

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

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

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G R A P H I C A L A B S T R A C T

A R T I C L E I N F O

Keywords:

Membrane formation

Polymer blending

Polystyrene

PMMA

Biofouling

Solubility parameter

A B S T R A C T

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 with 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 widely 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. How-

ever, the main disadvantages are the high hydrophobicity of the PS membrane and its brittleness. Hydrophobic membranes are susceptible

<https://doi.org/10.1016/j.desal.2017.12.024>

Received 25 May 2017; Received in revised form 10 December 2017; Accepted 12 December 2017

† This manuscript honors Prof. Rafi Semiat from the Department of Chemical Engineering at the Technion: A great friend and colleague!

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Available online 16 December 2017

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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, $M_w \sim 350,000$ 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 (CpTiCl₃), n-Butyllithium (BuLi), styrene and Methylalumoxane (MAO) were purchased 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 ¹³C 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-III) 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 methanol to deactivate the catalyst and subsequently

Fig. 1. Structural formula of syndiotactic polystyrene (sPS).
¹H NMR (500 MHz, C₂H₂Cl₄, 373 K) δ = 1.42 (CH₂, H₁), 1.91 (CH, H₂), 6.60 (Ha, H₄), 7.09 (Ha, H₅, 6, 7).
¹³C NMR (125.7 MHz, C₂H₂Cl₄, 373 K) δ = 41 (CH, C₂), 44.2 (CH₂, C₁), 125.5 (C₆H₅, C₆), 127.7 (C₆H₅, C₄, 8), 127.8 (C₆H₅, C₅, 7), 145.3 (C₆H₅, C₃).

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washed with water, methanol, and acetone, filtered and dried in a va-

cuum oven at 60 Å°C. Then it was extracted with methyl ethyl ketone (MEK) to remove the remained atactic component.

2.2.2. Chemical modification of polystyrene

Functionalized polystyrene could be obtained by activation of the aromatic CeH bonds via the simple electrophilic aromatic substitution (Fig. 2) [5]. The result of post-functionalization is partially functionalized polystyrenes with randomly distributed functional pendant groups. The abbreviation of the resulted copolymer products will be rPS(100-m)-co-r(FG)m, while r, FG, and m represent the tacticity (a for atactic, s for syndiotactic), functional group and degree of substitution (in percentage), respectively. The calculation for the degrees of substitution appears in the supplementary information.

2.2.2.1. Sulfonation of PS. Sulfonation of the PS (aPS and sPS) was reported in the literature, using acetyl sulfate as the sulfonating reagent, at 60 Å°C for 3 h. Based on this procedure aPS was sulfonated by acetyl sulfate in the presence of chloroform, while sPS in the presence of a mixture of solvents (tetrachloroethane (TCE)/chloroform; 60/40) in order to facilitate the control and reactivity between the reactants. The polymers were prepared following the exact procedure as presented in the literature [28]. The sulfonated dried polymers obtained were: aPS76-co-aPS(SO3H)24: 2.1 g (88.8%), and sPS60-co-sPS(SO3H)40:1.04 g (53%).

The 1H NMR and 13C NMR of the partially sulfonated aPS [29] and sPS [30] are known in the literature.

2.2.2.2. Iodination of PS. Iodination of aPS was prepared in the presence of I2 and I2O5 in a mixture of carbon tetrachloride (CCl4), 50% aqueous H2SO4 and nitrobenzene at 90 Å°C for 40 h, as previously reported however instead of 8 g of PS we used 5 g [31,32]. The PS-I was dried at 70 Å°C for 24 h to obtain aPS18-co-aPS(I)82: 2 g (20%). The 13C NMR of the partially iodinated aPS is known in the literature [33].

aPS70-co-aPS(I)30:

1H NMR (500 MHz, C2D2Cl4, 373 K) δ = 1.52 (CH2, H1, 1 \times), 1.95 (CH, H2, 2 \times), 6.17 \sim 6.66 (Har, H4, 8, 4 \times , 8 \times), 6.98 \sim 7.42 (Har, H5, 6, 7, 5 \times , 7 \times).

2.2.2.3. Nitration of PS. Nitration of PS was performed using a mixture of nitric acid and sulfuric acid at 50 Å°C for 24 h as previously reported [34]. The dried polymer weighed: aPS27-co-aPS(NO2)73: 4.5 g (68.2%), and sPS90-co-sPS(NO2)10: 3.3 g (63.2%). The 1H NMR of the partially nitrated aPS is known in the literature [34].

aPS27-co-aPS(NO2)73:

13C NMR (75.4 MHz, DMSO-d6, 373 K) δ = 30.7 (CH, C2, 2 \times), 41.2 (CH2, C1, 1 \times), 123.3 (C6H5, C5, 7, 5 \times , 7 \times), 128.8 (C6H5, C4, 8, 4 \times , 8 \times),

146.4 (C6H5, C3, 3 \times), 152.0 (C6H5, C6).

FTIR (KBr) $\tilde{\nu}$ = 1541 and 1309 cm⁻¹ (antisymmetric and symmetric NO2 stretch, respectively).

sPS90-co-sPS(NO2)10:

1H NMR (300 MHz, DMSO-d6, 373 K) δ = 1.42 (CH2, H1, 1 \times), 1.91 (CH, H2, 2 \times) 6.69 (Har, H4, 8, 4 \times , 8 \times), 7.75 (Har, H5, 6, 7, 5 \times , 7 \times).

13C NMR spectrum of polymers could not be obtained due to lack of solubility of the polymer.

FTIR (KBr) $\tilde{\nu}$ = 1520 and 1349 cm⁻¹ (antisymmetric and symmetric NO2 stretch, respectively).

2.2.2.4. Bromination of PS. Bromination of sPS was performed using bromine activated by ferric chloride as a Lewis acid catalyst in the presence of CCl4 in the dark for 3 days as in the literature [35]. The dried obtained polymer was sPS81-co-sPS(Br)19: 2.0 g (70%). The 1H NMR of the partially nitrated sPS is known in the literature [36].

sPS81-co-sPS(Br)19:

¹³C NMR (75.4 MHz, C₂D₂C₁₄, 373 K) δ = 41.0 (CH, C₂), 44.3 (CH₂, C₁), 119.5 (C₆H₅, C₆) 125.5 (C₆H₅, C₅, 7), 127.8 (C₆H₅, C₄, 8, 4 \times 2, 8 \times 2), 129.5 (C₆H₅, C₅ \times 2, 7 \times 2), 131.2 (C₆H₅, C₆), 145.0 (C₆H₅, C₃), 145.4 (C₆H₅, C₃ \times 2).

2.3. Membrane preparation

PS/PMMA blend membranes were prepared by the classical phase inversion process [23]. PS and PMMA were introduced into the chosen solvent (the total concentration of PS and PMMA was 20 wt%) and the weight ratio of PS/PMAA (1:1) was maintained. The blend solution was stirred at 80 °C for 24 h until a homogeneous casting solution was obtained and subsequently was cast onto a clean glass plate by a steel casting knife to the desired membrane thickness. The cast film was immediately immersed in water as the non-solvent and coagulation bath for 24 h at 25 °C in order to exchange the solvent completely. The thicknesses of the membranes varied from 40 to 135 μ m, depending on the casting conditions for phase inversion.

In membranes, which were prepared using the commercially available copolymer, (PS-r-PMMA), an additional 2% to the 20% of the blend was used.

2.4. Membrane characterization

2.4.1. Solubility parameter

In the phase inversion process induced by the immersion pre-precipitation, thermodynamic and kinetic aspects have to be considered since they are responsible for the membrane morphology and its performance [37]. In ternary systems (polymer/solvent/non-solvent), the thermodynamics interactions are directly proportional to the solubility parameter difference between the components [15].

The solubility parameter difference between the polymer (p) and solvent (s) determined their mutual affinity and can be calculated based on the Hansen solubility parameters (HSP) according to Eq. (1), where the subscripts δ^d , δ^p , and δ^H , represent contributions from the non-polar

interaction, polar interaction, and hydrogen bonding, respectively. The units for these parameters are (MPa)^{1/2}. Similarly, the polymer/non-solvent ($\delta^p - \delta^ns$) and solvent/nonsolvent ($\delta^s - \delta^ns$) solubility parameter differences can be calculated. Smaller values correspond to a high affinity to each component, hence to a better miscibility [38].

$$\Delta\delta = \sqrt{(\delta^d_p - \delta^d_s)^2 + (\delta^p_p - \delta^p_s)^2 + (\delta^H_p - \delta^H_s)^2} \quad (1)$$

1

2 (2)

This work numerically estimated the HSP of functionalized aPS by a group molar contribution method suggested by Hoy [39]. A detailed description is presented at the supporting information.

Fig. 2. Functionalized polystyrene structures obtained by electrophilic aromatic substitution.

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2.4.2. Water flux measurements

Water flux performance of the PS/PMMA blended membranes were examined using a dead-end filtration cell connected to a nitrogen gas cylinder to apply the feed pressure at room temperature as shown in Fig. 3.

The pure water feed solution was examined under various operating pressures ranging from 2 to 10 bar at room temperature. To avoid initial non-equilibrium conditions, collection of the permeate was only started after 30 min of permeation.

Flux values of pure water at different trans-membrane pressures were measured under steady state condition using the following equation:

=
 $\hat{A} < \dots$
 $J V$
 $(A \hat{I}''t)w$
 w

where J_w , V , A , and $\hat{I}''t$ are the pure water flux ($\text{L m}^{-2} \text{ h}^{-1}$), the volume of the permeated pure water (2 mL), effective filtration area ($A = 0.73 \text{ cm}^2$), and $\hat{I}''t$ (h) is the recorded time. Each test was performed three times and then the average performance values were taken. The relative standard error (RSE) was found to be lower than 25% except in the case of dioxane, which the flux increases drastically after every run.

2.4.3. Characterization of antibacterial properties

Antibacterial potential of the modified membranes was evaluated in static and flow-through conditions as previously described in the literature [40]. Static tests were performed by the inhibition zone method to provide evidence of the antibacterial activity of the modified PS based membranes. Luria-Bertani (LB) broth was used for generation of the starter cultures used for inoculation of the experimental cultures. The experiments were initiated by dilution of the starter *E. coli* CN-13 culture (0.21 OD) to reach an initial cell concentration of approximately 5×10^4 cells/ml in the plate. All experiments were performed under sterile conditions. The volume of 0.1 ml of the diluted sample is pipetted onto the surface of the agar plate. The membranes were cut into circular disks and then deposited on the agar plate for incubation. After 72 h, the membranes were removed, thoroughly washed with a sterile saline solution, stained with nucleic acid stains Syto 9 and Propidium iodide (PI) and taken for further visualization by confocal laser scanning microscopy (CLSM).

Flow-through experiments were performed in cross-flow flat sheet-membrane cells with internal recirculation operating in continuous mode, feed with diluted (1:250) LB medium under aseptic conditions with *P. putida* S-12 as model bacterium. The experiment was started by adding a volume of the starter culture (0.27 OD) of 1.25 ml into the reaction medium (170 ml) and left to run for one hour in closed recirculation to let the bacteria to establish. Then, continuous operation was started. The flow-through cells (13 cm length and 12.5 mm diameter) were equipped with the membranes. After 72 h, the membranes were visualized and analyzed by HRSEM.

3. Results and discussion

3.1. Polystyrene synthesis and characterization

The neat and modified polystyrenes with different tacticities were confirmed by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy [41,42]. Following the post-modification by the typical electrophilic aromatic substitution, copolymers based on the polystyrene skeleton were fabricated. The thermal properties and molecular weight of the neat and modified polystyrenes are summarized in Table 1.

Table 1 compares the molecular weights of the resulted modified PS obtained from the GPC. Generally, higher degrees of substitution increase the copolymer molecular weight. However, as can be seen in the case of for aPS70-co-aPS(I)30, iodination of aPS produced lower molecular weight polymer with a non-uniform substitution (i.e., high PDI value) probably due to uncontrolled regioselectivity and/or degradation [32] [34]. The thermal and chemical stabilities of polymers are of high interest and very important parameters in the field of membrane

Fig. 3. Schematics diagram of the experimental setup.

Table 1

Properties of the neat and modified stereoregular polystyrenes.

Polystyrene Type GPC DSC
 M_w
 (kg mol $^{-1}$)

PDI Tg (Å°C)
 aPS Neat aPS 75.31 2.9 100
 aPS76-co-aPS(SO3H)24 4077. 2.4 98
 aPS70-co-aPS(I)30 54.52 6.2 116
 aPS27-co-aPS(NO2)73 Insoluble 100
 sPS neat sPSa 17.80 1.9 99
 sPS60-co-sPS(SO3H)40 Insoluble 102
 sPS90-co-sPS(NO2)10b Insoluble 101
 sPS81-co-sPS(Br)19 60.5 1.3 Å°C
 a Tm= 257 Å°C (34.85 of crystallinity).
 b Tm= 229 Å°C.
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technology since they can dramatically influence the glass transition temperatures. Based on the presented results, the Tg of the copolymers is higher than that of neat PS except for aPS based copolymer, aPS76-co-aPS(SO3H)24, which is slightly lower. As expected, intermolecular interactions between bulky pendant groups (i.e., hydrogen bonding, polarity, etc.,) restrict the motion of the copolymer chains and therefore raise their Tg.

The polymerization results indicate that copolymers based on stereoregular polystyrene with the different functional groups and compositions were successfully prepared. Thus, the improved thermal and chemical stability in addition to the hydrophilic properties makes those copolymers a good candidate for membrane processes like water and wastewater treatment in terms of permeability and processability and hence we present in continuation those results.

3.2. Fabrication and characterization of polystyrene-based membrane Membrane formation processes involve a complicated relationship between thermodynamic and kinetic factors of a ternary system (polymer/solvent/non-solvent). The morphology and the performance of the membrane strongly depend on the above effects. The composition of the casting solution (containing solvent, non-solvent, and polymer composition) and the composition of the bath (containing non-solvent and solvent) are factors that determine which precipitation sequence is kinetically favored in the process.

In the current study, we attempted to qualitatively understand and analyze the phase separation behavior of the quaternary PS/PMMA/solvent/non-solvent systems with various solvents and non-solvents and to relate the thermodynamic and kinetic parameters, of the studied systems, with their membrane morphologies and consequently their performances. Our quaternary system contains a 20% of aPS blended with PMMA (1:1) in different solvent/nonsolvents, and water as a coagulant. The reason for choosing PMMA and weight ratio of 50: 50 (PS: PMMA) is based on the paper of K. Kaniappan et al. [16], which indicates that the rigidity value of PS is reduced after its blending with PMMA at this ratio. The discussion will be directed in terms of the thermodynamics (solubility parameter) and in terms of kinetics (mass transfer) properties. To the best of our knowledge, this is the first study on a quaternary phase separation behavior of PS/PMMA/solvent/non-solvent systems.

3.2.1. Effect of casting parameters on PS-based membranes morphology Å°C the solvent/non-solvent effect

Fig. 4 shows SEM images of cross sections of aPS/PMMA blend membranes prepared from casting solution in DMF, NMP, and dioxane when water was used as the coagulant at room temperature. The membranes obtained from the casting solution with DMF has finger-like morphology with a protuberance and large macro voids that appear in the cross-section image of the membrane (Fig. 4a).

Similar finger like morphology can be seen in the membrane prepared from casting solutions with NMP. However, cross-section image

shows short finger-like on the top and multi-layered support (Fig. 4b). On the other hand, the membrane prepared from dioxane results in finger like structure with typical sponge support layer (Fig. 4c). Such morphologies can be explained by the kinetic aspects of the phase inversion process, particularly at the solvent/ non-solvent exchange rates. A sponge structure indicates a slow exchange rate between the solvent and the non-solvent in the immersionâ€precipitation processes (delayed demixing), which suppress the formation of macrovoids. In general, instantaneous demixing results in the production of a membrane with a thin top layer of porous nodular structure and macrovoids (finger-like); while delayed demixing forms the membrane with a dense, thick top layer and a closed cell substructure (sponge-like) [23].

Apart from the kinetics, the effect of the solvent on the membrane morphology can be estimated thermodynamically using HSP solventâ€water solubility parameter difference ($\delta^H_{\text{solvent}} - \delta^H_{\text{water}}$), as presented in Table 2. The HSP comprises the following three parameters: the dispersion force, δ^H_d , the dipole interaction force factor, δ^H_p , and the hydrogen-bonding force factor, δ^H_H .

The liquid-liquid demixing is significantly influenced by the affinity between the solvent and the coagulant liquid, in this case, will be water. It is known that the decrease of the solubility parameter difference increased the mutual affinity between the solvent and the non-solvent [38]. As could be seen in Table 2, the solubility parameter difference between DMF/water, ($\delta^H_{\text{DMF}} - \delta^H_{\text{water}} = 31.1 \text{ MPa}^{1/2}$), is the lowest as compared to NMP/water and dioxane/water (35.4 and 37.8 MPa^{1/2}, respectively). Thus, it is clear that water has a higher mutual affinity with DMF than with dioxane or NMP. The high mutual affinity would increase the diffusivity between the solvent and the water phase leading to instantaneous demixing, which will be associated with the formation of finger-like pores in the support layer or macrovoids. In addition, the protuberance appearance on top of the membrane can be explained using the solubility parameter difference between the DMF/polymer blend. From Table 2, the solubility parameter difference between PS and PMMA is 3 MPa^{1/2} indicating that the blend will be thermodynamically incompatible. Furthermore, the solubility of the two polymers in DMF is quite different while PS is less soluble in DMF ($\delta^H_{\text{DMF}} - \delta^H_{\text{PS}} = 10.4 \text{ MPa}^{1/2}$) than PMMA (4.6 MPa^{1/2}). It can be suggested that in the initial stages of the phase inversion process, fast precipitation of the PS occurs. PS separates from PMMA and solidifies as a PS-rich phase, while the PMMA phase collapses below the PS-air interface [43]. In the later immersing stage, increase in the water inflow results in a secondary polymer-rich/polymer-lean phase separation [44]. However, as the diffusion between the solvent and the water decrease, slow precipitation occurs and the dominant mechanism is Fig. 4. Cross section of aPS/PMMA blend membrane (A = DMF, B = NMP, C = dioxane, all of them in a coagulant water bath).

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polymer-rich and polymer-lean phase separation. These observations are in good agreement with several studies regarding solvent effects on the morphology of polymer blends based membranes [9,23,24].

3.2.2. Influence of the composition of the coagulation bath

Addition of non-solvent additives to the coagulation bath can change the thermodynamic and kinetic properties of the solution and as a result, affects the membrane structures and properties. The type of non-solvent can change the precipitation sequence from instantaneous to delayed demixing, which affects macrovoids formation [45]. In this study, PS membranes were prepared using various 2-propanol (IPA) and water composition ratios. The cross-section morphology of the membranes prepared from aPS/PMMA/NMP/IPA (100% IPA) and aPS/

PMMA/NMP/IPA/water (IPA 70% wt in water) are shown in Fig. 5. From the kinetics point of view, IPA is a weak non-solvent and has a lower diffusion coefficient in NMP as compared to water (4.7×10^{-6} and 8.1×10^{-6} cm²/s, respectively) [46]. Therefore, the exchange between IPA and NMP is slower leading to a delayed demixing. In a classic ternary system (polymer/solvent/non-solvent), when delayed demixing occurs, a sponge-like structure is created [45]. As the IPA content in the coagulation bath increases (Fig. 5), the finger-like pore structure is suppressed, which resulted in the formation of horizontally layered structures with spongy protuberances. These unusual structure features are typically observed in quaternary systems of immiscible polymer blends [44].

In addition, as the content of IPA in the coagulation bath decreases, the membranes thicknesses increase (50 μ m and 90 μ m, respectively). It is expected that the in-phase inversion process, slow diffusion of IPA into the polymer blend casting solution occurs and high outflow of NMP to the coagulation bath will allow shrinkage of the membrane.

Kinetically, the film shrinks due to faster diffusion of NMP out to the coagulation bath than that of IPA into the polymer blend solution [47].

The NMP/non-solvent, PMMA/non-solvent and PS/non-solvent solubility parameters difference, δ^1 -NMP-non-solvent, δ^1 -PMMA-non-solvent, δ^1 -PS-

non-solvent, respectively, are listed in Table 3. These values decrease by increasing the IPA content in the coagulation bath. The lower δ^1 -NMP-non-solvent value indicates that NMP has a better affinity with the alcohol rather than with water while lower δ^1 -PMMA-non-solvent, and δ^1 -PS-non-sol-

vent values suggesting that the alcohol is a weak non-solvent for PMMA and PS. Under such conditions, instantaneous type of demixing is favored, however, the sponge-like structure was observed. Since a good agreement was obtained between the kinetic effect (diffusion coefficients) and the final morphology, it could be concluded that in this case, kinetics dominates over the thermodynamic effects. This discrepancy has been also observed in several studies [24] [45].

3.2.3. Influence of the functional groups

Increasing at the PS the degree of substitution at the aromatic ring could lead to a polymer with a better miscibility with PMMA due to additional intermolecular interactions. The effect of iodine in aPS70-co-aPS(I)30/PMMA blend solution in NMP and water as non-solvent is depicted in Fig. 6. Both the modified PS and the original membrane (aPS/PMMA, see Figs. 4b and 6c) possess a porous top layer with finger-like pores layer with a highly porous support layer (macrovoids in the sublayer). The modified membrane has a surface that contains protuberance (Fig. 6A), which represent the polymer-rich domains after a completed phase-separated process [48].

In order to explain the morphology of the resulted membranes based on aPS70-co-aPS(I)30/PMMA/NMP/water systems, thermodynamically, HSP of functionalized aPS70-co-aPS(I)30 using the group molar contribution method, suggested by Hoy [39], have been calculated (Table 4). According to the prediction of the cohesive energies by Small, Hoy, Fedors and Van Krevelen, the highest the halogen electro-negativity, the smaller the corresponding cohesive energy. This resulted

Table 2
Hansen solubility parameters (δ^1) and solubility parameter differences between solvents (s) and water (non-solvent) δ^1 -s-water.

Solvent δ^1 -d (MPa)^{1/2} δ^1 -p (MPa)^{1/2} δ^1 -H (MPa)^{1/2} δ^1 -t (MPa)^{1/2} δ^1 -s-water (MPa)^{1/2} δ^1 -s-PS (MPa)^{1/2} δ^1 -s-PMMA (MPa)^{1/2}

PMMA 18.8 10.2 8.6 23.1 Δ Δ Δ

PS 17.6 6.1 4.1 20.1 Δ Δ Δ

Dioxane 19.1 1.8 7.4 20.5 37.8 5.5 8.4

NMP 18.0 12.3 7.2 23.0 35.4 6.9 2.6

DMF 17.4 13.7 11.3 24.9 31.1 10.4 4.6
 Water 15.6 16.0 42.3 47.8

Fig. 5. Cross section of membranes casted from aPS/PMMA/NMP/non-solvent systems. At the coagulation bath (A = IPA, B = IPA: water (70:30 wt%)).

Table 3

Hansen solubility parameter difference between NMP and non-solvent, $\delta_{H,NMP-non-solvent}$ and polymer/non-solvent $\delta_{H,polymer-non-solvent}$.

Non-solvent

(IPA:water)

$\delta_{H,PMMA-non-solvent}$

(MPa)^{1/2}

$\delta_{H,PS-non-solvent}$

(MPa)^{1/2}

$\delta_{H,NMP-non-solvent}$

(MPa)^{1/2}

0:100 34.3 39.5 35.4

70:30 15.9 20.3 17.4

100:0 11.2 12.4 11.3

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in lowering the total solubility parameter, which leads to smaller solubility parameter differences between the solvent and the polymer, $\delta_{H,NMP-polymer}$ and $\delta_{H,water-polymer}$, respectively.

It can be seen (Table 4) that the solubility parameter difference between aPS70-co-aPS(I)30/NMP is smaller in comparison to PS/NMP. Therefore, the possibility for instantaneous demixing increases for aPS70-co-aPS(I)30/PMMA/NMP system resulting in a finger like with macrovoids morphology [24].

This result is in agreement with the morphology in the SEM of aPS70-co-aPS(I)30/PMMA/NMP/water based membrane (Fig. 6).

The miscibility of blending polymers can be improved using a compatibilizer. To improve the mechanical integrity of the blends in the chosen solvent, PS-r-PMMA copolymers were blended together with the aPS27-co-aPS(NO2)73/PMMA casting solution. PS-r-PMMA is considered a compatibilizer between the two immiscible polymers. The chemical identity of the copolymer segments with the homopolymers phases improves the interfacial adhesion of the dispersed homopolymer and allows a finer dispersion during mixing [50]. Addition of 2% PS-r-PMMA to aPS27-co-aPS(NO2)73/PMMA blend solution was sufficient to saturate the interface and to create a mechanically stable membrane. Hence, the phase separation behavior of aPS27-co-aPS(NO2)73/PMMA blend solution with and without the addition of PS-r-PMMA, as the compatibilizer, was studied.

Fig. 7 shows the SEM micrographs of the cross sections of aPS27-co-aPS(NO2)73/PMMA/PS-r-PMMA (Fig. 7a) and aPS27-co-aPS(NO2)73/PMMA (Fig. 7b) membranes prepared from an NMP solution through immersion in a water coagulation bath. It can be seen that the membrane prepared from an aPS27-co-aPS(NO2)73/PMMA/PS-r-PMMA casting solution has a sponge-like structure with smaller thickness (40 μm) in comparison to the membrane without PS-r-PMMA (70 μm).

The copolymer is assumed to be located between the blend components leading to a coalescence between the PS and PMMA macromolecules, which increased the compatibility between the two polymers resulting in a polymeric blend with thermodynamic stability [50].

In this case, delayed demixing is usually observed with sponge-like and smaller thickness [51,52]. Kinetically, as discussed before, the film shrinks due to more solvent flowing out of the solution than non-solvent flowing into the solution. From another point of view, the presence of the copolymer increases the blend solution viscosity that also slows

down the diffusional exchange rate of the solvent (NMP) and non-solvent (water) during the membrane formation process, leading to a delayed demixing and suppressing the macrovoids formations [53].

3.2.4. Influence of the tacticity of the polymer

Atactic polystyrene can be precipitated from a casting solution by a liquid-liquid phase separation that comprises a porous sublayer that is dominated by cellular pores and/or macrovoids. On the other hand, semicrystalline polystyrenes could be precipitated from the casting solution either by liquid-liquid phase separation, or by a crystallization process (solid-liquid demixing), or even both. When the precipitation is slower due to a slow mass exchange, crystallization commences much earlier than liquid-liquid demixing. In these cases, the resulted membrane morphology is also composed of inter-linked crystalline particles [54].

In the preparation of membranes, via the immersion precipitation process, the selection of solvent/non-solvent plays an important role because it affects not only the kinetics of the pore growth but also the crystallization behavior of the polymer [47] [55]. Hence, the correlation between the modified semicrystalline polystyrene and the membrane morphology controlled by kinetic aspects was evaluated.

The HRSEM images for sPS60-co-sPS(SO3H)40/PMMA/PS-r-PMMA, sPS90-co-sPS(NO2)10/PMMA/PS-r-PMMA, and sPS81-co-sPS(Br)19/PMMA/PS-r-PMMA blends in NMP/water systems are illustrated in Fig. 8. It could be seen that different morphologies were produced mainly by liquid-liquid demixing, which was the predominantly observed process.

As can be seen in Fig. 8a, the system sPS60-co-sPS(SO3H)40/PMMA/PS-r-PMMA/NMP/water exhibited sponge-like structures, with a thickness of 80 μm . In contrast, the systems sPS81-co-sPS(Br)19/PMMA/PS-r-PMMA/NMP/water and sPS90-co-sPS(NO2)10/PMMA/PS-r-PMMA/NMP/water (Fig. 8b and c, respectively) exhibited a finger-like pores with large macrovoids sublayers gradually progressing throughout the cross-section of the membrane with thicknesses of 100 and 135 μm , respectively. The uniformity of the membrane cross-section implies that the interaction of sPS60-co-sPS(SO3H)40 with NMP is stronger due to the expected hydrogen bonding. A high degree of sulfonic group substitution at the sPS induces to strong interactions with the NMP solvent, which slows down the mass exchange rate between the solvent and the non-solvent and induced a delayed demixing, resulting in a sponge-like structure. The typical finger-like morphology obtained in the casting systems sPS81-co-sPS(Br)19/PMMA/PS-r-PMMA and sPS90-co-sPS(NO2)10/PMMA/PS-r-PMMA indicates a fast precipitation of the membrane (instantaneous demixing) due to the better affinity between the NMP and water. We can conclude that a high degree of polymers Fig. 6. Surface and cross-section of a membrane casted from aPS70-co-aPS(I)30/PMMA/NMP/water system, A and B respectively. As a comparison, image C is the surface of the original membrane based on aPS/PMMA/NMP/water system showing the surface pores.

Table 4

Hansen solubility parameter difference using the group molar contribution method between NMP and polymer, $\delta^*_1 - \delta^*_2$ NMP-polymer and polymer-non-solvent $\delta^*_1 - \delta^*_3$

polymer-non-solvent

[49].

Polymer $\delta^*_1 - \delta^*_2$ polymer-NMP

(MPa)^{1/2}

$\delta^*_1 - \delta^*_3$ polymer-water

(MPa)^{1/2}

aPS-co-PS(I)30 4.3 36.5

aPS 6.9 39.5

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substitution with hydrophilic functional groups plays an important role in the phase inversion immersion precipitation process, and therefore affects the resulted membrane morphology.

3.3. Permeation studies of the prepared membranes

The membrane properties such as hydrophilicity and surface pore size are those mainly determining the permeability of the membrane [56–58]. The obtained permeation results are supported by the respectively obtained morphologies of the prepared membranes. Fig. 9 exhibits the influence of the solvent type (DMF, NMP or dioxane) on the pure water flux of the membrane prepared from the different aPS/PMMA/solvent/water systems.

As could be seen, for all the three systems, the pure water flux increased while increasing the operating pressure. By using DMF as the membrane casting solvent, the membrane displays a higher pure water flux (990 L/m² h at 10 bar) as compared to the membrane that was casted using dioxane with a flux of pure water of 72 L/m² h at 10 bar. Such disclosure can be attributed to the different morphology of the membrane prepared from aPS/PMMA/ dioxane system as compared to ones prepared from aPS/PMMA/NMP and aPS/PMMA/DMF systems (see Section 3.2.1.). In the latter two membranes, finger-like porous sublayers and enlargement of macrovoids were observed, which are responsible for the high pure water flux values.

Figs. 10 and 11 exhibits the effect of the hydrophilic side groups on the pure water flux of aPS and sPS based copolymers, respectively. As can be seen in Fig. 10, the permeate flux of the control membrane system (i.e. aPS/PMMA/solvent/water) was 117 L/m² h at 10 bar, which is almost 5-folds lower than that of the membranes prepared from the casting solutions aPS27-co-aPS(NO₂)₇₃/PMMA/NMP/water Fig. 7. Cross section of membrane casted from aPS27-co-aPS(NO₂)₇₃/PMMA/NMP/water (A) and aPS27-co-PS(NO₂)₇₃/PMMA/PS-r-PMMA (B).

Fig. 8. Cross section of membranes casted from the sPS(100-m)-co-sPS(FG)_m/PMMA/NMP/water system. FG is the functional group and n, m are the degree of substitution. A= sPS60-co-sPS(SO₃H)₄₀; B= sPS81-co-sPS(Br)₁₉; C= sPS90-co-sPS(NO₂)₁₀.

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and aPS70-co-aPS(I)₃₀/PMMA/NMP/water (495 L/m² h and 550 L/m² h at 10 bar, respectively). These changes in permeate flux are in correspondence with the hydrophilic nature of the PS copolymer-based membranes. When the polymer is substituted by a large amount of highly polar groups, the polymer becomes more hydrophilic [59]. As can be seen, when the level of polar substituents increased at the PS side chains (73% nitro groups vs. 30% iodine groups), the polymer water solubility increased. In addition, the flux increased significantly when adding PS-r-PMMA to the blend solution. This is probably due to a surface segregation and local surface reorganization of the copolymer with the amphiphilic copolymers (aPS27-co-aPS(NO₂)₇₃) [60,61]. The membrane prepared from aPS27-co-aPS(NO₂)₇₃/PMMA/PS-r-PMMA/NMP/water system exhibited a flux of 767 L/m² h at 10 bar, which is the highest among all four membranes. This result also emphasizes that the designed modifications with the functional groups are able to improve the water flux of the membranes.

Fig. 11 shows the pure water flux of three membranes prepared from the copolymer-based sPS membranes. The membranes prepared from the sPS81-co-sPS(Br)₁₉/PMMA/PS-r-PMMA/NMP/water system, exhibited almost the same pure water flux as from the membrane prepared from the sPS90-co-sPS(NO₂)₁₀/PMMA/PS-r-PMMA/NMP/water system (3302 L/m² h at 10 bar and 1115 L/m² h at 10 bar, respec-

tively). The membrane prepared from sPS60-co-sPS(SO₃H)40/PMMA/PS-r-PMMA, exhibited a water flux of 250 L/m² h at 10 bar. Unexpectedly the membrane based on PS81-co-sPS(Br)19/PMMA/PS-r-PMMA shows an increased flux beyond 9 bar that isn't observed in the other two membranes and further studies are needed to understand this observation that was repeated three times. This pressure-flux behavior it is probably a result of flexible macrovoids that upon pressure allows the rapid flux through the membrane [9]. The observed water permeation results agreed in general with the morphologies shown in Fig. 8 (see Section 3.2.4.) indicating that the higher the membrane porosity and the membrane hydrophilicity, the higher the water flux. As compared to other membranes in the literature, it is interesting to point out that for a blended polyethersulfone/polysulfide amide (1/1 wt%) a flux of 244 L/m² h was obtained whereas for a polyvinyl chloride/polyvinyl formal (1/1 wt%) a maximum flux of 323 L/m² h was observed [62,63].

3.4. Antibacterial effect of the aPS membranes

The antibacterial activity of polymeric surfaces can be enhanced by specific chemical modifications with different active groups. The nature of the active groups determines the mechanism of the antimicrobial action, which can be bacteriostatic or bactericidal [8]. To evaluate the antibacterial activity of the partially modified PS, a membrane based on partially iodinated aPS, aPS70-co-aPS(I)30/PMMA, was chosen as the model membrane. In addition, to be able to compare our antibacterial results two additional membranes were used as blanks. An unmodified PS blended with PMMA (e.g., aPS/PMMA and a fully modified polyvinylphenol/PMMA. The reason we decide to use the PvPh/PMMA is due to its well know antimicrobial capacity [64].

The antifouling activity and performance of the aPS70-co-aPS(I)30/PMMA and PvPh/PMMA membranes were evaluated using two assays (i.e., static condition and flowing through systems) and compared to a control membranes made from aPS/PMMA.

The antibacterial abilities in static conditions were tested by the inhibition zone method on LB agar plates against E. coli strain S17-1. An inhibition clearing zone with a radius could be seen around the aPS70- Fig. 9. Effect of pressure on pure water flux in aPS/PMMA/solvent/water systems. Inset:

effect of the operation pressure on pure water flux between 0 and 10 bar. Fig. 10. Effect of pressure on pure water flux of aPS(100-m)-co-aPS(FG)m/PMMA/NMP/ water and control (aPS/PMMA) systems. FG is the functional group and m is the degree of substitution.

Fig. 11. Effect of pressure on water flux of sPS(100-m)-co-sPS(FG)m/PMMA/PS-r-PMMA/ NMP/water systems FG is the functional group and m is the degree of substitution.

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co-aPS(I)30/PMMA and PvPh/PMMA membranes samples after 72 h proving the antibacterial influence as compared to the control aPS/PMMA based membrane. Following this experiment, the evaluation of the above was further visualized by Syto9 and PI staining in in CLSM (Fig. 12).

CLSM micrographs of the aPS70-co-aPS(I)30/PMMA, PvPh/PMMA and aPS/PMMA depicted a typical biofilm grown on the membranes after 72 h of incubation.

From Fig. 12A and B, relatively weak green fluorescence intensity was observed from the aPS70-co-aPS(I)30/PMMA and PvPh/PMMA based membrane as compared to the aPS/PMMA (Fig. 12C). It appears that the bacterial population is somewhat reduced on the modified

surfaces, which indicate less adhesion of the *E. coli*. At the same time, higher biomass of dead cells (red fluorescence of PI staining in Fig.12E and 12F) could be seen on the modified surfaces emphasizing that most of the attached cells are dead. Thus, these results indicated not only that membranes based aPS70-co-aPS(I)30 copolymer and PvPh exhibited satisfying antibacterial capability which is more effective than neat aPS/PMMA membrane but also confirmed that the activity is mainly through the presence of pendant iodine and hydroxyl groups (phenol), as expected.

Another set of experiments was performed in a cross-flow mode with continuous feed with *P. putida* S-12 as a model for bacterium for 72 h, following visualization and analysis by HRSEM.

Fig. 13 shows HRSEM images of the aPS70-co-aPS(I)30/PMMA, PvPh/PMMA, and aPS/PMMA based membranes, before (first row for comparison) and after continuous flow (second and third row, magnification $\tilde{\text{A}}-5$ K and $\tilde{\text{A}}-10$ K, respectively). As can be seen, after 72 h in flow conditions, all the membranes produced a biofilm of *P. putida*. A developed biofilm was seen on the neat aPS/PMMA (Fig. 13E and H), displaying clusters and almost full surface coverage while on the modified membranes several discrete areas covered with adhered bacteria. The aPS-co-aPS(I)30/PMMA membrane surface (Fig. 13D and G) showed initial stages of biofilm development, covered in a monolayer structure while images of the PvPh/PMMA (Fig. 13F and I) showed mostly sporadically dispersed bacteria. The difference between these results can be explained by the degree of rejection forces against bacteria adherence. The attachment of microbial cells depends on the hydrophilic nature of the surface, which can be controlled by the polymer chemistry. We see that 30% degree of iodination of aPS allows to obtain a good antibacterial membrane. Clearly, a higher degree of substitution is needed to achieve an excellent membrane.

Both static and cross-flow experiments highlight the potential of the modified PS based membranes in water treatment.

Upper panels: membrane before the cross-flow experiment (A, B and C). Two other panels: membranes after exposure to cross flow (D, E, F; magnification x5K and G, H, I; magnification $\tilde{\text{A}}-10$ K). All the images are top views.

4. Conclusions

For the first time, a research study related to the formation of filtration membranes made of functionalized polystyrene by the immersion precipitation technique has been performed. There was an effort to develop new and improved functional membranes, which fulfill the filtration requirements and minimize the devastating effect of biofouling. The final morphology of the membranes was governed by a trade-off between thermodynamic and kinetic aspects. In this research, the relationship between the membrane morphology and the performance of the polystyrene membrane was presented.

Membranes based on atactic polymers were analyzed by the prediction of the thermodynamic parameter, which is the HSP difference between the binary systems based on Hoy's method. This method leads to a good correlation between the membranes performances to their morphology visualized by SEM. By changing the solution casting parameters, such as the type of solvent/non-solvent pair, the composition of coagulation bath, functional group and copolymer addition, the morphology and therefore the permeability changed. As for the Fig. 12. CLSM micrographs of the antibacterial activity of each membrane against *E. coli* after 72 h. The left column represents aPS(I)30/PMMA based membrane, the middle column represent PvPh /PMMA based membrane and the right represent aPS /PMMA based membrane. The total cells (live and dead) are stained green, while the dead cells are stained red. (For

interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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crystalline polystyrene, the analysis was based only on kinetics effects (mass transfer). Moreover, functionalized membranes based on sPS possess higher fluxes with good mechanical and chemical stabilities. Furthermore, aPS-co-aPS(I)30/PMMA was examined as a model membrane for the antibacterial assays using static and cross flow experiments. Both the static and flow-through systems, supported by microscopic visualization, highlight the potential of aPS-co-aPS(I)30/PMMA membrane in controlling and hindering membrane biofouling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2017.12.024>.

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