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Synthesis, characterization and performance of polystyrene/PMMA blend membranes for potential water treatment☆

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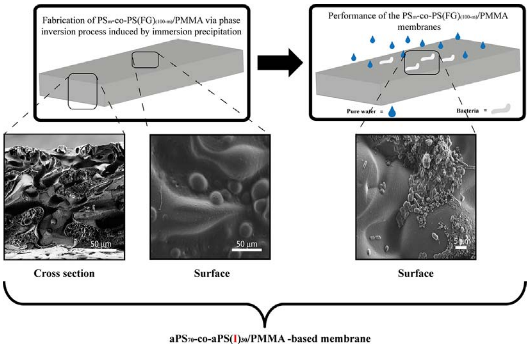
GRAPHICAL ABSTRACT



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ABSTRACT

PS membranes were prepared from polymeric blends of PS and PMMA via a phase inversion induced by an immersion precipitation in water coagulation baths. The effects of the casting parameters (e.g., solvent selection, the composition of the coagulation bath) and the type of polystyrene (substituents at the aromatic ring, tacticity) on the morphology and water permeation flux were studied. The findings reveal that modified PS promoting instantaneous demixing with NMP/water systems result in membranes wit- h macrovoids while the addition of 2% of PS-r-PMMA results in membranes with high water fluxes. The membranes morphologies were governed by a trade-off between thermodynamic and kinetic aspects. The antibacterial effect of $(aPS)_{70}$-co-$aPS(I)_{30}$/PMMA-based membrane was examined using static and cross-flow systems. These results illustrate the diversity in the design of these PS/PMMA based membranes and highlight the possibility to control the polymer chemistry for tailoring specific morphology, permeation, and antibacterial properties for the desired function.

1. Introduction

Amorphous polystyrene (PS) is one of the most wildly used polymers with good thermal and radiation resistant properties. In addition, semicrystalline PS has a high melting point and therefore possess good chemical resistance, thermal stability, excellent hydrocarbon resistance, a high degree of dimensional stability, and excellent electrical performance [1]. All these properties make PS as an attractive membrane material. To the best of our knowledge, the fabrication and performance of PS-based membranes have never been explored. However, the main disadvantages are the high hydrophobicity of the PS membrane and its brittleness. Hydrophobic membranes are susceptible

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☆ This manuscript honors Prof. Rafi Semiat from the Department of Chemical Engineering at the Technion: A great friend and colleague!
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to contamination by proteins and some other organic impurities in water and wastewater treatments, which results in reduced water membrane fluxes [2,3]. Therefore, it is necessary to improve the stability and antifouling properties of PS membranes.

Many studies have investigated improvements in the polymer membrane performances by polymer chemical modification, surface modifications and physical blending [3,4]. Functionalization of polystyrene can be achieved by post-polymerization through the introduction of a functional group via activation of the aromatic C—H bonds [5]. The degree of modification depends generally on the type, amount and distribution of functional groups in the polystyrene leading to copolymerization and resulting in styrene-functional styrene sequences with superior properties. Modification by antimicrobial substances such as phenols, mercuric chloride, chlorine, polysubstituted benzene derivatives, hypochlorite, and iodine can effectively prevent microbial growth on filtration membranes [6–8].

Additionally, blending is a simple and commonly used method for membranes preparation, obtained via a phase inversion methodology [9,10], which leads to the formation of new materials with enhanced physical, chemical and mechanical properties [9]. In recent years, blending of polystyrene with poly(L-lactide) [11], polyethylene [12], poly(vinyl methyl ether) (PVME) [13,14], poly(bromo)styrene (PBrS) [15] and poly(methyl methacrylate) (PMMA) [16] have been studied.

The permeability and selectivity characteristics of polymeric membranes are influenced not only by the molecular structure of the polymer but also by the morphology of the membrane. The different mechanisms for the formation of the final morphology of the asymmetric membrane, which ranges from finger-like to sponge-like voids, are affected both thermodynamically and kinetically. Porous polymeric membranes can be fabricated via phase separation methods such as non-solvent induced phase separation (NIPS) [17,18], thermally induced phase separation (TIPS) [19,20] or combination of both methods [21,22]. In the phase inversion process induced by immersion precipitation, phase separation occurs by the exchange of solvent and non-solvent. This liquid-liquid demixing process rate can produce dense membranes with sponge-like structure (low demixing rate) or finger-like pore membranes (high demixing rate) [23]. Therefore, to design or to tailor a membrane material, the selection of the different parameters will determine the properties and characteristics of such membrane. The solubility parameter theory is a convenient way of estimating the expected compatibility between polymers, solvents and non-solvents [23,24].

The aim of the current work is to develop new membrane materials via NIPS based on functionalized polystyrene with different tacticities (atactic (aPS) and syndiotactic (sPS)) with high permeability, long-term stability, and antibacterial activity. By post-modification of the PS moiety with various hydrophilic substituents, a copolymer was achieved. These copolymers were subsequently blended with PMMA and their effects on the membrane morphology, and pure water flux were studied. In addition, the effects of antimicrobial properties of the membranes using static and flowing systems are also presented.

2. Experimental

2.1. Materials and methods

The compounds atactic polystyrene, polymethyl methacrylate (PMMA, Mw ~ 350,000 Da) and poly(styrene-random-methyl methacrylate) (PS-r-PMMA) were purchased from Sigma-Aldrich and used as received. Polyvinylphenol (PvPh) was purchased from Frontier Chemicals, LLC, and used as received.

Dimethylformamide (DMF), isopropyl alcohol, toluene (Ar, Frutarom), 1-methyl-2-pyrrolidinone (NMP) (≥ 98%, Fluka), dioxane (Riedel-de Haen), dichlorobenzene (DCB), 1,1,2,2 tetrachloroethane (TCE), cyclooctane, cyclohexane and acetic anhydride (98%), cyclopentadienyl titanium(IV) trichloride ($CpTiCl_3$), n-Butyllithium (BuLi), styrene and Methylalumoxane (MAO) were purchase at Sigma-Aldrich. Ethanol, methanol, and methyl ethyl ketone (Ar, Bio Lab). Most of the solvents were used as received except for cyclooctane, cyclohexane, and styrene that were used after their corresponding purifications via distillation [25]. Static measurements were performed using *Escherichia coli* CN-13 as the model organism. Flows through experiments were performed using *Pseudomonas putida* S-12 (ATCC 700801).

Differential scanning calorimetry (DSC) was carried out in a Seratam TG-92 instrument in air and was used for determination of the glass transition (T_g) and melting temperatures (T_m). DSC spectra were recorded with a heating rate of 10 °C/min over a temperature range from 25 °C to 300 °C. Nuclear Magnetic Resonance (NMR) spectra were recorded using either a Bruker Avance 300 and 500 MHz spectrometers. Chemical shifts for ^1H and ^{13}C were referenced to internal solvent resonances and are reported relative to tetramethylsilane (TMS). The NMR measurements for the polymers were performed in deuterated 1,1,2,2-tetrachloroethane or deuterated dimethyl sulfoxide (DMSO) at 80 °C. The spectra were analyzed with Topspin software. Calculation of degree of substitution (DS) of the aPS was performed by ^1H NMR, however, for sPS was performed by elemental analysis using a Thermo Scientific Flash 2000 CHNS OEA instrument (The detailed calculation is presented at the supplementary information). Molecular weights and polydispersity of the polymers were determined by gel permeation chromatography (GPC) on a Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene (HPLC grade, J. T. Baker) as a mobile phase at 160 °C. Polystyrene standards were used for the standard calibration curve of the GPC (Varian, 2000–180,000 range). Fourier transform infrared spectroscopy (FTIR) experiments were carried out on a Bruker Vector 22 instrument in transmission mode using KBr pellet under a nitrogen flow.

In this work, a morphological study of the modified and unmodified membranes was performed using scanning electron microscopy (SEM) (a Tescan (Vega-II) electron microscope) and high resolution scanning electron microscopy (HRSEM) (Carl Zeiss Gemini Ultra plus HRSEM 1 kV). Prior to imaging, all the samples were prepared by freeze fracturing the sample in liquid nitrogen and coated with carbon. Visualization of the autopsied membranes was done by HRSEM. This involved washing, fixation with 2.5% (v/v) glutaraldehyde, followed by subsequent dehydration using an ethanol gradient in the cold and finally drying [26].

2.2. Synthesis of neat and modified polystyrene

2.2.1. Syndiotactic polystyrene, sPS

Syndiotactic polystyrene (Fig. 1) was successfully synthesized by using titanium compounds/methylalumoxane, as homogeneous organometallic catalytic systems at 50 °C following the exact procedure as presented in the literature [27]. The resulting polymer was stirred in acidified in methanol to deactivate the catalyst and subsequently

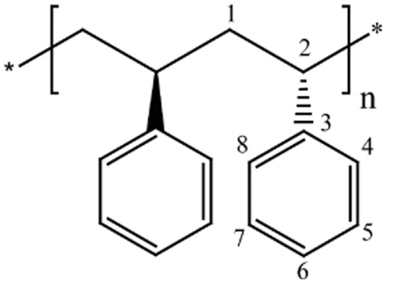

Fig. 1. Structural formula of syndiotactic polystyrene (sPS).
^1H NMR (500 MHz, $C_2H_2Cl_4$–d_2, 373 K) δ = 1.42 (CH_2, H1), 1.91 (C*H*, H2) 6.60 (H_{ar}, H4, 8), 7.09 ($H_{a,}$ H5, 6, 7).
^{13}C NMR (125.7 MHz, $C_2H_2Cl_4$–d_2, 373 K) δ = 41 (*C*H, C2), 44.2 (*C*H_2, C1), 125.5 (C_6H_5, C6), 12 7.7 (C_6H_5, C4, 8), 127.8 (C_6H_5, C5, 7), 145.3 (C_6H_5, C3).