Functionalized Assembly of Solid Membranes for Chiral Separation using Polyelectrolytes and Chiral Ionic Liquid

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The successful assembly of a new solid membrane for chiral separation, assembled via the formation of complexes of a polyelectrolyte and β-cyclodextrins chiral ionic liquid (β-CD-IL) is presented. Before the assembly, the β-CD-IL, used as a chiral selector, was synthesized and characterized by ^{1}H NMR. To tune the chiral separation capability of the solid membrane, β-CD-IL was subsequently immobilized on to porous supporting membranes through layer-by-layer assembly of the β-CD-IL and polyelectrolytes. The resulting membrane was used in the chiral separation of D, L-tryptophan racemate enantiomer. The membrane structure and surface morphologies were systematically analyzed by FT-IR, UV–vis, SEM and AFM. The effects of layer number on the chiral separation were investigated. It was found that the more β-CD-IL was immobilized on the membranes; the higher average separation factor could be obtained. The stability of the multilayer membrane was improved by coating with crosslinked polymer layer. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4772–4779, 2013

Keywords: chiral separation, immobilization, β-cyclodextrins chiral ionic liquid, layer-by-layer assembly

Introduction

Direct separation of optical isomers has been widely recognized as one of the most difficult technical problems in organic chemistry.[1] During recent years, membrane separation has been considered to have great potential for industrial chiral separation. Liquid membranes for chiral separation, such as supported liquid membranes and emulsion liquid membranes, have been widely studied.[2–4] The application of liquid membrane separation has been mainly restricted by their poor long-term stability. By comparison, solid membrane separation has many advantages such as the ease of continuous operation, ability to scale-up, the flexibility of the device design and system, and low-energy consumption. Therefore, the use of solid membrane techniques for the separation of optical isomers has now gained widespread attention.[5]

For a chiral solid membrane, the chiral selector is usually fixed in the polymer membrane by blending and coating methods. The enantiomer selective recognition and affinity of the chiral selector are the most important factors for solid membrane separation. Commonly used chiral selectors include proteins, antibiotics, polysaccharides, amino acids, apo-enzymes, DNA and surfactant supramolecular compounds such as cyclodextrins and crown ethers.[6–9] These compounds possess enantiomers which are able to bind to specific sites including enantiomeric binding sites, chiral rings or holes. Cyclodextrins (CD) have a chiral cavity which is hydrophobic inside and hydrophilic outside. A chiral guest can be separated by making use of differing intermolecular force for the two enantiomers and this technique has been widely used in solid membrane chiral separation.[10–12] However, due to its low solubility in aqueous solution, the loading of the chiral selector is very limited. Therefore, the immobilization of the chiral selector results in lower selectivity. The preparation of a chiral solid membrane often proves difficult when taking into account the desired high-throughput and good separation factor. Consequently, many researchers have investigated ways to modify CD to improve its solubility.[13,14]

Chiral ionic liquids (ILs) act not only as a solvent but also a chiral selector.[15] Recent synthesis of chiral ILs has provided new potential selectors for enantiomeric separation. For example, Francois et al. have studied the influence of chiral ILs in the electrolytes for capillary electrophoresis (CE) in the presence of classical chiral selectors (diortrimethyl-_-cyclodextrin).[16] They observed an increase in separation selectivity and resolution and, in some cases, possible synergistic effects. Tran et al. have recently reported that a chiral IL, S—[3-(chloro-2-hydroxypropyl) trimethylammonium] [bis((trifluoromethyl)sulfonyl)amide] (S—[CHTA]+ [Tf_2N]—) can be successfully used both as a co-electrolyte and as a chiral selector for CE.[17] These previous studies have demonstrated that chiral ILs exhibit significantly better enantio-separation properties than do classical chiral selectors. In addition to the aforementioned advantages, it is well-known that an increase of temperature can effectively increase the membrane flux. Chiral ILs has low-vapor pressure. Therefore, it is expected that the immobilization of the chiral ILs on to the polymer membrane can not only improve the fixed loading of the chiral selector but can also effectively avoid the instability resulting from higher-temperature operation.[18] However, most of the studies focused on applications in CE fields. The application of the use of chiral ILs in separation membranes has been less investigated.

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The direct fabrication of a blending membrane including polymer and chiral selectors usually requires a certain thickness to ensure that the membrane has sufficient mechanical strength for separation uses. Therefore, the membrane flux obtained is relatively low, which limits its application. The preparation of composite membranes might be an effective alternative method to achieve an ultra-thin selective layer for chiral separation processes. In recent years, researchers have coated the chiral selector on to a porous supporting membrane.[19] However; it is difficult to obtain an ultra-thin selective layer using surface coating. Moreover, the selective layer easily peels away from the supporting membrane due to the weak forces between them. Therefore, it is necessary to explore a new way to prepare composite membranes consisting of polymer and chiral selector. In recent years, the electrostatic layer-by-layer (LbL) adsorption of oppositely charged polyelectrolytes has proven to be a promising method for the preparation of polyelectrolyte multilayer membranes (PEMMs). Previously, it has been demonstrated that LbL assembled composite membranes can function for a wide range of uses, such as pervaporation, gas separation, nanofiltration, reverse osmosis and forward osmosis.[20–26] However, no previous work has dealt with the assembly of chiral selectors into PEMMs for chiral separation.

This work investigates the immobilization of chiral ILs into a solid polymer membrane and its subsequent use in chiral separation. The first step was the synthesis of the β-CD-IL. The successive adsorption of negatively charged β-CD-IL and positively charged polyelectrolyte on to the porous supporting membrane leads to the formation of an ultrathin selective layer for chiral separation. The resulting membrane was characterized with SEM, AFM and FTIR. The chiral separation performance of the D,L-tryptophan (D,L-Trp) was also evaluated.

Experimental

Materials

Poly(ethyleneimine) (PEI), with a molecular weight of 60,000, and poly(acrylic acid) (PAA), with a molecular weight of 4,000,000, were obtained from American ALDRICH. Chitosan (CS) with a molecular weight of 300,000, was received in the yellow powder form from Golden-Shell Biochemical Co., Ltd. (Yuhuan, Zhejiang, China). D,L-tryptophan (D,L-Trp), D-tryptophan (D-Trp) and L-tryptophan (L-Trp) were obtained from Shanghai Crystal Pure Reagent Co., Ltd. Beta-cyclodextrins(β-CD), Methylbenzenesulfonyl chloride, formic acid, acetic acid, sulfonylurea chloride, sodium hydroxide acetonitrile, hydrochloric acid, potassium chloride, Dimethylformamide (DMF), acetone, Poly(vinyl alcohol) (PVA) and glutaraldehyde (GA) were provided by the Beijing Chemical Factory.

Quartz substrates for UV–vis measurements were purchased from Beijing Kinglass Quartz Co., Ltd. The flat sheet polyacrylonitrile (PAN) ultrafiltration (UF) membranes, with a molecular weight cutoff of 20,000, were supplied by Sepro Membranes.

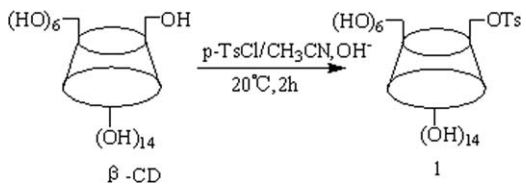


Figure 1. Synthesis route of mono-6-OTs-β-CD.

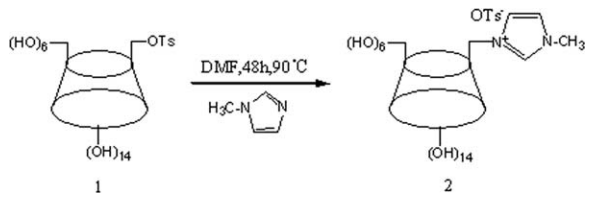


Figure 2. Synthesis route of mono-6-deoxy-6-(3-methylimidazolium)-β-cyclodextrin tosylate.

Syntheses of β-cyclodextrins chiral ionic liquids

The mono-6-OTs-β-cyclodextrin and mono-6-deoxy-6-(3-methylimidazolium)-β-cyclodextrin tosylate (β-CD-IL) were synthesized according to previously published procedures.[27–29] The synthetic route of mono-6-OTs-β-CD is shown in Figure 1. 75.0 g (0.066 mol) of β-CD was dissolved slowly in 625 mL deionized water below 20°C to generate a turbid white suspension. 25 mL of 8.21 mol/L NaOH solution was then added to make sure the solution became clear, and then the solution was stirred for an hour to dissolve it completely. Subsequently, 12.6 g (0.066 mol) of p-toluenesulfonyl chloride dissolved in 37.5 mL of acetonitrile was slowly added. The reaction solution was further agitated at 20°C for 2 h. After the removal of the impurities, 10 wt % of hydrochloric acid was added to adjust the pH value to between 8 and 9, after which a white precipitate appeared. The suspension was kept at 4°C for 12 h. The suspension was filtered to obtain a white precipitate. After recrystallization, the white solid was dried *in vacuo* at 50°C for 12 h.

The synthetic route for β-CD-IL is shown in Figure 2. A mixture of 12.89 g (0.01 mol) of mono-6-OTs-β-CD and 2.50 g (0.03 mol) of N-methyl imidazole was dissolved in 25 mL of DMF. The mixture was stirred for 48 h at 90°C under nitrogen. After cooling to room temperature, acetone (100 mL) was added to the resulting solution, which was then vigorously stirred for 60 min. The solid formed after filtering the suspension was then washed with acetone two or three times and finally dried under high vacuum to obtain a white solid. The synthesized β-CD-IL was studied by ^{1}H NMR spectroscopy and the solubility was investigated.

Preparation of the Chiral solid membrane

The polyacrylonitrile (PAN) membranes were first immersed in 2M NaOH aqueous solution for 60 min at 65°C.[20,21] The membrane obtained a negatively charged surface through alkaline hydrolysis. The membrane was then washed repeatedly with deionized water until the flushing solution was neutral. The membrane was then put into a laboratory-scale filtration unit containing PEI aqueous solution or CS acetic acid solution for 30 min to achieve a positively charged surface. The assembly process is shown in Figure 3. Dynamic LbL assembly was performed by sequentially filtrating PAA and β-CD-IL aqueous solutions through the substrate membrane for 30 min each. Before each cycle, the membranes were thoroughly rinsed with deionized water and dried *in vacuo*. Alternating PAA/β-CD-IL multilayer films could be obtained by repeating these steps in a cyclic fashion. The resulting membranes were washed with deionized water three times and dried *in vacuo* before testing.

FT-IR, UV–vis, SEM and AFM characterizations

The infrared spectra (FT-IR) of KBr disks were recorded over the range 400 cm^{-1}−4000 cm^{-1} using a Nicolet Nexus 8700 FT-IR spectrometer. To monitor the overall feasibility

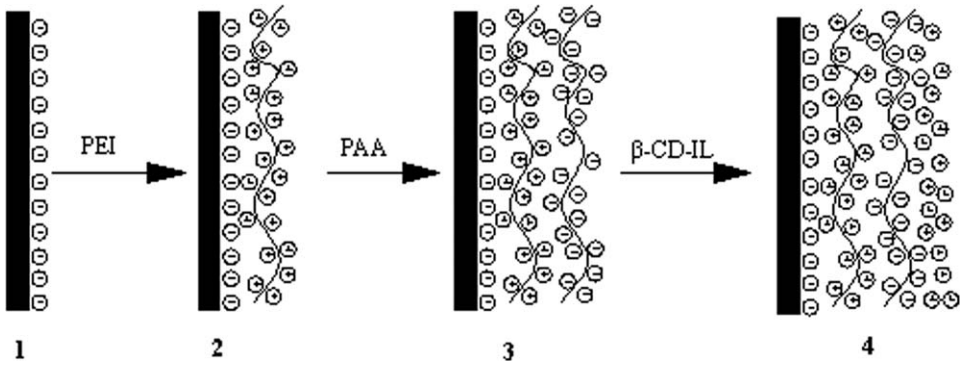


Figure 3. Schematic illustration of the LbL assembly of chiral solid multilayer membranes.

of growing films, the PAA/β-CD-IL multilayer films were also assembled on to quartz slides. Quartz slides were treated with boiling piranha solution (30:70 v/v H2O2:H2SO4) for 70 min, followed by rinsing with copious amounts of ultrapure water. The assembly of the PAA/β-CD-IL multilayer films is then almost identical with the process of growing films on a hydrolyzed PAN membrane. The growth of the PAA/β-CD-IL multilayers on quartz slides was monitored using a spectrophotometer (Blue Star A, Beijing Laboratory Tyco Instrument Co., Ltd. Morphological analysis was carried out on a scanning electron microscope (SEM S-4700, Hitachi, Ltd., Japan). The change of roughness of the membrane surface was studied using a Nanoscope IIIa AFM Instrument (ASAP2020M). The drive frequency was 330 ± 50 kHz, and the voltage were between 3.0 and 4.0 V. The drive amplitude, set point and scan rate were 300 mV, 3.34 μV and 1.0 Hz, respectively.

Chiral separation experiments

Chiral separation experiments were conducted at room temperature in a laboratory-scale filtration unit, shown in Figure 4, which contains a cross-flow permeation cell with an effective filtration area of 38.47 cm^2 supported by a porous stainless steel disc. The transmembrane pressure can be controlled between 0–0.2 MPa.

The L-tryptophan and D-tryptophan feed solutions were prepared by dissolving them in pure water with a concentration of about 0.1 g/L. After the experiment, permeate was collected, and accurate concentrations of tryptophan were analyzed by HPLC.

The apparent separation factor α was calculated using the following equation

$$\alpha = \frac{C_{P(D)}/C_{P(L)}}{C_{F(D)}/C_{F(L)}} \quad (1)$$

where $Cp_{(D)}$ (g/L) and $C_{P(L)}$ (g/L) are the D-Trp and L-Trp concentrations in the penetration solution and $C_{F(D)}$ (g/L) and $C_{F(L)}$ (g/L) refer to the D-Trp and L-Trp concentrations in the feed solution, respectively.

The penetration flux Q ($g/m^2 \cdot h$) was calculated using the following equation

$$Q = \frac{q}{A \times t} \quad (2)$$

where q refers to the penetration quality of D-Trp (g) (or L-Trp (g)), A (m^2) is the active area and t (h) signifies the experimental time.

Each separation experiment was repeated three times and the average was calculated for further analysis.

High-performance liquid chromatography (HPLC) analyses

The analyses of the D- and L-Trp racemate enantiomer were carried out using an external standard method on a HPLC apparatus equipped with a Daicel CROWNPAK CR (+) column (150 mm×4 mm I.D.) and a UV detector (280 nm). Chiral analysis was performed using a mobile phase containing perchloric acid (pH = 2.0) and methanol (volume ratio 86:14). The flow rate was 1.5 mL/min. All the chiral analyses were performed in triplicate to guarantee accuracy.

Results and Discussion

Analysis of synthetic products

The ^{1}H NMR spectra of β-CD, mono-6-OTs-β-CD, and mono-6-deoxy-6-(3-methylimidazolium)-β-cyclodextrin tosylate are shown in Figure 5. Comparing Figure 5a with b, it was noted that most of the peaks of β-CD, mono-6-OTs-β-CD overlap. However, the characteristic peaks at δ: 7.42–7.44 and δ: 7.74–7.76, due to the benzene ring = CH hydrogen chemical shift, appeared in the ^{1}H NMR results for mono-6-OTs-β-CD. Moreover, the hydrogen appearing at δ: 3.84 represents the absorption peak of methyl hydrogen attached to the benzene ring. This was further confirmed by the appearance of the tosyl absorption peak in the products, which, in turn, demonstrated the successful synthesis of the mono-6-OTs-β-CD products. As shown in Figure 5c, the new absorption peak at δ: 3.84 is attributed to the methyl hydrogen chemical shift. The chemical shifts of the hydrogen δ: 7.69 represent the imidazole group on the 4- and 5-bits = CH. δ: 9.01 represents the 2 bits-CH hydrogen chemical shifts. These three new absorption

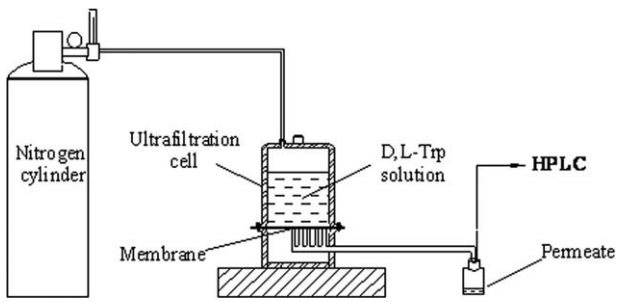


Figure 4. Experimental apparatus for the preparation of chiral solid multilayer membranes.

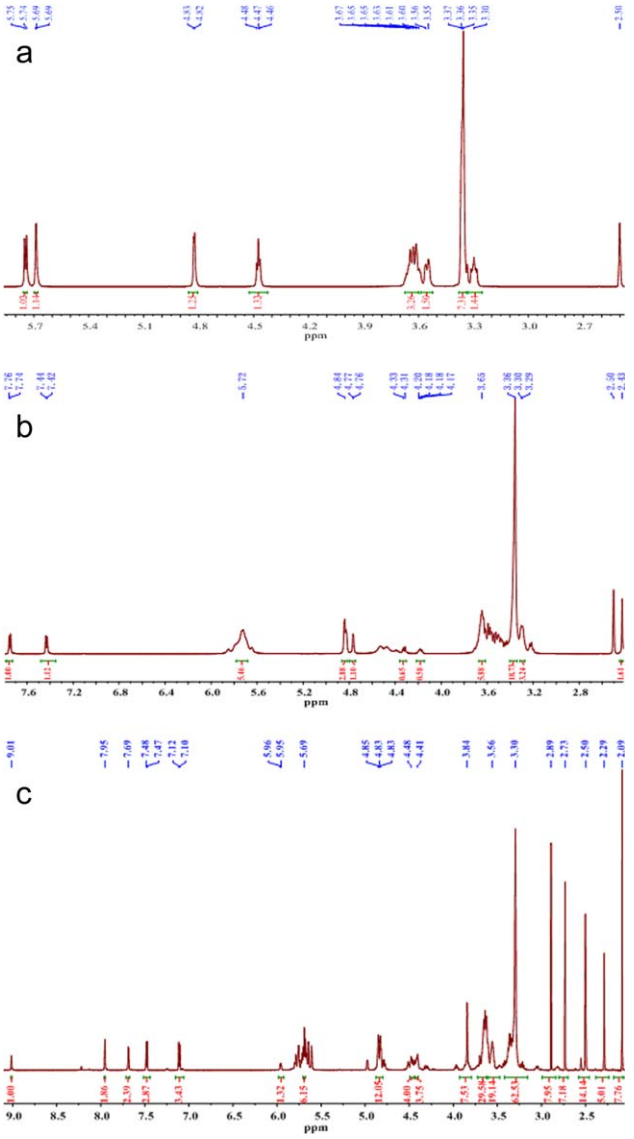


Figure 5. ^{1}HNMR spectra of (a) β-CD, (b) mono-6-OTs-β-CD, and (c) mono-6-deoxy-6-(3-methylimidazolium)-β-CD tosylate.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peaks indicated that the 1-methyl imidazole groups had been successfully grafted on to mono-6-OTs-β-CD, which proved the success of the synthesis of mono-6-deoxy-6-(3-methylimidazolium)-β-cyclodextrin tosylate.

Solubility measurements for the two products were then carried out. The solubility of β-CD is 1.86 g/100 mL while that of mono-6-OTs-β-CD is less than 0.06 g/100 mL. These results agreed well with other data reported in the literature.[27] By comparison, the solubility of β-CD-IL can reach 20 g/100 mL, which is far higher than those of β-CD and mono-6-OTs-β-CD. The higher solubility would be helpful for subsequent film assembly by permitting high loading of chiral selector on the solid membrane.

Feasibility study of assembly of the β-CD-IL and polyelectrolyte complex membranes

To verify the formation of the (PAA/β-CD-IL) complex, the PAN-based (PAA/β-CD-IL)n membrane was characterized by FT-IR. As shown in Figure 6, the PAN membrane showed alkyl and ester groups at a wave number of 1736 cm^{-1} while the hydrolyzed PAN membrane exhibited the carboxy vibration at 1568 cm^{-1}. This is because, in certain concentrations of NaOH solution, the —CN group in the PAN molecular chain can react to form a COO^- group, due to the hydrolysis.[20–22] The positively charged PEI was easily immobilized on to the negatively charged membrane. After applying the PEI coating, the 2244 cm^{-1} and 1450 cm^{-1} characteristic peaks attributed to the —CN group decreased significantly. By comparison, the 2940 cm^{-1} methylene peaks increased significantly and the 3278.4 cm^{-1} and 3336.2 cm^{-1} formamide peaks appeared. These changes provide evidence that a large number of PEI were assembled on to the PAN substrate membrane. After the PAA was immobilized on the membrane, the 2244 cm^{-1} characteristic peaks of the cyano group almost disappeared and the poly(acrylic acid) peaks around 1554 cm^{-1} increased, which clearly suggested a successful assembly of PAA. As for the β-CD-IL composite membrane, the imidazole vibration was not observed. This is due to β-CD itself, whose characteristic absorption bands cover the entire region, obscuring the ionic liquid methyl imidazole substituent. To further confirm the successful assembly of the β-CD-IL and polyelectrolyte complex membranes, multilayer films were then assembled on to a PEI-modified quartz substrate. The film growth was then monitored by UV–vis spectroscopy. Figure 7 shows the UV–vis spectra of $(PAA/\beta\text{-CD-IL})_n$ multilayers on a quartz substrate ($n = 1$–6). The assembly of β-CD-IL into multilayers leads to an absorption peak at 210 nm, which is attributed to imidazole. The increase in absorbance at 210 nm as a function of the number of bilayer pairs indicates the progressive deposition process of the $(PAA/\beta\text{-CD-IL})_n$ films.

Morphologies of β-CD-IL/PAA membranes

The membrane morphologies before and after assembly were compared using the SEM pictures shown in Figure 8. It can be seen from Figures 8a and 8b that there are a number of pores on the membrane surface before assembly. After assembling a PEI/PAA bilayer, the number of pores was much reduced, just as shown in Figure 8c. After a further β-

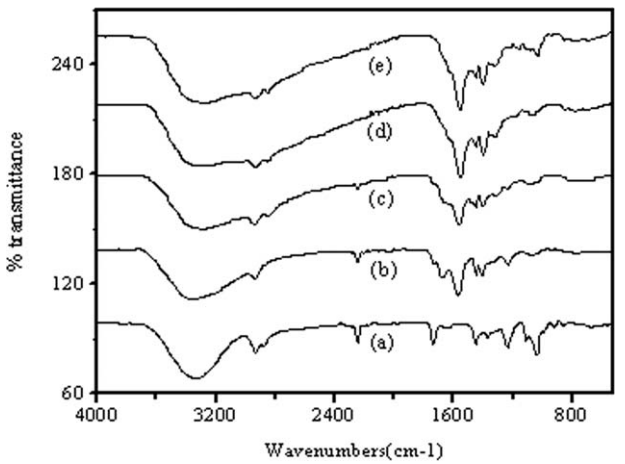


Figure 6. FT-IR spectra of (a) PAN membrane, (b) hydrolyzed PAN membrane, (c) PEI/PAN membrane immobilized, (d) PAA/PEI/h-PAN membrane, (e) (β-CD-IL/PAA)/PEI/h-PAN membrane.

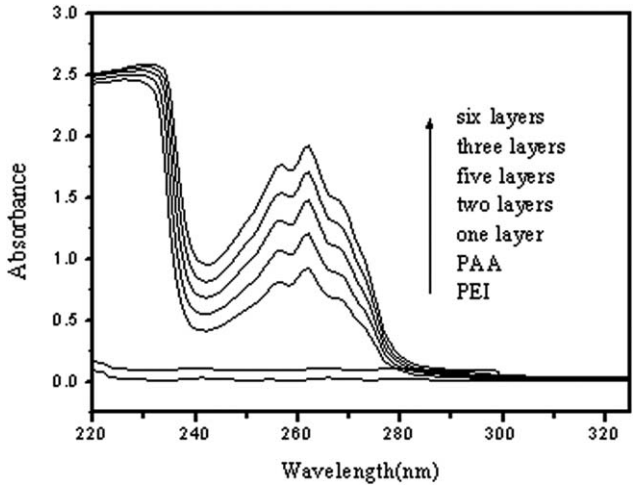


Figure 7. UV–vis spectra of (PAA/IL) n films with $n = 1$–6 on quartz substrates.

CD-IL layer, significant changes were observed. As shown in Figure 8d, almost all of the nanopores were covered and a more compact and uniform layer was formed, due to the formation of the PAA/β-CD-IL complexes. The membrane surface morphologies were also studied using an atomic force microscope (AFM). As shown in Figure 9, the values of roughness were obtained for a number of 40 μm$\times$40 μm scan areas. It was noted that the roughness of the top surface was significantly changed after deposition of the PAA/β-CD-IL complexes. For example, the surface roughness of the PAN substrate after hydrolysis was 28.2 nm. Significant changes in the surface morphology were observed after deposition by the polymer. The roughness increased to 81.4 nm after deposition with PEI/PAA. This value decreased to 66.3 nm after further assembly of β-CD-IL. This is because some of the PEI/PAA may have swelled and partly peeled off, due to the β-CD-IL assembly process.[30–32] It was clear that although the β-CD-IL can be assembled on to the PEI/PAA due to the electrostatic adsorption force, the β-CD-IL will, to

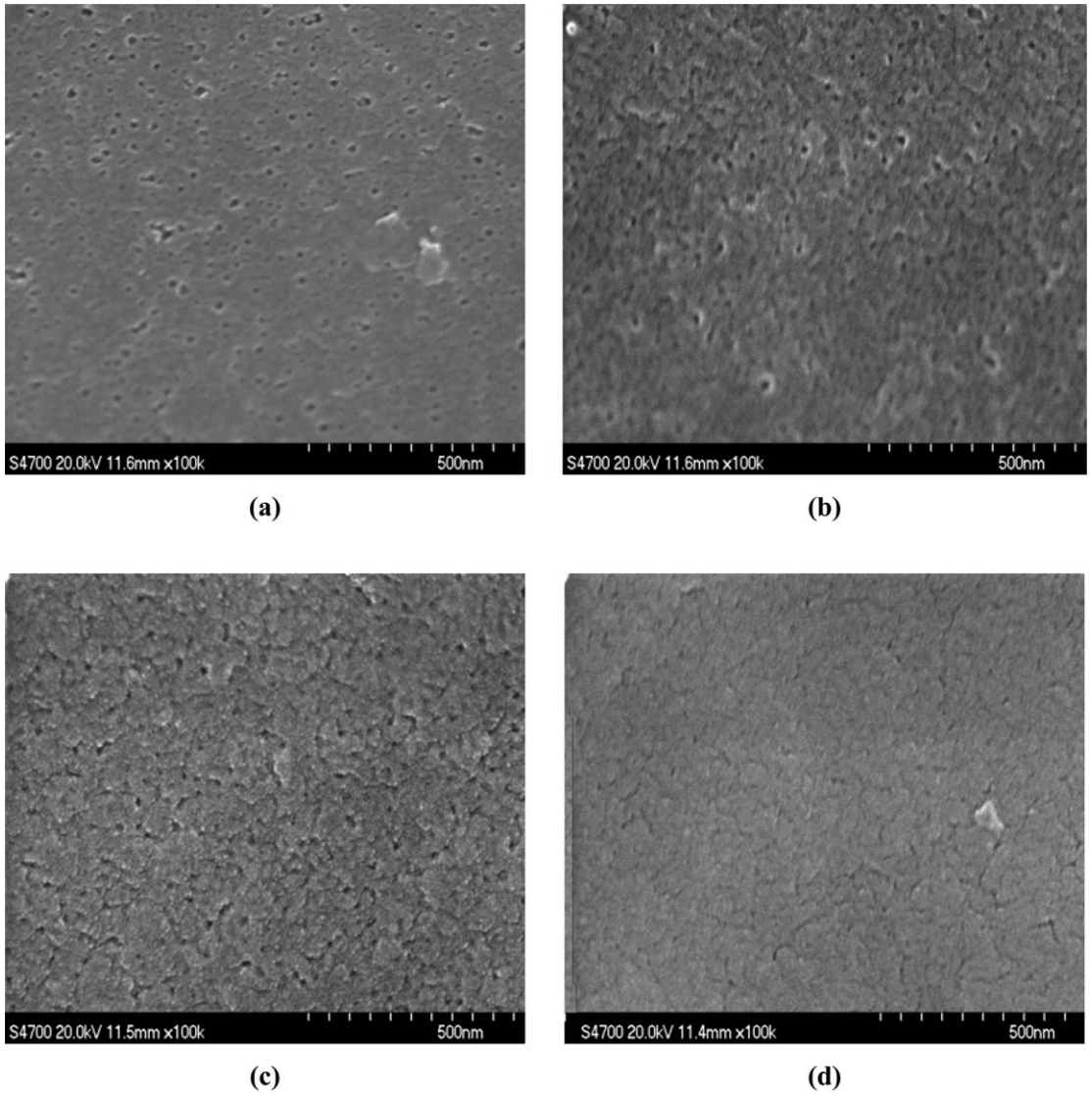


Figure 8. SEM images of (a) PAN membrane, (b) hydrolyzed PAN membrane, (c) PEI/PAA membrane, and (d) PAA/β-CD-IL membrane.

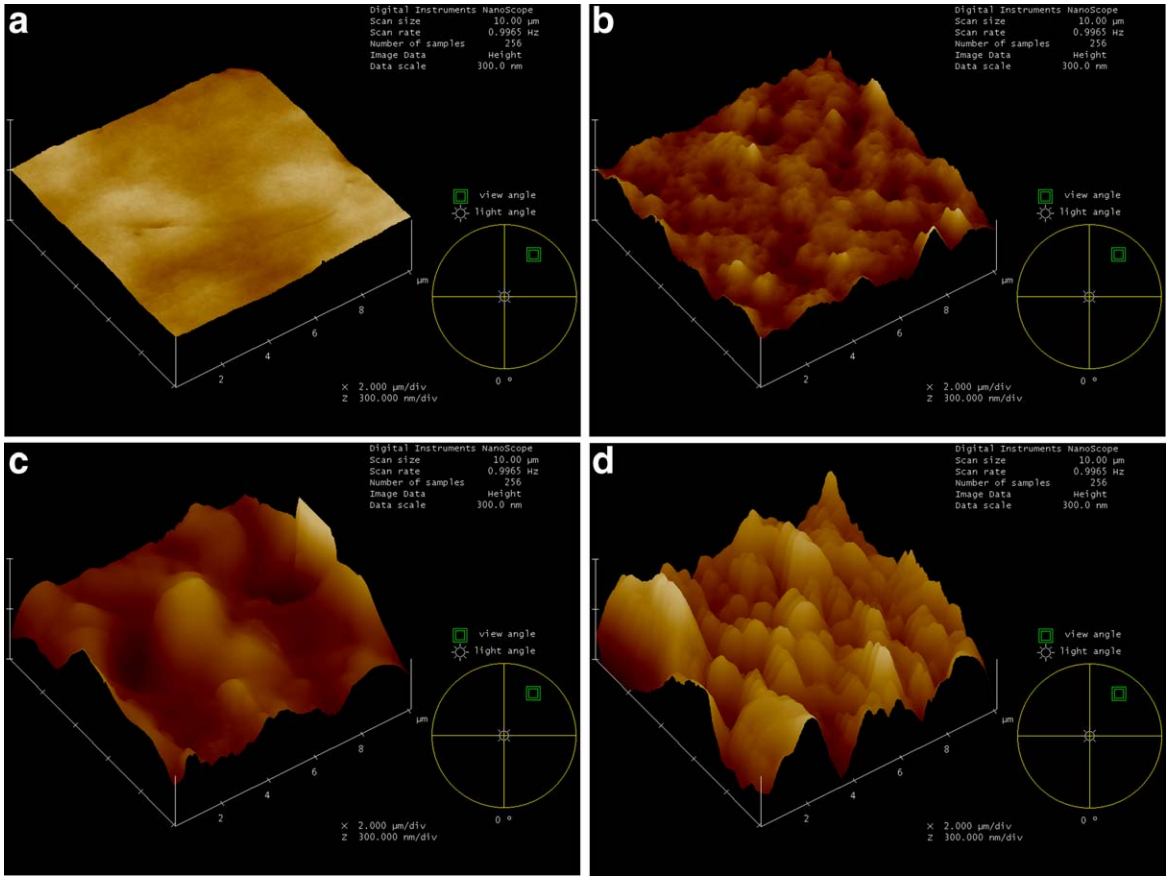


Figure 9. AFM images (a) PAN membrane, (b) hydrolyzed PAN membrane, (c) PAA/PEI/h-PAN membrane, and (d) (β-CD-IL/PAA)/PEI/h-PAN membrane.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

some extent, swell the polyelectrolye complex due to its own solvent and salt characteristics. These surface morphology changes further confirmed that the β-CD-IL can be successfully immobilized with polyeletrolyte complexes on to a solid supporting membrane.

Chiral separation by immobilized β-CD-IL membranes

Our subsequent experiments were intended to examine the chiral separation capacity for D-, L-tryptophan using the PAA/β-CD-IL multilayer membrane. The change of separation factor with bilayer number is shown in Figure 10. It demonstrates that the separation factor increased with the increase in bilayer number. The average separation factor was 1.066, 1.18, 1.346 and 1.41 when the bilayer number was 2, 3, 4 and 6, respectively, which represents a very competitive chiral separation factor. According to the recent critical review reported by Higuchi et al., the separation factors of the immobilized CD membranes were usually in the range

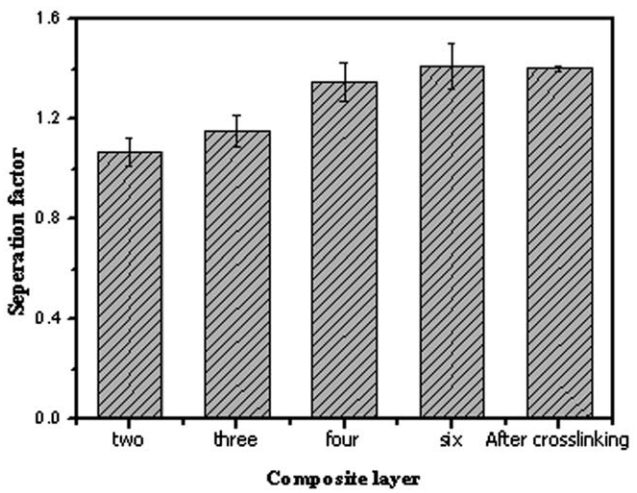


Figure 10. Effects of bilayer numbers on chiral seperation factor.

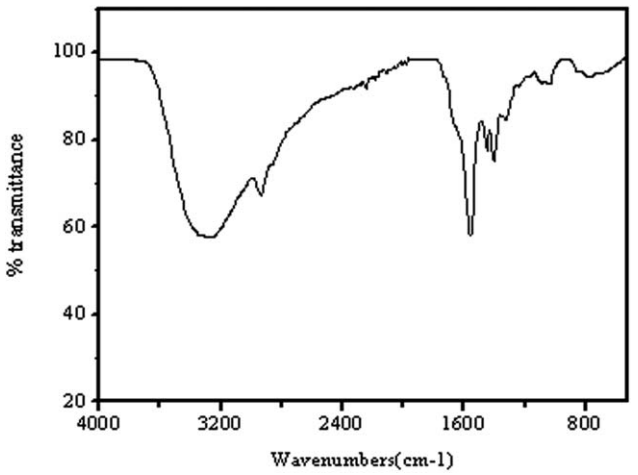


Figure 11. FT-IR spectrum of (β-CD-IL/PAA)$_6$/PEI/PAN membrane after chiral separation experiments.

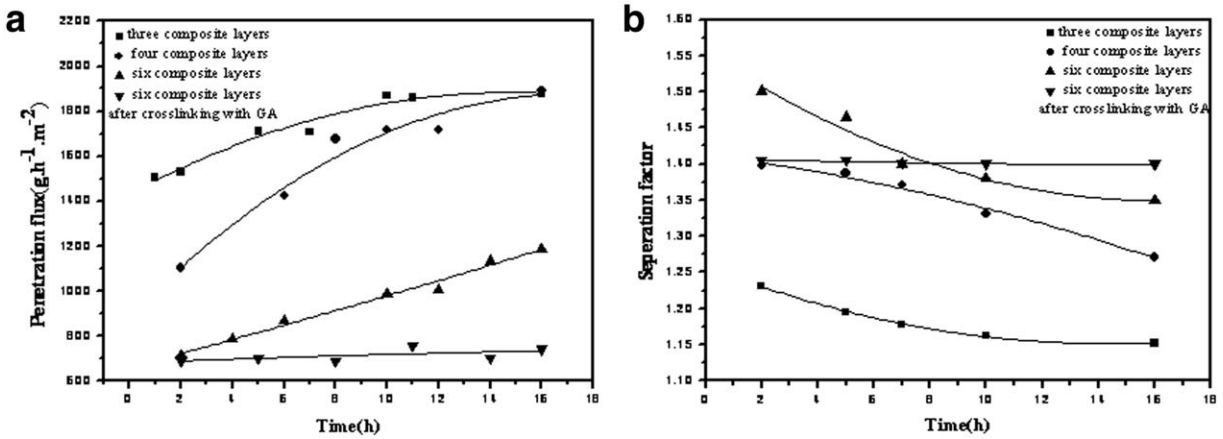
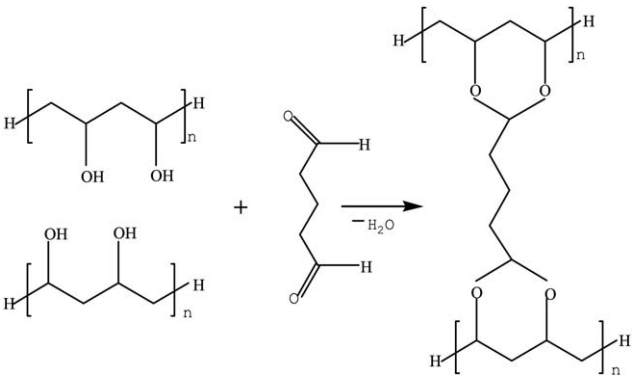


Figure 12. Variation of permeate flux and separation factor with operation time.

of 1.0–1.5.[33] For instance, by comparison, Xiao et al. synthetized a type of functionlized cellulose dialysis membrane for chrial separation using β-cyclodextrin immobilization and found that the highest separation factor was 1.1 for a permeation flux of 1.66×10^{-7} mg·cm^2·s^{-1}.[34] Xiao et al. further improved enantioselectivity to the range of 1.26–1.33 using the acetylated CD-immobilized membrane, which mainly attributed to the improved discrimination ability of acetylated CD and the decrease in membrane pore size.[35] Wang et al. performed a kind of enantiomer separation using chitosan/β-cyclodextrin deposited on membranes. The highest separation factor was 1.47 while the permeation flux was 0.039 mg·cm^2·h^{-1}.[36] It is well-recognized that the inclusion ability of the β-CD-IL with L-tryptophan is much stronger than that with D-tryptophan, which would result in the lower permeation flux of L-tryptophan with pressure-driven filtration. Meanwhile, D-tryptophan will be enriched in the permeate side. With the increase of the number of bilayers, the loading of β-CD-IL increased. Obviously, the increasing selectivity with the number of layers was mainly due to the increase in the absolute amount of chiral selectors in the membrane. Moreover, the chiral separation of D,L-trp through a set of multiple layers is similar to a multi-stage separation. Each PAA/β-CD-IL pair can increase the chiral separation capacity. Therefore, the separation factor can easily be tuned by adjusting the bilayer number. In addition, due to the high solubility of β-CD-IL, the chiral selector can be easily immobilized on to a solid support. After completing the separation experiments, the used PAA/β-CD-IL multilayer membrane was characterized with FT-IR. As shown in Figure 11, the benzene ring vibration appeared at a wave number of 1650 cm^{-1}, which further suggested that the inclusion ability of the solid multilayer membrane involved the amino group. The variation of membrane performance with operation time is shown in Figure 12. As shown in Figure 12a, comparing the 3- 4- and 6-bilayer multilayer membranes, the permeation flux decreased with the increase in the bilayer number, which is mainly because of the increase of film thickness. Interestingly, in contrast to normal pressure-driven ultrafiltration, it was found that the permeate flux increased with the operation time. Meanwhile, it was noted that the separation factor decreased when the operation time was extended (Figure 12b). These observations suggested that the loss of β-CD-IL is relatively serious during the operation. Moreover, the saturation of the chiral selectors due to binding with L-trp might also contribute to the decreased selectivity. To improve the stability of the PAA/β-CD-IL multilayer membrane, a crosslinked polymer layer was subsequently formed onto the top of PAA/β-CD-IL multilayers. The PAN-based (PAA/β-CD-IL)$_6$ membranes were immersed into 0.5% poly(vinyl alcohol) solutions and crosslinked by glutaraldehyde. A stable polymer layer could be obtained by binding glutaraldehyde to PVA chains through an acetalization reaction, according to the following scheme[37–40]



Although the flux of the crosskinked membrane was a little lower than that of the uncrosskinked membrane, the separation factor could maintain at 1.4 (Figure 10). More importantly, it was observed that both membrane flux and separation factor almost keep at a constant value with the long-term operation. This suggested that the chiral ionic liquids could be effectively immobilized into crosslinked PVA matrix, which provided an effective way to improve the stability of the chiral separation membrane. In addition, the introduction of more chiral selective sites into solid membrane would be a possible way to further improve the efficiency of chiral separation. For example, chitosan usually exhibits excellent chiral selectivity due to the presence of a large number of chiral sites. We have recently conducted the immobilization of both chiral ionic liquids and chitosan on the hydrolyzed PAN substrate membrane for chiral separation. It was found that the separation factor of (PAA/β-CD-IL)$_6$/CS/h-PAN membrane could reach 1.8, which was much higher than that of (PAA/β-CD-IL)$_6$/PEI/h-PAN membrane. This is because chitosan and chiral ionic liquids exhibit synergistic chiral selectivity.

Conclusions

In this study, a β-CD-IL was synthesized and characterized, and afterwards first assembled with polyelectrolyte to prepare a PAA/β-CD-IL multilayer membrane. The

feasibility of this assembly process was thoroughly investigated by UV–vis, FTIR, SEM and AFM measurements. The chiral separation of D,L-Try using polyelectrolyte/β-CD-IL multilayer membrane was investigated by pressure-driven filtration experiments. It was noted that the separation factor could easily be tuned by adjusting the bilayer number. This provides a facile way to prepare a solid membrane for chiral separation. To the best of our knowledge, this is the first report of the LbL assembly of chiral IL and polyelectrolyte on to porous substrates for chiral separation.

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