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Sulfonated polymerized liquid crystal nanoporous membranes for water purification

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ABSTRACT

New isoporous nanofiltration composite membranes were fabricated by photo-polymerization of thin films of the hexagonal columnar mesophase of the supramolecular complex 4sTB. This was followed by deposition on a polyether sulfone macro-porous support and removal of the template molecule. The membranes had an average permeability of 2.3 L m⁻² h⁻¹ bar⁻¹ and a sharp molecular weight cut-off of around 5000 g mol⁻¹ based on PEG filtration. The full rejection of Bovine Serum Albumin and Green fluorescence proteins and their flux recovery suggested the absence of defects on the LC layer of the membrane. The filtration of charged molecules presented total rejection for molecules larger than 1000 g mol⁻¹ and a size-charge selectivity with higher rejection for cationic molecules due to ionic interactions with the pore walls. These interactions mean absorption within the membrane, which has an effect on the rejection of neutral solutes such as Riboflavin and PEG 3000, being less relevant for smaller molecules.

1. Introduction

Water is one of the most important resources to sustain life. Increasing amounts of new emerging micropollutants (MPs) [1], i.e. toxic trace contaminants such as pesticides, plasticizers, pharmaceuticals, chemicals or hormones are released into the environment, and seriously endanger access to clean water [2]. Water and wastewater treatment thus are becoming increasingly important. These methods to clean water focus on the removal of undesired species and/or the selective recovery of valuable components for reuse. Among available separation processes, membrane filtration is increasingly adopted for water purification due to its low energy consumption, low footprint and low cost [3].

Current practice in water purification makes use of anisotropic membranes that are divided mainly into two types: porous, which are typically ultrafiltration (UF) and microfiltration (MF) membranes [4], and dense membranes, e.g. thin-film composites (TFC), used as reverse osmosis (RO) and nanofiltration (NF) membranes [5,6]. The first ones have in general a single chemical composition (normally polymeric) but a gradient of porosity. On the contrary, composite membranes consist of a thin selective layer of usually cross-linked polyamide (PA) on top of a microporous support (phase separation membrane) that provides mechanical stability.

Among the different types of membranes, especially NF membranes are commonly used for the effective removal of molecular-sized solutes from aqueous streams [7–9]. NF selectively separates small solutes from water based on pore sizes in the nm range. Nevertheless, current membranes present an intrinsically and most difficult to address drawback: the trade-off between permeability and selectivity. The absence of distinct, well defined pores in commercial NF membranes (asymmetric and dense morphology) hampers the strict control over selectivity for the filtration of different solutes.

Self-assembly is a very versatile approach to design membranes with well-defined pores to achieve molecular-level separations (nm scale) [10]. Self-assembled porous structures offer control over the morphology and the pore size distribution which improves the sieving process. Moreover, a very interesting feature of self-assembled membranes is the possibility to introduce the so-called “chemical functionality” to the pores, which refers to the chemical environment that can be modified to tune the selectivity. Pores with tunable chemical functionality may provide self-assembled membranes with an important advantage over commercial ones: selectivity of the NF process in such membranes will not only originate from the well-defined pores but also on the specific interactions between the membrane and the solutes. This

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provides a way to decouple the typically inherent inverse relation between flux and rejection for current NF membranes.

Previous research has shown that the self-assembly of well-designed molecular building blocks is an effective strategy to develop membranes with homogeneously distributed pores and uniform size imposed by the morphology and size of the building units [11–13]. As an example, different block-copolymers have been used for the development of nanoporous materials for filtration purposes, reaching pore sizes down to 2 nm [13–15]. However, this is the lowest limit. To reach smaller pore sizes, other chemistries must be adopted though.

On a smaller length scale, liquid crystals (LC) can self-organize in well-ordered nanostructures with access to even smaller pore sizes [16, 17]. Liquid crystalline molecules so-called “mesogens”, combine the mobility of liquids with some degree of order [18]. Different morphologies can be built by the self-assembly of these mesogens, mostly in 3 configurations: columnar, lamellar and bicontinuous (Fig. 1). This organization of the molecules can vary with the effect of the temperature (thermotropic LCs [19]) or with the solvent content, normally water (lyotropic LC [20]). Due to their robustness and stability, polymerized LC have attracted attention for their use in the preparation of membranes with pore sizes between 0.5 and 2 nm, which gives them the potential for molecular level separations [21]. In addition, the use of this bottom-up approach gives control over the pore functionality, which makes it possible to have a more specific distinction in the separation process between ions and molecules similar in size or charge.

Substantial progress has been made recently in the application of these polymerized LCs as separation systems in filtration membranes, especially for desalination and removal of organic micropollutants from water.

Among the previously mentioned different morphologies in which the mesogens can arrange, the anisotropy present in columnar mesophases gives a higher order that is advantageous for the formation of uniform pores and thus membranes with higher water flux [23]. However, to achieve this improved performance, unlike for bicontinuous phases, the alignment of the columns is needed. Therefore, even though 1D geometries are in principle preferred, there is more work reported based on 3D membranes because of the easier processability they offer [23–29].

Gin and co-workers reported nanocomposite membranes based on lyotropic liquid crystals (LLC) with 3D morphologies that showed high salt rejections (95% for NaCl and 99% for MgSO4 and CaCl2) and size selectivity for charged and uncharged solutes but low permeability values in the RO range (<0.5 L m⁻² h⁻¹ bar⁻¹) [24–26].

Thermotropic liquid crystals (TLC) have been also exploited by the group of Kato for the fabrication of NF membranes with potential applications in virus rejection and salt removal [27–29]. Using columnar and smectic phases (1D and 2D) higher fluxes (6–20 L m⁻² h⁻¹.bar⁻¹) in defect-free composite membranes could be achieved [30–32]. Nevertheless, charge and size selectivity at a scale below virus sizes was not further studied. Size and charge selectivity for small organic dyes of composite water filtration membranes with smectic 2D active layers have been reported for instance, but water fluxes were low, in the range of RO membranes (1–2 L m⁻² h⁻¹.bar⁻¹) [33].

An elegant method to create porous structures with a specific pore size was firstly reported by Kim et al. by removing a template molecule from a columnar structure [34]. Columnar mesophases can be obtained from LC hydrogen bonded complexes between benzoic acid derivatives and template aromatic molecules in the centre [35–37]. This specific strategy to obtain nanoporous polymerized liquid crystals using the template strategy has been further explored by other groups. More specially, fabrication of free-standing films with size and charge selectivity for alkali metal ions and organic molecules was studied by Serrano et al. using as templates melamine (M) or tris(triazolyl)triazine (T) [38] and by our group with 3:1 complexes between gallic acid derivatives and 1,3,5-Tris(1 H-benzo[d]imidazole-2-yl)benzene (TBIB) as template [39, 40]. Further work on homeotropic alignment of the nanoporous films was reported, where absorption of dyes increases compared to planar-oriented films [41]. Important advances in the template strategy have been reported by the team of Osuji to create perfectly oriented columnar pores in thin films [42] and to optimize the thickness of supported membranes to improve the filtration performance in future applications [43]. Up to now, only water permeability has been measured in these systems but rejection and selectivity data of various solutes in water are not yet available.

Here, we move beyond the state of the art of the template strategy to develop a polymerized columnar LC-based water purification membrane for the size and charge selective separation of organic solutes (Fig. 2).

We use the stronger electrolyte sulfonic acid instead of previously used carboxylic acids to reduce interactions with cations and to increase the water permeability of the membranes [44,45]. Wedge-shaped sulfonic acid monomer derivatives are used to complex with the 1,3,5-tris(1H-benzo[d]imidazole-2-yl) benzene (TB) template into a discotic supramolecular unit. The alkane functionalities of the sulfonate monomers are cross-linked, and the template molecule is removed resulting in pores of around 1.3 nm size with sulfonate groups in the interior.

2. Experimental

2.1. Materials and methods

All the reagents and solvents for synthesis were purchased from Sigma-Aldrich or TCI America. The ultrafiltration PES support, PES UF (30 kDa MWCO) was purchased from Sartorius Stedim Biotech, monodispersed PEG with a polydispersity of ∼ 1.05 was purchased from Agilent. Ultrapure water was used for all filtration experiments.

NMR spectra were recorded at room temperature on a Bruker FT-NMR spectrometer AVANCE III HD-NanoBay (400 MHz, Bruker UltraShield magnet, BBFO Probehead, BOSS1 shim assembly) in CDCl3. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS, 0 ppm). MALDI-TOF-MS analysis was performed on a Bruker speed autoflex operated in reflectron mode with a positive voltage polarity, 500 shots. ATR FT-IR spectra were recorded at room temperature on a
PerkinElmer Spectrum Two spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory. Polarized Optical Microscopy (POM) was performed with a Jeneval microscope equipped with crossed polarizers and a Linkam THMS 600 heating stage. Differential Scanning Calorimetry (DSC) measurements were performed in hermetic T-zero aluminium sample pans using a TA Instruments Q2000–1037 DSC instrument equipped with a RCS90 cooling accessory. Transition temperatures and enthalpies were typically determined from the first cooling and second heating run using Universal Analysis.

X-ray scattering measurements were performed on a GaNesh lab instrument equipped with a Genix-Cu ultralow divergence source producing X-ray photons with a wavelength of 0.154 nm and a flux of 1·10^9 photons s^-1. Diffraction patterns were collected using a Pilatus 300 K silicon pixel detector with 487·619 pixels of 172 μm² in size, placed at a sample to detector distance of 91 mm (wide-angle, WAXS), or 500 mm (medium angle, MAXS). The beam centre and the q-range were calibrated using silver behenate (d = 0.50, 0.70, 1.076 nm; 5.839 nm) as a reference. The d100 was used for calibration. Temperature was controlled with a Linkam HFSX350 heating stage and cooling unit. Measurements were performed on bulk samples sealed in 1.0 mm diameter glass capillaries, 0.01 mm wall thickness (Hilgenberg).

UV-VIS experiments were performed on a Jasco V-750 spectrophotometer. All experiments were performed in 10·10 mm quartz cuvettes at 20 °C. The photopolymerization was performed for 15 min with an ultrapure water (total volume of 20 mL) and was pressurized with nitrogen at the desired pressure. Samples that after 2 h under a pressure of 5 bar showed a water flux of zero were considered defect free. After that, the membranes were shaken in 1 M aqueous NaOH for 3 h to remove the glass and PVA sacrificial layer were removed by immersing the composite membrane in water and the obtained membrane was dried in a vacuum oven at 40 °C.

2.2. Membrane fabrication

To develop NF membrane with reproducible performance, the use of proper support and a technique that produces thin and homogeneous films are essential. Due to its high permeability, a microporous polyethersulfone (PES) UF membrane was used as support. The fabrication of the CLC membranes was carried out using photo-polymerization and following a reported transfer method [46,47], which consists of spin coating onto a glass surface and transferring by pressing and heating the LC layer to the porous support. Spin coating was used to achieve the deposition of thin layers to get a higher water flux of the membrane [48].

Glass plates were cleaned with acetone and isopropanol under sonication for 10 min in a bath. Solutions for spin coating were prepared by mixing the sulfonic acid monomer (3.2 equivalents) with the template (TB, 1 equivalent) and 1,10-decanedithiol (4.6 equivalents) in DCE/EtOH (8:2 v/v) in a 10 wt % concentration. Finally, Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819, 3 wt%) was added as initiator. A sacrificial layer of PVA was used which was spin-coated from a 10 wt% aqueous solution onto clean glass at 1500 rpm for 60 s. Then the monomer mixture was spin-coated on top at 2500 rpm for 30 s. The resulting LC/PVA was transferred to a polystyrene (PS) support. The “sandwich” was heated to 70 °C and hand-pressed with a seal roller to help the transfer. After further cooling to room temperature, the membrane was polymerized with UV light for 15 min with an 8 mW cm^-2 of intensity giving a thin layer around 100 nm of the LC phase-coated onto a PES support (Fig. 3iv). The glass and PVA sacrificial layer were removed by immersing the composite membrane in water and the obtained membrane was dried in a vacuum oven at 40 °C.

2.2.1. Water permeability

The permeability of the membranes was determined by measuring the flux of pure water at different pressures (1–5 bar) using a 20 mL custom-made, stainless steel, stirred “Amicon type” dead-end filtration cell of 1.5 cm diameter (Fig. S12) [49]. Samples of the membrane were cut to the desired size and pre-cleaned with deionized water. For each filtration test, a membrane was placed in the cell which was filled with ultrapure water (total volume of 20 mL) and was pressurized with nitrogen at the desired pressure. Samples that after 2 h under a pressure of 5 bar showed a water flux of zero were considered defect free. After that, the membranes were shaken in 1 M aqueous NaOH for 3 h to remove the template and subsequently were rinsed with water. Permeate weight was measured in triplo increasing P from 1 to 5 bar. The permeate at each pressure was collected once a steady state flux was reached and was converted to volume to obtain the water flux (J [L·m⁻²·h⁻¹]) [50], which was proportional to the pressure difference. Plotting J over ΔP (bar) gave a linear relation from which the permeability P [L·m⁻²·h⁻¹·bar⁻¹] was calculated following:

\[ P = \frac{J}{\Delta P} \] (1)

All measurements were performed using at least two different membranes to ensure reproducibility.

2.4. Calculation of the theoretical membrane water flux

We assumed a flow through an ideally homogeneously aligned monodomain of a columnar hexagonal mesophase [51], as described in previous studies on similar LC based nanocomposite membranes [24]. Theoretical water flux, Q [L·m⁻²·h⁻¹·bar⁻¹] was calculated using the Hagan-Poiseuille equation:

\[ Q = \frac{4 \pi R^4}{8 \eta L} \]
Fig. 3. Schematic illustration of the membrane fabrication.

(i) Spin-coating of sacrificial layer
(ii) Spin-coating of LC monomers
(iii) Transfer of support by heating and pressing the sample
(iv) Polymerization
(v) Recovery membrane

Fig. 4. Representation of a hexagonal lattice with the characteristic parameters and representation of the homeotropic orientation for a theoretical water flux.

\[ d_1 = 4.65 \text{ nm} \]
\[ d_2 = 1.3 \text{ nm (TB diameter)} \]
\[ Q = \frac{\pi (\Delta P) R^4}{8 \mu L} \]  

(2)

The length of all cylinders was assumed to be equal to the thickness of the film (L [m]). The porosity (ε) of the mesophase is related to the distance between the cylinders:

\[ \varepsilon = \frac{2}{\sqrt{3}d_c} \]  

(3)

The pressure difference \( \Delta P \) is 1 bar, \( R \) is the characteristic radius and equal to the ratio of \( d_2/d_1 \) (Fig. 4) and \( \mu \) is the viscosity of the medium, in this case water 0.89 \( \times 10^{-3} \) Pa s.

2.3.2. Salt rejection

2 g L\(^{-1}\) aqueous solutions of NaCl and MgSO\(_4\) were used for filtration tests in the Amicon cell set-up described above. 15 mL of feed solution was introduced in the cell and filtered through the membrane at 4 bar and samples were collected every 10 min from the beginning of the process. Conductivity of the feed and permeate solutions was measured with a C319 Consort conductivity meter. The concentration was determined from the calibration curve previously determined for both salts:

\[ \sigma_{\text{NaCl}} = 1.945[C] \]  

\[ \sigma_{\text{MgSO}_4} = 0.759[C] \]  

(where the salt concentration [C] is given in g L\(^{-1}\) and conductivity \( \sigma \) in \( \mu \)S cm\(^{-1}\)).

Rejection (R) was calculated from the difference of feed (C\(_F\)) and permeate (C\(_P\)) concentrations:

\[ R(\%) = \frac{C_F - C_P}{C_F} \times 100(\%) \]  

(4)

2.4. Protein rejection

Bovine serum albumin (BSA) and Green fluorescence protein (GFP) were used for filtration tests in the Amicon cell set-up described before. A solution of 1 g L\(^{-1}\) of BSA was prepared in PBS buffer. 50 nM solution of GFP was prepared from 5 mM stock solution by dissolving 50 μL of 1 g L\(^{-1}\) aqueous solutions of NaCl and MgSO\(_4\) were used for filtration tests. Aqueous solutions in ultrapure water flux, pure water was filtered after the filtration of BSA and flux was measured to confirm the steady state. Moreover, to check the recovery of the initial water flux, pure water was filtered after the filtration of GFP and the permeate (P) solutions:

\[ R(\%) = \frac{I_F - I_P}{I_F} \times 100(\%) \]  

(5)

The flux in both processes was measured every 10 min for 2 h to confirm the steady state. Moreover, to check the recovery of the initial water flux, pure water was filtered after the filtration of BSA and flux was measured over time.

2.5. MWCO determination

Membranes were subjected to Polyethylene glycol (PEG) filtrations at 4 bar using the same Amicon cell. Aqueous solutions in ultrapure water were made containing 8 PEGs with a number average molecular weights (Mn) ranging from 600 to 20000 g mol\(^{-1}\) with a concentration of 0.5 g L\(^{-1}\) for each polymer. 10 mL of 2 solutions of 4 different Mn PEG (from 600 to 4000 and from 4500 to 2 \( \times 10^3 \) g mol\(^{-1}\)) were filtered separately and 3 fractions of 1 mL of permeate solution were collected. The composition of the feed and the permeate solutions was analyzed by Size Exclusion Chromatography (SEC) in DMF. The collected fractions of 1 mL of each permeate sample were evaporated separately and dissolved in 1 mL of DMF. For each analysis, 10 μL of the sample was injected into the SEC, which ran at 10 mL min\(^{-1}\). The concentration of PEG was detected with a photodiode array detector (PDA). The corresponding calibration curve is applied to convert the rejection time to molecular weight. The average peaks obtained from each solution were normalized to the peak of PEG 600 g mol\(^{-1}\), which was shown to pass through the polymerized LC membrane without rejection (Hydrodynamic radius of the coil, \( R_h \) = 0.81 nm) in a single filtration experiment of this Mn PEG (Fig. S14).

The rejection (R) was calculated from the difference of the maximum intensity of the peaks of the feed (F) and permeate (P) as:

\[ R(\%) = \frac{I_F - I_P}{I_F} \times 100(\%) \]  

(6)

Filtration and analysis of a mixture solution containing PEG 3000 and the cationic dye methylene blue (MB) was performed in the same way described.

2.6. Size and charge selectivity

A series of different dyes with molecular weights between 186 and 1299 g mol\(^{-1}\) were used for filtration tests. 50 μM aqueous solutions of the dyes were filtered separately at 4 bar pressure in the Amicon setup. Once a steady state was reached, samples of the permeate were collected in triplo to determine the average rejection. Samples were immediately measured in UV–Vis between 300 and 600 nm in a quartz microcuvette.

Rejection (R) of the solute was determined by comparing the intensity (I) of the maxima of each dye in UV absorbance of the feed (F) and the permeate (P) solutions using equation (6).

The filtration of a mixture containing Riboflavin and Methylene Blue was performed in the same way and the rejection of Riboflavin was calculated as described above.

3. Results and discussion

3.1. Synthesis and characterisation of supramolecular complex 4\(_3\) TB

Sulfonic acid derivative monomer 4 was synthesized in four steps following the synthetic route depicted in Scheme 1.

First, the three phenolic groups of methyl gallate were alkylated with 11-bromo-1-undecene followed by deprotection of the carboxylic acid according to a literature procedure to give 2. The acid chloride 3 was formed quantitatively with thionyl chloride and coupled with N-methyl sulfanilic acid in DCM with trimethylamine as a base, yielding desired compound 4, which was further characterized with \(^1\)H NMR, \(^{13}\)C NMR, FT-IR and MALDI-TOF. The thermal and liquid crystalline properties of 4 were investigated with differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray scattering. Compound 4 was found to be liquid crystalline when visualized under the POM at RT with micro-meter sized domains in a typical conic texture for a columnar mesophase (Fig. S5) with a transition peak from isotropic to LC at 57 °C (\( \Delta H = 3.48 J g^{-1} \)) in the heating cycle of the DSC (Fig. S7). The medium angle X-ray scattering pattern (MAXS) of compound 4 (Fig. S8) showed peaks with a ratio of q values 1:2:3:2:1:… corresponding to a Col\(_{3}\) phase with a lattice diameter of 3.84 nm.

Compound 4 was mixed with TB as a template for 3:1 complexation. To suppress phase separation of the template from the mixture a small excess of 4, was used. Mixing of 4 and TB in a 3:2:1 ratio in EtOH:CHCl\(_3\) (1:4) afforded the supramolecular complex 4\(_3\) TB.

Liquid crystallinity of the complex was studied under POM, where a
focal conic texture with micro-meter size domains, as for compound 4, was obtained after heating the sample to 150 °C and cooling to RT (Fig. 5b). This texture is characteristic of columnar mesophases with small domains [18]. The mesophase appears only after hours, regardless of the cooling rate. The POM pictures show a mesophase with a predominantly homeotropic alignment and randomly ordered planar domains. DSC data (Fig. 5c) showed two transition peaks in the second heating; a glass transition at low temperatures (give temp) and isotropization at 55 °C. X-ray diffraction measurements at room temperature (Fig. 5d) confirmed the existence of a columnar hexagonal mesophase for the complex with a ratio of 1:√3:2 of the principal diffraction peaks giving a lattice parameter a of 4.47 nm. A peak related to the interdisc distance at higher q values is absent, identifying this mesophase as disordered columnar hexagonal, Colhd.

3.2. Characterization of free-standing LC polymer films

Nanoporous LC films were prepared via thiol-ene reaction, a light-induced radical polymerization in which a thiol group reacts with an alkene to give homogeneously cross-linked networks (Fig. 6a). The thiol-
ene reaction is compatible with a wide range of functional groups which is important for the fabrication of membranes with functionalized nanopores [52].

A solution containing TB, compound 4, 1,10-decanedithiol as the cross-linker (1.5 dithiol molecule per molecule of compound 4 to have a ratio 1:1 of thiol:ene) and Irgacure 819 as initiator, was drop-cast onto a clean glass substrate. Free-standing yellow-transparent films were obtained by photo-polymerization and subsequent removal from the glass surface by floating in an aqueous NaCl solution. The obtained self-standing films were characterized by FT-IR to confirm the success of the photopolymerization by the disappearance of the terminal double bonds (–C–H bending vibration at 908 cm\(^{-1}\)) as shown in Fig. 6b. Both POM and X-ray diffraction confirmed the retention of the columnar hexagonal lattice after the polymerization (Fig. 6c and d) with narrower peaks on the WAXS pattern indicating a slightly higher order. The lattice spacing \(d_{100}\) increased from 3.90 to 4.65 nm in the polymer due to the introduction of the cross-linker in the network. Removal of the template was performed by gently shaking the free-standing films in DMSO for 3 h. Qualitatively, removal of the fluorescent template can be followed by eye, since under 254 nm UV light the as-made film is yellow-green but turns blue after removal of the template (Fig. 6e). Quantitative removal of TB after three extractions with DMSO was confirmed with UV–Vis spectroscopy to determine the concentration of template in the solution (Fig. S10).

### 3.3. Membrane characterization

Nanocomposite membranes were obtained following the process previously described in section 2.2. Scanning electron microscopy (SEM) micrographs of the surface and cross-section were taken. The top view shown in Fig. 7b confirmed that the nanostructured filtration layer covered the PES surface completely without micrometre-scale defects. The successful transference of the LC to the PES support was confirmed in Fig. 7c, where an average thickness of the LC polymerized layer of approximately 200 nm on top of the thick, porous PES support was shown.

#### 3.3.1. Water permeability

The ultrapure water filtration properties of the composite polymerized LC membrane were studied. Ultrapure water was permeability through the membrane until the flux remained stable for at least 1 h (Fig. 8a). From a linear fit of flux vs \(\Delta P\) (Fig. 8b), the pure water permeability was determined to be 2.36 ± 0.27 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) while for the bare PES support the permeability was 106 ± 3.92 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\) (Fig. S13). This indicates that the LC layer is the dominant factor in overall membrane performance and that the PES support is not

![Figure 6](image-url) Fig. 6. A) Schematic representation of the cross-linking via photo-polymerization through thiol-ene chemistry and template removal from the polymerized material; B) comparison of the complex mixture before (grey) and after polymerization (black) on FT-IR; B) POM of the texture of a photopolymerized film; d) WAXS pattern and e) visualization of the films with and without TB under UV light.
significantly affecting permeability.

The permeability of the nanocomposite membrane is close to that of current NF membranes (between 1 and 10 L m$^{-2}$ h$^{-1}$ bar$^{-1}$), as indicated in Table 1 and similar to the values of recent LC-based membranes reported by the groups of Kato and Osuji [29–31,43].

The theoretical permeability was calculated for a 200 nm thick membrane with perfect homeotropic alignment of the pores (calculated pore density $\epsilon = 6.73 \times 10^{16}$ m$^{-2}$) with a diameter of 1.3 nm. This value is the estimated pore size from the calculated diameter for the template molecule with Chem3D software and from Ref. [39] for an analogous system. Experimental pore size determination is not straightforward since available methods are not capable of determining sizes of a few nm. The commonly used N$_2$ adsorption isotherm (BET) provides information about all pores in the membrane, not just active pores but also dead-end pores and those of the PES support under the separating layer. Porosimetric methods such as porometry, permoporometry and mercury porometry depend on filling of pores with liquid, which requires excessively high pressures well above 100 bar. Pore filling using capillary condensation has a limit of a few nm, making this approach also inappropriate for pores with sizes around a nanometer. Therefore, experimentally determined pore sizes are not useful to interpret filtration behaviour.

Fig. 7. A) Representation of the composite membrane composition, B) HR-SEM top view of the LC layer surface and c) HR-SEM cross-section showing the LC layer of 200 nm thick.

Fig. 8. A) Relation between water flux vs pressure from which the permeability value $P$ was is obtained and B) Plot of water permeability vs time.
Table 1
Comparison of permeability values for NF commercial membranes and reported LC-based composite membranes with this paper.

| LC based membranes | Reference | Support | Permeability (L m⁻² h⁻¹ bar⁻¹) |
|--------------------|-----------|---------|-------------------------------|
| CoI₀₁₆ | This paper | PES | 2.3 |
| Cubisc® | [29] | PS | 0.17 |
| Co₁₅₀ | [30] | PS | 2.35 |
| SmA | [31] | PS | 2.8 |
| Col aligned | [43] | PEI6 | 1.8 |
| Commercial membranes | Membrane Material |
| NF90 | Dow FilmTec Polyamide TFC | 6.6 |
| NF200 | Dow FilmTec Polyamide TFC | 4.2 |
| N30F | Microdyn-Nadir Polyethersulfone | 5.6 |
| N603 | Microdyn-Nadir Polyethersulfone | 1.8 |
| TFC-HB | Koch Polyamide TFC | 3.5 |
| DK | GE Osmonics Polyamide TFC | 5.5 |

α Values based on 400 nm LC layer.
β Value based on 750 nm LC layer.
γ Values taken from ref. [53].

Rejection was determined once the steady state of both proteins was reached with the stabilization of the flux (Fig. S16). The analysis of rejection data showed that 99.6% of the BSA protein and 99.2% of GFP were rejected (Table 2). Due to the big size of the solutes, the flux, the very high number on rejection confirmed a defect-free membrane with pores smaller than 2 nm.

Moreover, the filtration of BSA resulted in a reduction of the permeability from 2.39 to 0.82 [L.m⁻².h⁻¹.bar⁻¹], with nearly complete (>99%) recovery of flux when the protein solution was again replaced by pure water (Fig. 10).

3.3.4. MWCO determination
The MWCO of the LC membrane was determined by measuring the rejection of polyethylene glycol (PEG). The composite LC membrane showed a MWCO (by definition the Mn at which 90% of the solute is retained) of 5000 g mol⁻¹ PEG (Fig. 11), corresponding to a hydrodynamic radius of 1.7 nm as calculated from the relation between molecular weight and hydrodynamic radius for PEG, given by eq. (7) [56].

\[ R_0 = 0.06127 M_n^{0.5931} \]

In principle, we could expect a smaller Rh following the calculated molecular size of the TB template (1.3 nm). The observed Rh at the cut-off Mn aligns well with the estimated pore size, considering the fact that the PEG coils do not have a fixed size and can pass pores with a radius that is smaller than Rh [57].

3.3.5. Size and charge selectivity
Size and charge selectivity of the polymerized LC membrane for small organic molecules was further tested with the filtration of a series of different sizes of anionic, neutral, zwitterionic and cationic dyes with molecular weights between 186 and 1299 g mol⁻¹ (Table 3, Fig. 12). Aqueous solutions of the dyes were filtered separately through the membrane and permeate solutions were collected once a steady state for rejection and flux was reached.

Analysis of the obtained data showed the influence of the charges of the dyes on their rejection. This effect is more noticeable for the cationic dyes: the large dye AB, (±4, M_w = 1157 g mol⁻¹) was fully rejected, while for cationic dyes smaller than the estimated pore size, CV, MB and DMBip, rejection decreased considerably with decreasing size (Mn) of the molecule (Fig. 12b). Moreover, the rejection values of the cationic dyes with different charges follow the same MWCO curve (green trend line in Fig. 12b), which lies above the data for the dyes without charge (Rib and RhB). This suggests an effect of positive charge, but a limited role of overall charge on rejection.

Similarly, rejection of anionic dyes increased gradually with molecular size: from 17% rejection of the smallest dye Fluorescein (F) (−1, M_w = 330 g mol⁻¹) to total rejection of the large dye PhCy (−4, M_w = 892 g mol⁻¹). However, unlike for cationic dyes, there was little effect of the negative charge on rejection since the rejection values of the anionic dyes are lower and lie on a steeper curve (orange line in Fig. 12c) than the cationic dyes. For example, the rejection of monocationic MB is 77%, much higher than for monoaionic F, although the molecular weights of the ions are similar (284 vs 330 g mol⁻¹). The neutral dye Riboflavin (Rb) and the zwitterionic dye Rhodamine B (RhB) follow the same tendency.

Therefore, it is proposed that the higher rejection of cationic dyes is caused by their absorption in the pores via electrostatic interaction with the sulfonate groups. The absorption of the molecules inside the pores leads to a smaller effective pore diameter, as has been previously shown.

![Fig. 9. Rejection of the monovalent salt NaCl and the divalent salt MgSO₄ as a function of time.](image-url)
This hypothesis is supported by a number of observations: The dyes used in the filtration test. Table 3 respectively.

Fig. 10. Flux vs time for pure water followed by BSA solution, and pure water, respectively.

Fig. 11. MWCO curve of the polymerized LC membrane. Solute: PEG.

Table 3

| Dye   | Charge | Mw (gmol$^{-1}$) | Molecular width$^a$ (nm) | Rejection (%) |
|-------|--------|------------------|--------------------------|--------------|
| PhCy  | -4     | 892.25           | 1.42                     | 99.8         |
| Pyr   | -3     | 455.37           | 0.99                     | 77.4         |
| OG    | -2     | 406.38           | 1.07                     | 23.1         |
| F     | -1     | 330.27           | 0.92                     | 16.9         |
| Rhb   | +1     | 442.57           | 1.14                     | 50.9         |
| RB    | 0      | 376.36           | 1.02                     | 17.4         |
| MB    | +1     | 284.4            | 0.58                     | 77.1         |
| CV    | +1     | 372.45           | 1.12                     | 88.1         |
| DMbip | +2     | 186.26           | 0.98                     | 35.7         |
| AB    | +4     | 1157.06          | 2.26                     | 99.3         |

$^a$ Largest dimension orthogonal to the long axis of the molecule.

for absorption of counterions at the pore wall of lyotropic LC membranes [58]. This hypothesis is supported by a number of observations: The large dye AB (+4, M$_W$ = 1157 g mol$^{-1}$) was totally rejected and partially adsorbed at the surface, which could be observed by eye with the coloration of the surface of the membrane (Fig. S17a left). During the filtration of a smaller mono cationic dye (CV) rejection increased from an initial value of 60%–80% at the steady state. (Fig. S17c). The strong coloration of the whole membrane after the filtration process (Fig. S17a) and the low concentration of dye in the retentate solution (Fig. S17b right) confirmed the absorption of the dye within the membrane. Thus, on the filtration of a cationic dye with a molecular size similar to or smaller than the pore size, absorption occurs, increasing the rejection of the dye upon time.

The observed behaviour was studied in more detail by checking the influence of the presence of cationic dyes on the rejection of other molecules using a feed mixture containing the cationic dye (MB) and the neutral solute PEG 3000 or Riboflavin. Table 4 gives the rejection and flux values at the steady state of the solutes. Comparing data with and without MB, we observed a lower flux for the mixture and an increase of the rejection, more remarkably for PEG 3000 (from 50 to 75%) confirming our hypothesis.

The reason might be related to the proposed slowdown process inside the pores of the membrane when cationic solutes are filtered due to the charge interactions which “decreases the apparent pore size”. We attribute these results to the molecular size: riboflavin is not big enough to be affected while PEG 3000 is in the steeper part of the MWCO curve for PEG rejection.

In conclusion, the polymerized LC membranes are size-selective and reject cations more strongly than anions of similar size due to absorption within the pores via electrostatic interactions with SO$_3^-$ groups. The membrane presents an average MWCO between 400 and 700 g mol$^{-1}$ for charged solutes and total rejection for both charges is reached for molecules with a diameter larger than 1.4 nm, in excellent agreement with the estimated pore size of 1.3 nm.

4. Conclusions

We reported the application of a template-pore strategy to develop a new isoporous NF membrane for water purification consisting of a supramolecular columnar LC selective layer on top of a porous PES support. The retention of a columnar hexagonal structure after its fixation by photo-polymerization permitted the removal of the template molecule leading to the formation of controlled-sized pores of around 1 nm with sulfonate functionalities.

The thin LC film was successfully attached on top of the porous PES support. The absence of defects confirmed the quality of the membrane. This resulted in membranes with nearly full rejection (>99%) of large solutes such as globular proteins BSA and GFP (>6 nm) and water permeability around 2 L m$^{-2}$ h$^{-1}$-bar$^{-1}$, similar to NF commercial membranes and other LC-based membranes previously reported. Experimental water flux achieves a value that corresponds to half fraction of the calculated theoretical flux for perfectly aligned cylindrical pores.

The columnar organization of pores with a homogenous size gave steep size-dependent retention for the filtration of PEG with a MWCO of 5000 g mol$^{-1}$. In addition, the presence of SO$_3^-$ functionalities created a charge selectivity on the rejection process besides the size sieving effect, lowering the MWCO to around 1000 g mol$^{-1}$ for charged solutes. Moreover, the charges played an important role: rejection is higher for cationic dyes than anionic ones with the same molecular size due to a decrease of the effective pore size created by the absorption of the first ones in the membrane. This is a result of the interaction of positive charges with the anionic sulfonate groups at the pore walls.

With this work, we provide a new approach to obtain a polymerized LC-supported membrane for the selective removal of small organic molecules from water. The template-pore strategy permits the creation of well-organized porous columnar structures with controlled size. The presence of charged functionalities within the pores introduces specific interactions that modulate the selectivity on the filtration of charged and uncharged solutes.

Author statement

Patricia Marín*: Conceptualization, investigation, visualization, writing – original draft and revisions

Rint Sijbesma: Conceptualization, supervision, writing – review and editing, project administration, funding acquisition.

Kitty Nijmeijer: Conceptualization, writing – review and editing.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4

|                        | Without MB | With MB |
|------------------------|------------|---------|
| Permeability (L m⁻² h⁻¹ bar⁻¹) |            |         |
| Rib.  | 2.0        | 0.7     |
| PEG 3000 | 1.9        | 0.7     |
| Rejection (%) |            |         |
| Rib.  | 17.4       | 74.6    |
| PEG 3000 | 50.1       | 21.6    |

Fig. 12. a) Molecular structures of the different dyes used, b) plot with rejection values vs molecular weight for anionic dyes and c) for cationic.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.120097.

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