($M_w = 350 \text{ g mol}^{-1}$); α -CD ($M_w = 973 \text{ g mol}^{-1}$), PEG ($M_w = 1000 \text{ g mol}^{-1}$), and trimethylolpropane ethoxylate ($M_w = 1014 \text{ g mol}^{-1}$). For the dye molecules' shape-selectivity test, a solution of mixed dyes was used with the concentration of 5 ppm for each dye molecule. The concentrations of both feed and permeate were analyzed simultaneously via UV-vis spectroscopy. For the other

set of molecules (α -CD, PEG, and trimethylolpropane ethoxylate), gel-permeation chromatography (GPC) was utilized to test their concentration in the feed and permeate. Because their signals in the GPC are overlapped, these were tested separately. 1000 ppm PEG 1000 in MeOH, 1000 ppm α -CD in MeOH, and 1000 ppm trimethylolpropane ethoxylate in MeOH were tested in sequence. After each filtration, pure MeOH was passed through the membranes to remove impurity before the next filtration. The concentrations of these molecules were verified via GPC on Agilent Technologies 1200 series installed with dual columns in series (PL Aquagel-OH 60 μm and PL Aquagel-OH 30 μm) and a G1362A refractive index detector (RID). The column and the RID were working under 30 and 35 °C, respectively. Milli-Q water was used as the mobile phase with a flow rate of 1 mL min⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D structure, cyclodextrin films, organic solvent nanofiltration, shape selectivity

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