



Systematic variation of membrane casting parameters to control the structure of thermo-responsive isoporous membranes

Merve Mocan^a, Hares Wahdat^b, Hanne M. van der Kooij^a, Wiebe M. de Vos^c,
Marleen Kamperman^{a,*}

^a Physical Chemistry and Soft Matter, Wageningen University & Research, Stippeneng 4, 6708 WE Wageningen, The Netherlands

^b Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld, Germany

^c Membrane Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands



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ABSTRACT

Fouling is a critical issue in membrane process operation as it greatly compromises the efficiency of the treatment processes. A promising approach to overcome this problem is the production of easy-to-clean membranes by incorporating stimuli-responsive pores. In this study, we fabricated thermo-responsive polystyrene-*b*-poly(*N*-isopropyl acrylamide) (PS-*b*-PNIPAM) block copolymer membranes using the self-assembly and non-solvent induced phase separation (SNIPS) method and systematically varied several membrane casting parameters, i.e. evaporation time, polymer concentration, solvent type and water content, to obtain nano- and isoporous membranes. Membranes with a disordered surface were obtained for PS selective solvents, whereas isoporous membranes were obtained when the block copolymers were dissolved in PNIPAM selective solvent mixtures. Using 1,4-dioxane/ tetrahydrofuran mixtures resulted in isoporous membranes for a large parameter space, indicating the robustness of structure formation in the PS-*b*-PNIPAM system. Permeability tests at various temperatures demonstrated fully reversible thermo-responsive behavior of the membranes.

1. Introduction

To separate nano-sized impurities such as proteins and viruses from water, nanoporous membranes are essential. From all available material classes, block copolymers received a great deal of attention in this field, since they can microphase separate into regular structures [1] and have the ability to form membranes exhibiting uniform nano-sized pores with pore sizes in the range of 2–100 nm [2,3]. Block copolymer (BCP) membranes offer high pore densities, tunable pore sizes, narrow pore size distributions, tunable chemical properties and the ability for selective functionalization such as stimuli-responsivity [4].

Introducing stimuli-responsive pores in the membrane is a promising approach to create easy-to-clean membranes [5–13], since fouling, the accumulation of impurities on the membrane surface, is one of the most important problems in membrane technology. When a stimulus (e.g. temperature, pH, light, magnetism or electricity) is applied, the size of the pores can be tuned and in case the pore size increases, the accumulated impurities can be removed. A stimuli-responsive character can be acquired by fabricating membranes using BCPs that possess a stimuli-responsive character. The most commonly used stimuli-responsive BCPs for membrane production are polystyrene-*b*-poly(4-

vinylpyridine) (PS-*b*-P4VP) [9,14–16] and poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) [17,18] because of their pH-responsive character and their ability to produce well-ordered isoporous membranes. PS-*b*-P4VP BCP membranes were also modified postproduction to attain thermo-responsivity in addition to pH-responsivity [19]. Recently, it was shown that thermo-responsivity could also be directly obtained using polystyrene-poly(*N*-isopropyl acrylamide) (PS-PNIPAM) BCPs either in a spin-coating process [20] or using a phase inversion method [21]. Other pH and thermo-responsive membranes were produced from polystyrene-*b*-poly(2-(dimethylamino)ethyl methacrylate) [22,23] and BCPs consisting of polystyrene and poly(ethylene glycol methyl ether methacrylate) [24].

BCP membranes can be successfully produced by a phase inversion method, also referred to as self-assembly and non-solvent-induced phase separation (SNIPS). In the SNIPS process, a film is formed from a viscous solution of the BCP by using a casting knife with a known gate height. The solvent in the film is evaporated for a certain period, often less than one minute, which causes a concentration gradient that is perpendicular to the film surface. Solvent evaporation is an essential step for self-assembly. The film is then transferred into a non-solvent bath where the organic solvent in the polymer film and the non-solvent

* Corresponding author.

E-mail address: marleen.kamperman@wur.nl (M. Kamperman).

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are exchanged. This ends the self-assembly process and results in the formation of the porous structure [14]. SNIPS membranes are free-standing and, therefore, an additional transfer step to a porous support can be omitted. Different from other methods, pores are directly produced without requiring additional (i.e. etching or additive removal) steps.

Although SNIPS is an easy and quick method, there are many parameters in the process that should be considered and chosen carefully, since they strongly affect the final structure and properties of the membrane. The main parameters that influence the self-assembled surface layer of the membrane are solvent type(s) and ratio, polymer concentration, evaporation time, and type of non-solvent. For a successful SNIPS process, all parameters should be optimized. In our previous study, we produced membranes from PS-*b*-PNIPAM BCPs by using SNIPS. Whereas the films exhibited fully reversible thermo-responsive behavior, the obtained pore sizes were not uniform [21]. In this work, we aimed to improve the surface structures of the membranes by systematically tuning the membrane casting parameters. We investigated the influences of casting solution composition and evaporation time of the SNIPS process and produced nano- and isoporous membranes from a PS-*b*-PNIPAM BCP. The membranes with uniform nanopores were obtained for a relatively large range of parameters. The membranes exhibited thermo-responsive character which was also found to be fully reversible.

2. Experimental part

2.1. Materials

Styrene (Sigma-Aldrich, > 99%) was vacuum distilled just before the synthesis after overnight stirring over calcium hydride. *N*-isopropyl acrylamide (NIPAM) (Sigma-Aldrich, 97%) was recrystallized from toluene. 2,2'-Azobis(2-methylpropionitrile) (AIBN), (Sigma-Aldrich, 98%) was purified by recrystallization from methanol. Diethylether (Biosolve B.V.) and methanol (Fisher Scientific) were used as received. 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DTMA) (98%), calcium hydride (95%), 1,4-dioxane (anhydrous, 99.8%), *N*-methyl-2-pyrrolidone (NMP) ($\geq 99.0\%$), tetrahydrofuran (THF) (anhydrous, $\geq 99.9\%$), acetone and deuterated chloroform (CDCl_3) (99.96% D) were purchased from Sigma-Aldrich and used as received.

2.2. Synthesis of PNIPAM macro-RAFT agent

A monofunctional RAFT agent 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DTMA) was used for the synthesis of PNIPAM macro-RAFT agent. AIBN, NIPAM and DTMA were dissolved in 40 mL 1,4-dioxane. The initial monomer concentration ($[\text{M}]_0$), the ratio of initial monomer and chain transfer agent concentrations ($[\text{M}]_0/[\text{CTA}]_0$) and the ratio of initial chain transfer agent and initiator concentrations ($[\text{CTA}]_0/[\text{I}]_0$) were 1.18 M, 145 and 10, respectively. After dissolution, the liquid was transferred to a Schlenk ampoule with a syringe. After three freeze-pump-thaw cycles, the ampoule was heated to 70 °C by using a temperature controlled oil bath and kept at 70 °C for 4 h. The solution was cooled with liquid nitrogen to stop further reaction. The solution was reprecipitated in diethyl ether after addition of a small amount of acetone. The product was dried for 12 h in a vacuum oven at room temperature (Yield: 81%). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 4.0$ (1 H, s, -NCH-), 0.8–2.5 (9 H, m, -CH₃, -CH-CH₂-), 5.8–7.5 (1 H, br, -NH-). $M_n = 25$ kDa, PDI = 1.10 (determined with GPC)

2.3. Synthesis of PS-*b*-PNIPAM block copolymer

PNIPAM macro-RAFT agent, styrene and AIBN were dissolved in 90 mL 1,4-dioxane by stirring at room temperature. Styrene was purified by vacuum distillation just before the polymerization. For this polymerization step $[\text{M}]_0$, $[\text{M}]_0/[\text{macro-RAFT}]_0$ and $[\text{macro-RAFT}]_0/$

$[\text{I}]_0$ were 4.35 M, 1917 and 10, respectively. After dissolution, the liquid was transferred to a Schlenk ampoule with a syringe. After three successive freeze-pump-thaw cycles, the ampoule was heated to 70 °C by using a temperature controlled oil bath. The polymerization proceeded for 48 h. Then the solution was cooled in liquid nitrogen to stop further reaction. By using a rotary evaporator, 1,4-dioxane was evaporated from the solution. The polymer was dissolved in THF and precipitated in cold water several times until no PNIPAM homopolymer peak was detected in the GPC elugram. Then the solid was precipitated twice from diethyl ether to purify the copolymer from the unreacted styrene. The product was dried in a vacuum oven overnight at 35 °C (Yield: 33%). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.2$ –7.1 (5H, m, Ph), 4.0 (1H, s, -NCH-), 0.8–2.5 (3H, m, -CH-CH₂- for PS and 9H, m, -CH₃, -CH-CH₂-for PNIPAM). $f_{\text{PS}} = 0.83$ (determined with NMR), $M_n = 194$ kDa (determined with NMR), PDI = 1.34 (determined with GPC)

2.4. Polymer characterization

$^1\text{H NMR}$ measurements were performed on a Bruker AMX-400 NMR spectrometer (400 MHz) at room temperature. Gel permeation chromatography (GPC) was carried out on a Viscotek GPCmax equipped with 302 TDA model detectors. A guard column (PSS-GRAM, 10 μm , 5 cm) and two analytical columns (PSS-GRAM-1000/30 Å, 10 μm , 30 cm) were used. The eluent was dimethyl formamide (containing 0.01 M LiBr) at 50 °C and the flow rate was 1 mL/min. For the calibration of the column, poly(methyl methacrylate) standards were used. Viscotek Omnisec software was used to process the data. Molecular weight and PDI of PNIPAM macro-RAFT agent and PDI of PS-*b*-PNIPAM BCP were determined by using refractive index and light scattering signals, respectively. The molecular weight of the BCP was obtained using the molecular weight of PNIPAM macro-RAFT agent and the block ratio calculated from NMR. The block ratio between PS and PNIPAM in the BCP was found by comparing the integrals of the aromatic PS protons between 6.2 and 7.1 ppm (5 H, m, Ph) to the lone PNIPAM proton at 4.0 ppm (1 H, s, -NCH-).

2.5. Membrane preparation

A polymer solution of specified concentration was poured onto a glass substrate, after which a casting knife (gate height: 200 μm) was used to form a polymer film. After a waiting step, in which part of the solvent evaporated, the film was transferred to a non-solvent bath. Water was used as non-solvent for all the membranes except the one prepared from toluene-THF solutions. Ethanol was used as the non-solvent for that system due to immiscibility of toluene in water. Polymer films were kept in the non-solvent bath for at least 4–5 h for a complete solvent-non-solvent exchange. The membrane films were stored in vials filled with Milli-Q water and prepared into the desired dimensions for relevant characterization.

Humidity might have an influence on the morphology especially because PNIPAM is hygroscopic. However, a significant difference was not observed, therefore we did not report the results. Nevertheless, all samples presented here were prepared at a constant humidity of 40% RH.

2.6. Membrane characterization

Before morphological analyses, the membranes were cut into 1 × 1 cm sized samples, fixed on Si wafers using double-sided tape and then dried overnight in a vacuum oven at 40 °C. The surface structure of the membrane films was analyzed with a Bruker Multimode 8 Atomic Force Microscopy (AFM) instrument using non-conductive silicon nitride probes (Bruker, DNP-10 model, spring constant: 0.24 N/m). Images were obtained in Nanoscope V ScanAsyst imaging mode with a scanning rate of 1.50 Hz. Data were processed using NanoScope Analysis 1.5 software. To assure representative characterization of the

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