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Breath figure templating for fabrication of polysulfone microporous membranes with highly ordered monodispersed porosity

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ABSTRACT

Polysulfone membranes having highly ordered pores in uniform micron size range were fabricated using breath figure (BF) templating in combination with phase separation. Specifically, membranes with average pore opening of 1.5 μm, 2.5 μm, 2.8 μm and 3.4 μm and tubular pore cross-sections were prepared. Different solvent systems, dilutions and casting conditions were tested to realize BF templating for fabrication of microporous membranes with controlled and uniform pore sizes. PSF dissolved in a solvent-nonsolvent pair of dichloromethane and tertiary amyl alcohol at 6–10% (w/v) concentration cast at 85–95% relative humidity and 30 °C resulted in microporous membranes with uniform monodispersed, nearly hexagonally packed pore openings. The cross-sections revealed tubular channels or macrovoids followed by closed or interconnected cellular structure formed due to phase separation. In absence of internal nonsolvent BF templating could occur only in very dilute solution. The work also underscores need for immiscibility of casting solvents with water.

1. Introduction

Fabrication of polymer membranes with highly ordered pores using breath figure templating (BFT) is an area of great interest as the process is simple and dynamic control over formation and morphology of pores is attainable [1–6]. The possibility of membranes having controlled, well ordered and nearly monodispersed hexagonal close pack pore openings along with nearly maximum attainable pore density can translate in less energy consuming filtration membranes with definite size selectivity. Porous polymer films with micron and submicron size pores are finding application in solid support for sensors and catalysts, scaffolds for tissue engineering, low dielectric constant materials for microelectronic devices, photonic band-gap materials etc. [7–14]. Various groups have already demonstrated the concept to be functional in generation of very thin films with 3D highly ordered monopore morphology since first demonstration by Widawski et al. [1]. However, there is a scarcity of reports extending this concept for fabricating viable free standing microfiltration membranes [15,16]. Microporous track-etched membranes (TEMS) with monodispersed porosity are routinely made by nuclear fission fragment or accelerated ion beam tracking along with chemical track etching and amply used for high-specification filtration in many laboratory applications besides being used as template for synthesis of various micro and nanostructures [17–22]. TEM films can be made in selective pore sizes ranging from 10 nm to tens of micrometers and the pore density ranging from 1 to 1×10^{10} pores/cm^2 [21]. The major benefit of the breath-figure-templated membranes over the nuclear track-etch membranes would be very high pore density (Fig. S1 A–D). Pore density distribution is remarkably near maximum possible in case of breath figure templating due to highly ordered near hexagonal close packing of pore openings [1–3,7] compared to randomly scattered pores in case of track etched membranes [20,21]. Also a large number of polymers can be applied for BF templated membrane fabrication using simple solvent casting route [23–27]. In comparison not many polymers are amenable for track etching and mostly polycarbonate (PC), polyimide and polyethylene terephthalate (PET) films are used for viable track etched membrane fabrication [21].

The term "breath figures" refers to the arrangement of water droplets formed by of the condensation of water vapor on to either, a cold solid or, liquid surface and subsequent nucleation, growth and self assembly [28]. When a dilute polymer solution in a volatile solvent is cast in humid atmosphere the cooling associated with the evaporation of the volatile solvent from the polymer solution can start the condensation of water vapor at the solution surface, in form of an array of individual suspended water droplets. The growing droplets pack themselves in orderly manner above the surface of the solution creating a template consisting of non-coalescing ordered array of water droplets. These droplets can sink in the polymer solution, later creating a very regular porous pattern called breath figure template (BFT) pattern when all solvent and water evaporates; leaving behind porous polymer film.

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Initially breath figure templating was claimed to be achievable only with only specific polymers – such as star shaped or dendritic polymers, copolymers and rigid rod type polymers [1,2,4,7]. Later on many other polymers were found capable of forming honeycomb pattern porosity by BF templating (3, 23–27]. Since the first report by Widawski et al. [1] majority of reports emphasized that BF templating can occur only in very dilute solutions (1–3% polymer solution) [1–3,29–31]. The need of extremely dilute solution for BF templating creates a practical limitation for fabrication of free standing microporous membrane using breath figure templating route as these dilutions may not result in required mechanical integrity of the final membranes. This may be among the vital reasons that the BF templating phenomena known since long, has remained largely unexplored for synthesis of microporous membranes among other various practical applications [32]. However we found that BF templating can be harvested readily for fabricating microporous membranes using higher concentration polymer dopes (up to 10%) in presence of an internal hydrophilic nonsolvent additive in the polymer/hydrophobic solvent system.

Most of the work on breath figure templating is limited to drop casting. In general single drop of few hundred micro liter (μl) polymer solution either drop cast or spin cast on a glass support and subsequently exposed to humidity to prepare BFT pattern in very thin polymeric films [1,3,23–26,31]. There is a paucity of data demonstrating feasibility of the process to large area templating that can bring out application like BF templated microporous membrane formation based on common membrane polymers like polysulfone. Microporous membranes are membranes having 0.1 to 10 μm pores [33].This is the first report describing an elegant route combining BF templating with phase separation process for preparation of microporous membranes having near monodispersed ordered pores and porous cross section (Xn) using a conventional membrane polymer namely polysulfone. The well known phase separation process is often used for synthesis of asymmetric membrane [33,34]. Also very recently BFT and phase separation combination has been used for preparation of micropatterned film from a incompatible ternary blend of different polymers [35]. In this study we used an internal nonsolvent to achieve phase separation in freshly cast membrane simultaneously undergoing BF templating in a concentrate solution of polysulfone.

Present study reports optimization of solution composition and casting variables for BF templated polysulfone microporous membrane preparation from different solvent systems. Polysulfone is a well established membrane polymer due to its high Tg, excellent oxidative and environmental stability, superior physical properties and adequate solubility for solution casting. The polymer is dissolved in a chosen solvent system and cast in an environmental chamber (Bioasset Tech., India) under variable casting conditions of relative humidity (RH from 85–95%) and temperature (from 25–40 °C). Different solution compositions of PSF/DCM, PSF/DCM/TAA, PSF/DCM/Acetone, PSF/THF/TAA, PSF/THF/Acetone were studied. Homogeneous solutions having 2.5–10% (wt/v) polymer in solvent were prepared. In certain solutions an internal nonsolvent namely tertiary amyl alcohol (TAA) or a cosolvent namely acetone was added as volume% (v/v) of the first solvent. Following which membrane casting was performed in glass Petriplates inside an environmental chamber (make - Bioasset Tech., India).

The membranes were analyzed for surface porosity and cross sectional morphology using Quanta 400 SEM/EDAX to establish the effect of casting variables and solution composition on number, distribution, size and morphology of pores.

2. Experimental

Polysulfone (PSF) Mw 35000 (Aldrich) membranes were cast from water miscible solvents - tetrahydrofuran (THF) or water immiscible solvent dichloromethane (DCM - Qualigen AR grade). Acetone was used as a cosolvent. Tertiary amyl alcohol (TAA-Across Organics AR grade) was used as water miscible internal nonsolvent. Different solvent systems including PSF/DCM, PSF/DCM/TAA, PSF/DCM/Acetone, PSF/THF/TAA, PSF/THF/Acetone and different dilutions were tested. The selected solvents have low boiling points, specifically DCM-40 °C, Acetone-56 °C and THF-65 °C and high volatility essential for BF templating.

In a typical experiment selected amount of Polysulfone was dissolved in required volumes of solvent/s, with or without addition of the internal nonsolvent tertiary amyl alcohol. The homogeneous solution was then pour-cast in flat bottom Petridish (Schott Duran Catalog number 2375548, 100 × 20 mm with inner diameter of ~9 cm of the bottom casting plate) kept inside the environmental chamber at predefined relative humidity (RH) and temperature. After 2 h the formed membranes were taken out and subsequently dipped in methanol bath for 12 h to remove any residual solvent, followed by drying at 70 °C for 24 h. Physical pictures from casting process and a formed membrane are given in Supplementary material (Fig. S2 A–E).

Initially five different combinations were screened for feasibility evaluation of BF templated polysulfone membrane formation. These were PSF/THF/TAA, PSF/THF/Acetone, PSF/DCM, PSF/DCM/Acetone and PSF/DCM/TAA.

1. **PSF/DCM**: The PSF/DCM system was chosen for study of dilution effect in a single hydrophobic solvent on formation of breath figure templated (BFT) pores. Membranes were prepared with polysulfone/dichloromethane solution having wt/v concentrations of 10%, 8.5%, 6% and 2.5% by dissolving 0.8 g polysulfone in required volumes of hydrophobic volatile solvent DCM.
2. **PSF/DCM/Acetone**: 10% wt/v solution of PSF was prepared by dissolving 0.8 g polymer in 8 ml DCM-hydrophobic solvent and 0.8 ml acetone - hydrophilic solvent (10% v/v to DCM) was then added to solution. The homogeneous solution then cast.
3. **PSF/THF/Acetone**: 10% w/v solution of PSF was prepared by dissolving 0.8 g polymer in 8 ml of hydrophilic volatile solvent THF and 0.8 ml acetone (10% v/v to THF) was then added to solution. The homogeneous solution used for casting the membrane.
4. **PSF/THF/TAA**: 10% (w/v) solution of PSF was prepared by dissolving 0.8 g polymer in 8 ml THF and 0.8 ml TAA (10% v/v to THF) was then added to solution.
   All the homogeneous solutions were cast at 30 °C temperature and 95% RH unless specified otherwise. For optimization of PSF/DCM/TAA different combinations casting variables such as 25–35 °C temperature and 85–95% humidity and different casting compositions were studied.
5. PSF/DCM/TAA: 10%, 8%, 6%, and 4% w/v solutions of PSF (0.6 g or 0.8 g) in DCM were prepared. Different amount of hydrophilic internal nonsolvent TAA was added to these solutions and membranes were cast from homogeneous solutions under different casting conditions either in glass Petri dish or on a support filter-paper disk soaked with DCM and kept inside the glass Petri dish. In depth compositional variation and casting condition variation were carried out on this system.

3. Characterization

3.1. Morphological characterization

The top, bottom surfaces and cross-sections (Xn) of the membranes were characterized using Scanning Electron Microscope