Smectic Liquid Crystalline Polymer Membranes with Aligned Nanopores in an Anisotropic Scaffold

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ABSTRACT: Bottom-up methods for the fabrication of nanoporous polymer membranes have numerous advantages. However, it remains challenging to fabricate nanoporous membranes that are mechanically robust and have aligned pores, that is, with a low tortuosity. Here, a mechanically robust thin-film composite membrane was fabricated consisting of a two-dimensional (2D) porous smectic liquid crystalline polymer network inside an anisotropic, microporous polymer scaffold. The polymer scaffold allows for relatively straightforward planar alignment of the smectic liquid crystalline mixture, which consisted of a diacrylate cross-linker and a dimer forming benzoic acid-based monoacrylate. Polymerized samples displayed a smectic A (SmA) phase, which formed the eventual 2D porous channels after base treatment. The aligned 2D nanoporous membranes showed a high rejection of anionic solutes bigger than 322 g/mol. Cleaning and reusability of the system were demonstrated by intentionally fouling the porous channels with a cationic dye and subsequently cleaning the membrane with an acidic solution. After cleaning, the membrane properties were unaffected; this, combined with numerous pressurizing cycles, demonstrated reusability of the system.

KEYWORDS: smectic liquid crystal, liquid crystal polymer, nanoporous membrane, polymer scaffold, filtration

INTRODUCTION

Nanoporous membranes with well-defined pores have numerous applications ranging from water purification and food processing to recovery of valuable compounds from waste streams.1,2 These membranes are able to remove solutes in the size range of 1–10 nm. Most commercial nanoporous membranes are made by top–down techniques, such as phase inversion methods and layer-by-layer membranes.1,3 While these techniques are highly suitable for mass production, there is only a limited degree of control over the pore sizes formed and typically have a three-dimensional (3D) pore architecture. In addition to transmembrane flow, this 3D pore configuration also had lateral diffusion paths, which are less desired. As an alternative, membranes can be fabricated with bottom-up approaches having a one-dimensional (1D) or 2D pore configuration, resulting in a lower tortuosity. Self-assembling block copolymers,4–6 carbon-based systems,7–9 and liquid crystal (LC) polymers10–17 have gained attention due to the high degree of control over the pore sizes and narrow pore size distribution. However, each of these approaches face their own challenges.

Liquid crystal (LC)-based polymer membranes have been investigated due to their numerous phases, ease of fabrication, high order, and variety in chemical composition. Thus, 1D nanochannels,12,13,17–25 2D-layered systems,12,26–29 and 3D bicontinuous phases30–32 have been reported. For the fabrication of free-standing LC polymer films, typical polymerization is performed inside an LC cell having alignment layers. Alternatively, shear alignment, photoalignment, and alignment via electrical and magnetic fields have been reported.24,33,34 However, liquid crystalline membranes with aligned nanopores that are mechanically robust enough to withstand the conditions of high-pressure filtration have not yet been reported.

An approach to fabricate mechanically stable aligned nanoporous membranes is by using a porous polymer support, resulting in a composite membrane. By applying thin-film fabrication techniques, 1D, 2D, and 3D porous LC polymers with thickness ranging between 100 and 500 nm were placed on top of a polysulfone porous support.13,27,30,32 These systems were able to retain various solutes such as ions and virus particles.

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Here, we demonstrate the use of a porous anisotropic microporous polypropylene scaffold with pores 100 nm long and 10–20 nm wide (S1), commercially available as Celgard, to fabricate liquid crystalline polymer membranes with aligned 2D nanopores. This scaffold method is based on an earlier report, which fabricated humidity-responsive liquid crystal polymer actuators.35 In this work, a smectic liquid crystalline mixture consisting of a mono acrylate benzoic acid (I) hydrogen-bonded dimer and a smectic diacrylate (II) cross-linker (Figure 1a) is planarly aligned and polymerized inside the anisotropic porous polypropylene scaffold, resulting in a composite film (Figure 1b). After base treatment, a membrane is created having 2D aligned pores. The scaffold provides the membrane enough mechanical rigidity to withstand conditions of dead-end filtration. The aligned 2D nanoporous membranes show a high rejection for anionic molecules. Cleaning of the system is demonstrated by removal of a cationic dye with an acidic treatment, revealing the reusability of the membrane.

RESULTS AND DISCUSSION

Fabrication and Characterization of the Nanoporous Membrane. The thin-film composite (TFC) membranes were fabricated with a transfer method as illustrated in Figure 1c. The dissolved LC mixture, consisting of a 4:6 ratio between molecules I and II, a photoinitiator, and an inhibitor (see Materials and Methods Section), was bar-coated onto a poly(vinylpyrrolidone) (PVP) sacrificial layer. After evaporation of the solvent, the sample was heated to the nematic phase at 80 °C, at which the pretreated microporous anisotropic polypropylene scaffold was applied. Subsequently, the sample was placed inside a temperature-controlled N2 box in which the sample was gently cooled from 115 to 85 °C, at which the SmA phase forms with a layer spacing of 4.2 nm.
(Figure S2). The sample was then photopolymerized to form a liquid crystalline network (LCN) by exposure to UV light. The TFC membrane was released from the glass plate by dissolving the sacrificial layer in lukewarm water. Polymerization was confirmed with Fourier transform infrared (FTIR) spectroscopy (Figure S3).

The TFC membrane was investigated by scanning electron microscopy (SEM). Images obtained from the LCN side of the composite showed a near-featureless flat layer, indicating the absence of major defects, as shown in Figure 2a. The bottom side of the composite in Figure 2b shows two main features: on the vertical axis, larger girders can be seen, connected by smaller fibrils that run horizontally, which were also visible in the pristine anisotropic scaffold (S1). The fabrication process of the TFC membrane appears to have no impact on this morphology. The layer thickness of the LCN of the TFC membrane was investigated by making cryogenically cut cross sections. The SEM images of the cross sections in Figure 2c show an uninterrupted LCN layer inside the top part of the scaffold. A thin layer in the nanometer range might be on top of the scaffold. The composite film has a total thickness of 25 μm, which corresponds with the thickness of the pristine scaffold, meaning that the LCN layer is inside the scaffold, confined and fortified by the fibrils of the scaffold. The higher-magnification image in Figure 2d shows that the LCN has a thickness of 2−4 μm.

Figure 2. SEM images of (a) the LC side of the composite. (b) The bottom side of the scaffold showing anisotropic pores with dimensions of 100 × 10−20 nm². (c) Cryogenically cut cross sections of the composite with a total thickness of 25 μm, corresponding to the thickness of the scaffold. (d) Higher-magnification image showing a dense LC layer with a thickness of 2−4 μm.

The 2D nanostructure and alignment of the LCN inside the scaffold were further investigated by wide-angle X-ray scattering (WAXS) and medium-angle X-ray scattering (MAXS). The pristine polypropylene scaffold has a relatively complex 2D spectrum, as shown in Figure 3a,d. A range of rings and spots are visible both parallel and perpendicular to the fibril direction, revealing the anisotropic nature of the scaffold. These rings and spots have d-spacings of 0.64, 0.53, 0.48, 0.43, and 0.41 nm, which correspond to α-isotactic polypropylene. The WAXS spectrum of the TFC in Figure 3b shows an overall more intense background scattering. Outer weak spots appear at a distance of 0.38 nm, perpendicular to the fibril direction of the polypropylene scaffold. These spots correspond to typical intermolecular stacking of the liquid crystal building blocks. However, the typical 2D layer spacing was not observed for this sample, most likely due to a combination of low scattering intensity of the LCN and intense background scattering of the scaffold. The corresponding MAXS spectrum in Figure 3e does show the 2D layer spacing. Two spots are visible parallel to the fibril direction at a spacing of 3.9 nm (Figure S4), which corresponds with the molecular length of both molecules I and II, indicating a planar alignment of SmA liquid crystal network. Given both that the intermolecular stacking is perpendicular to the fibril direction and the layer spacing is parallel to the fibrils, one concludes...

Figure 3. WAXS (top row) and MAXS (bottom row) spectra of the pristine microporous anisotropic polypropylene scaffold (a, d), TFC (b, e), and the reference sample in which the scaffold was completely filled (c, f). The alignment direction of the thin fibrils of the scaffold and mesogenic core of the LC are depicted with the black arrow. The morphology and corresponding features during X-ray diffraction (XRD) measurements (g).
that the liquid crystal building blocks align parallel to the fibrils.

To achieve better contrast between the scaffold and LCN and confirm the morphology, samples were made in which the scaffold was completely filled (Figure S5). In the WAXS of the reference sample (Figure 3c), both the intermolecular stacking and layer spacing of the lamellar structure are visible, confirming the formation of a 2D-layered SmA system. The morphology of the composite film and WAXS features are illustrated in Figure 3g. The MAXS spectrum of this reference sample (Figure 3f) corresponds to the findings for the TFC with a layer spacing of 3.9 nm. Therefore, it is concluded that for both the TFC and the reference sample, the SmA liquid crystal mixture is well aligned along the fibrils and is preserved after polymerization. This result differs from the LC mixture without a scaffold. Here, the initial SmA phase changed into smectic C phase after polymerization (Figure S6).26,28 Most likely, the changes in phase were prevented due to geometrical confinement of the scaffold.

**Formation of the Pores.** The 2D nanostructured composite was converted into a 2D porous TFC membrane by disrupting the hydrogen bonds between the benzoic acid moieties. This was done by submerging the pristine TFC in a 0.1 M KOH solution for 24 h. FTIR spectroscopy confirmed the disruption of hydrogen bonds by the disappearance of the C=O stretch vibration at 1700 cm⁻¹ and formation of the carboxylate salt at 1580 cm⁻¹ (Figure S3). Subsequently, WAXS and MAXS analyses were performed to investigate the changes in the nanostructure. The alkaline treatment results in a transition from a highly ordered 2D-layered system into a system with lower order, manifested by the substitution of the lamellar spacing indicated by the isotropic ring at 3.9 nm in Figure 4a,c. However, even though the loss in order is clearly observed, as for the pristine composite, there is only low scattering intensity. Therefore, we employed the reference sample in which the scaffold was completely filled and subjected it to the alkaline treatment. In the WAXS and MAXS spectra of the sample in Figure 4b,d, a similar loss on order is observed. The normally well-defined intermolecular stacking at 0.38 nm appears to have lost some of its order. When looking at smaller scattering angles, it can be observed that the formerly well-defined SmA spots at 3.9 nm transformed in a slightly less defined spot at a smaller layer spacing of 3.7 nm accompanied by an isotropic ring (Figure S4). The disorder in the system is most likely caused by the breaking of H-bonds between benzoic acid moieties, which no longer act as chemical cross-linkers, resulting in softening of the network and giving the benzoic acid moieties the ability to rotate more freely around the polymer backbone. The remaining 2D order in the system is caused by the cross-linker, which is fixed in position by physical cross-links. This combination of properties leads to the formation of a 2D porous network. The described morphology is illustrated in Figure 4e. SEM analysis on the activated membrane in Figure 4f shows the girders of the scaffold.

**Membrane Properties.** The membrane properties of the TFC were tested in a custom-made “Amicon-type” magnetically stirred dead-end filtration setup. All permeation tests have been performed with the same membrane that was treated with KOH solution (vide infra). Prior to the treatment with an alkaline solution, a clean water flux measurement was performed with demineralized water. The clean water test was carried out by applying a 6-bar feed pressure for over 3 h, during which no permeation took place, confirming the presence of a dense LC hydrogen-bonded network. Subsequently, the membrane was activated in situ by placing a 0.1 M solution of KOH in the filtration cell for 24 h. After rinsing the filtration setup thoroughly with demineralized water, a new clean water flux measurement using the same conditions was performed, at which a flux of 0.95 L m⁻² h⁻¹ bar⁻¹ was achieved, indicating the activation of the membrane by the formation of porous channels. The clean water flux of the TFC membrane, of 0.95 L m⁻² h⁻¹ bar⁻¹, appears to be at the lower end for nanoporous membranes compared to the literature.1 However, the system presented here has a relatively thick active separation layer of 2–4 μm, while both lab-made and commercial nanoporous membranes can be fabricated with active layers between 60 and 500 nm.3,32,37 When normalizing the layer thickness to 200 nm, the clean water flux would be between 9.5 and 19 L m⁻² h⁻¹ bar⁻¹. This would make this membrane competitive with commercial membranes such as the Dow FILMTEC NF90-400, which has a permeability of roughly 10–15 L m⁻² h⁻¹ bar⁻¹.38 However, the presence of a possible thin top layer, vide supra, is not taken into account. The optimization toward an LC layer in the range of nanometers could be realized with industrially applied thin-film fabrication techniques such as flexography, spin coating, or spray coating. The disadvantage remains that the scaffold used is only 55% porous, which means that 55% of the material is not involved in the separation process, reducing its efficiency.

After activation, the system was tested for defects with a permeation test using bovine serum albumin (BSA), which given its large size of 4 × 4 × 14 nm³ should not be able to permeate through the membrane based on the layer spacing of the 2D layers. A rejection of 100% was measured by (Figure
confirming the successful fabrication of a defect-free TFC membrane. Subsequent solute rejections experiments were performed to determine the size and charge selectivity of the membrane.

A series of neutral, cationic, anionic, and zwitterionic dyes with molecular weights between 322 and 1299 g/mol were tested, the chemical structures, feed-, permeate-, and retentates solutions of which are shown in Figure 5a−g. The largest dye Alcian Blue 8GX (AB) has a +4 charge, which might lead to an affinity with the negatively charged benzoic acid moieties. However, permeation test showed a rejection of 100% and no significant changes in flux, as shown in Figures 5h,i and S7. Dyes with a negative charge, rose bengal (RB), indigo carmine (IC), and fluorescein (Fl), showed high rejection rates of 98.3, 92.0, and 92.6%, respectively. The molecular weights of these anionic dyes appear to have no influence on the permeability despite having a relatively large difference in size, as shown in Figure 5h. Riboflavin (Rbf) with no charge was able to permeate the membrane completely while not decreasing the flux, indicating that the dye was able to permeate without being adsorbed by the pore interior. This means that the permeation of this solute is a size-based effect, indicating that the molecular-weight cutoff (MWCO) is above 376 g/mol. The zwitterionic dye rhodamine B (RHb) shows a rejection of 17.7% and a decreased flux of 0.44 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. The latter might be a result of absorption due to the zwitterionic character of RHb. Moreover, the pore size of the membrane must be larger than the molecular dimensions of RHb given that the dye was able to permeate and have interaction with the pore interior. Methylene blue (MB), which is known to strongly absorb onto the negatively charged membrane, was completely absorbed, resulting in blocking and fouling of the pores (vide infra). The strong difference between anionic, neutral, zwitterionic, and cationic solutes can be explained by charge- and size-based rejection, both of which take place in nanofiltration. The almost complete rejection of anionic species is most likely due to the negatively charged character of the membrane, indicating that Donnan exclusion is the main separation mechanism for such dyes. For zwitterionic, neutral, and cationic solutes, size-based separation
plays an important role and a rejection cutoff between 479 and 1299 g/mol is found. An estimation of pore size would be subjected to a large margin of error given that both the 2D pores and dye geometry are highly anisotropic.

Cleaning and Reuse of the Membrane. As the membrane has anionic nanopores, fouling and potential blocking of pores due to adsorption of cationic species sometimes occurs, as demonstrated with cationic MB dye. During a permeation test with MB, the flux decreased to about a quarter of the regular clean water flux, being 0.24 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), and after a period of 7 h, the membrane was completely blocked (Figure S8). The membrane was cleaned by protonating the benzoic acid moiety with a buffer solution of pH 4, thereby releasing the MB from the membrane. Subsequently, the membrane was conditioned with an alkaline treatment. A concurrent clean water flux measurement and the respective FI rejection test showed complete recovery of the membrane’s properties prior to fouling, as shown in Figure 6a.

After all membrane tests and cleaning steps were performed on the same membrane, the membrane was taken out of the setup and subjected to SEM analysis to inspect for defects and fouling. In Figure 6b, the LCN side of the membrane is shown, where the structure of the girders of the scaffold is more apparent. No defects or significant fouling were observed. Overall, the membrane has gone through numerous pressurizing and depressurizing cycles with various solutes over a period of 3 months, indicating that the membrane appears to be both chemically and mechanically robust.

**CONCLUSIONS**

We report a first-of-its-kind mechanically robust thin-film composite LC membrane with aligned 2D pores that has been successfully applied as a nanoporous membrane. The fabrication relies on an anisotropic scaffold, which ensures mechanical strength and the correct alignment of the liquid crystal mixture. A combination of XRD and SEM confirmed the fabrication of a 2–4 μm thick 2D aligned LCN inside the scaffold.

After alkaline treatment, the hydrogen bonds between benzoic acid moieties are broken, resulting in a water-permeable, defect-free membrane with porous aligned channels with a clean water flux of 0.95 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\). Both size- and charge-based rejections have been demonstrated with a range of permeates, resulting in a size-based MWCO between 479 and 1299 g/mol and charge-based MWCO for anionic species below 332 g/mol. Cleaning of the membrane of MB was achieved with a buffer solution of pH 4; subsequent conditioning with an alkaline treatment resulted in full recovery of flux and performance of the membrane.

The combination of a 2D porous LC system with an anisotropic microporous polymer scaffold is an appealing method to make 2D nanoporous membrane. This method can potentially be applied for other 2D systems to fabricate membranes or other devices with relatively straightforward fabrication steps.

**MATERIALS AND METHODS**

Materials. 4-(6-(Acryloyloxy)hexyl)oxybenzoic acid (molecule I) was received from Ambeed, Inc. 4-((4-(6-(Acryloyloxy)hexyl)oxy)phenoxy)(carbonyl)phenyl 4-(6-(acyloyloxy)hexyl)oxy)benzoate (molecule II) was supplied by Synthon Chemicals. THF and ethanol were purchased from Acros Organics. Irgacure 819 was supplied by Sibia. Bovine serum albumin (BSA), phosphate-buffered saline (PBS), poly(vinylpyrrolidone) (PVP, Mn = 1,300,000 kg/mol), indigo carmine, fluorescein, rhodamine B, alcin blue, rose bengal, methylene blue, and riboflavin were purchased from Sigma-Aldrich. All chemicals were used without additional purification. Sodium citrate dihydrate and citric acid were used to make the pH 4 buffer solution.

Fabrication. On clean glass slides, a sacrificial layer was applied by spin-coating a 5 wt % solution of polyvinylpyrrolidone in ethanol. The LC mixture, consisting of a 4:6 ratio between molecules I and II, a 1 wt % photoinitiator, and a 0.1 wt % inhibitor, was dissolved for 20 wt % in tetrahydrofuran (THF). Subsequently, the LC layer was deposited with a wet film of thickness 6 μm onto the sacrificial layer with a wire-wound bar coating rod. After evaporation of the solvent, the sample was heated to 80 °C to the nematic phase at which the scaffold was applied with a pressure roller. Prior to application, the substrate was cleaned with ultrasonication in a 1:1 mixture of ethanol and acetone and cleaned with UV–ozone for 30 min to increase wettability. After application of the scaffold onto the LC, the sample was allowed to cure at room temperature for 8 h. After curing, the sample was cut into a temperature-controlled N2 box, in which the sample was cooled from 115°C to 85°C with a cooling rate of 1°C/min. Through in situ XRD analysis, the formation of the SmA phase was confirmed with a layer spacing of 4.2 nm (S2). Subsequently, the sample was polymerized to form a liquid crystalline network (LCN) by exposure to a UV lamp for 15 min with a light intensity of approximately 15 mW/cm². The TFC was released from the sacrificial...
layer by immersing the sample in lukewarm water. The activation of the membrane, in which the hydrogen bonds between the benzoic acid moieties were broken, was achieved by submerging the membrane in a 0.1 M KOH solution for 12 h.

**Scanning Electron Microscopy.** SEM analysis was performed on a QuantA FE-SEM in secondary electron mode, with a beam current of 5 kV. Cross sections of samples were prepared by first submerging the sample in ethanol and freezing the wetted sample in LN2. Subsequently, the sample was cut with a scalpel inside the LN2 parallel to the fibril direction.

**X-ray Scattering.** Small- and wide-angle X-ray scattering (SAXS/WAXS) experiments were performed on a GaneshaLab instrument equipped with a GeniX-Cu ultralow divergence source producing X-ray photons of wavelength 1.54 Å at a rate of 1 × 10^6 photons per second. Diffraction patterns were collected on a Pilatus 300 K silicon pixel detector with 487 × 619 pixels of 172 μm^2. Heating and cooling of the specimen in the setup were performed with a Linkam stage.

**Filtration Experiment.** Dead-end filtration experiments were performed in a custom-made Amicon-type magnetically stirred dead-end filtration setup with an internal volume of 22 mL. TFC membranes were cut into a circle with a diameter of 16 mm and pressurized to 6 bar. The cell was kept at this pressure for at least 1 h before any other tests were performed. BSA solution was prepared by dissolving BSA at a concentration of 1 g/L in PBS. Dye solutions were prepared in demineralized water. The eventually measured permeate sample was taken after at least 4 mL was permeated.

**UV−vis Spectroscopy.** The rejection of BSA and dyes was determined via a Shimadzu UV-3102 PC UV−vis spectrophotometer.

**Infrared Spectroscopy.** Attenuated total reflection−Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Varian 670-IR spectrometer equipped with a golden gate setup.

### ASSOCIATED CONTENT

© Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c20898. SEM images of scaffold and membranes; XRD pattern of the membranes; FTIR spectra of the scaffold and membranes; UV−vis spectra of dye permeation tests; and fouling of the membrane (PDF)

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**Author Contributions**

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**Notes**

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