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www.elsevier.com/locate/memsci

PII: S0376-7388(15)00367-1
DOI: <http://dx.doi.org/10.1016/j.memsci.2015.04.036>
Reference: MEMSCI13646

To appear in: *Journal of Membrane Science*

Cite this article as: Poornima Madhavan, Rachid Sougrat, Ali Reza Behzad, Klaus-Viktor Peinemann, Suzana P. Nunes, Ionic Liquids As Self-Assembly Guide for the Formation of Nanostructured Block Copolymer Membranes, *Journal of Membrane Science*, <http://dx.doi.org/10.1016/j.memsci.2015.04.036>

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Ionic Liquids As Self-Assembly Guide for the Formation of Nanostructured Block Copolymer Membranes

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Accepted manuscript

Abstract:

Nanostructured block copolymer membranes were manufactured by water induced phase inversion, using ionic liquids (ILs) as cosolvents. The effect of ionic liquids on the morphology was investigated, by using polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-PV4P) diblock as membrane copolymer matrix and imidazolium and pyridinium based ILs. The effect of IL concentration and chemical composition was evident with particular interaction with P4VP blocks. The order of block copolymer/ILs solutions previous to the membrane casting was confirmed by cryo scanning electron microscopy and the morphologies of the manufactured nanostructured membranes were characterized by transmission and scanning electron microscopy. Non-protic ionic liquids facilitate the formation of hexagonal nanoporous block copolymer structure, while protic ILs led to a lamella-structured membrane. The rheology of the IL/block copolymer solutions was investigated, evaluating the storage and loss moduli. Most membranes prepared with ionic liquid had higher water flux than pure block copolymer membranes without additives.

Key words: Ionic Liquid, PS-*b*-P4VP, self-assembly, phase separation, nanostructured membrane

Introduction

Block copolymers (BCP) are an attractive class of material that can self-assemble into various nanoscale structures. They have been combined with additives such as salts and nanoparticles to provide a variety of self assembled morphologies [1-3]. The micellization of block copolymers in solvents has been well investigated. Routes to tune the morphologies of block copolymer include chemical modification [4] and the use of additives such as metal salts [5, 6] homopolymer [7], surfactants [8] and H-bonding organic molecules [9, 10]. Ionic liquids (ILs) have been also reported to influence the bulk morphology of block copolymers [11-14]. ILs have unique characteristics compared to traditional solvents with negligible vapor pressure, recyclability, non-flammability, thermal and chemical stability [15] and also can lead to specific interaction with polymeric segments, being considered as “designers solvent” [16]. ILs have been reported to influence the morphology of block copolymers in solution or in the bulk and dense films. He et al. [17] investigated the micellization of poly(1,2-butadiene)-block-PEO diblock copolymers (PB-*b*-PEO) in 1-butyl-3-methylimidazolium hexafluoro phosphate [B₄MIM]PF₆. Gwee et al. [18] showed that the morphology of poly(styrene-*b*-methyl methacrylate) (SbMMA) can be changed by using different concentrations of IL, going from lamellae to cylindrical microdomains. Virgili et al. [14, 19, 20] studied the phase behavior of polystyrene-*b*-poly(2-vinylpyridine) copolymers in a selective ionic liquid such as imidazolium bis(trifluoromethane) sulfonimide ([IM][TFSI]). They observed ordered microstructures corresponding to lamellae, hexagonally close-packed cylinders, body-centered cubic, and face-centered cubic oriented micelles in the bulk or in thin dense films. A mixed behavior was observed for [IM][TFSI] as selective solvent

toward P2VP blocks: at high polymer concentration, it acted similar to a salt with induced pyridine-metal ion complexation, which results in an increase of the glass transition temperature (T_g), while at intermediate block copolymer concentrations, it acted more like a plasticizer, decreasing T_g .

In membrane technology ionic liquids have been considered before for other reasons. First there is a need for substituting well-established solvents for membrane manufacture to turn the manufacture process more environmentally friendly [21, 22]. Xing et al. [23, 24] were the first to report the fabrication of cellulose acetate membranes using ionic liquids as casting solvents. A second reason to integrate ionic liquids in membrane systems is their strong interaction with CO_2 , which leads to high gas selectivity. In this case the ionic liquid has been supported in porous membranes [25] or polymerized to constitute a gas separation membrane [26, 27]. Ionic liquids have been also reported to facilitated bioconversion processes in combination with membrane separation technology like pervaporation [28].

In this work we use ionic liquids for the first time to tune the pore morphology of nanostructured block copolymer membranes, produced by self-assembly and water induced phase separation. The general idea of combining block copolymer self-assembly and phase inversion to manufacture isoporous membranes was proposed and demonstrated by Peinemann et al. [29] using polystyrene-*b*-poly (4-vinyl pyridine) casting solutions in dimethylformamide (DMF) and tetrahydrofuran (THF). However this initially proposed copolymer/solvent system is sensitive to minor changes of molecular weight. Only with better understanding of the mechanism of pore formation based on micelle supramolecular assembly in solution [30] it was possible to find alternative

solvent mixtures, leading to stricter and more reproducible morphology control. This could be achieved for instance with the addition of copper acetate [30, 31], ternary solvent mixtures with dioxane [32, 33] and hydrogen bond forming molecules [34]. The disclosure of the mechanism facilitated the application of this method extended to other systems, containing for instance triblock copolymers [35, 36]. Ionic liquids have not been explored so far as additive for this application. We propose to use ionic liquids to guide the morphology in solution as a result of block-solvent thermodynamic interactions, coulombic and hydrogen-bond interactions mainly between ionic liquids and pyridine. By immersion in water, the solvent non-solvent (water) exchange should kinetically trap the order to manufacture asymmetric porous membranes.

EXPERIMENTAL SECTION

Materials

Polystyrene-*b*-poly (4-vinylpyridine) block copolymer P10900-S4VP (PS-*b*-P4VP 188,000-*b*-64,000 g/mol) was purchased from Polymer Source, Inc., Canada. Dimethyl formamide (DMF) and Tetrahydrofuran (THF) was supplied by Fisher Scientific. 1-methyl imidazole and sulphuric acid were purchased from Sigma Aldrich. ILs such as 1-Butyl-4-methylpyridinium tetrafluoroborate ([B4MPy][BF₄]) (≥97% purity), N-Butyl-3-methylpyridinium trifluoromethanesulfonate ([B3MPy][TFMS]) (98% purity), 1-Ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM][BF₄]) (≥97% purity), 1-Butyl-3-methylimidazolium tetrafluoroborate ([B3MIM][BF₄]) (≥98% purity) were purchased from Sigma Aldrich and Merck; they were used as received. Imidazolium bistrifluoro methane sulphonimide ([IM][TFSI]) and 1-methylimidazolium bisulfate ([HMIM][HSO₄]) were

synthesized by previously reported procedure [14, 37]. The monomer Imidazole was purified by sublimation under vacuum before the [IM][TFSI] was prepared.

Membrane Preparation

All the membranes were prepared using 17.4 to 18.0 wt% block copolymer solutions in a mixture of IL/ DMF/ THF. Different types of ionic liquids were mixed to the solution and stirred at room temperature for 24 h. The block copolymer solutions were cast on a glass plate using a casting knife with 200 μm air gap. The solvent was allowed to evaporate for different times and the films were immersed in water at room temperature.

ATR-FTIR

Perkin-Elmer 100 ATR-FTIR spectrometer was used for recording the IR spectra of block copolymer membrane. Data were collected over 16 scans with a resolution of 4 cm^{-1} . The ATR-FTIR measurements were made at room temperature, using an ATR unit at a nominal incident angle of 45°.

Transmission Electron Microscopy

The cross section of the membranes was imaged using TEM. All the membranes were embedded in a low-viscosity epoxy resin (Agar R1165) and cured at 60°C for 24 h. Ultrathin sections (80 nm) were prepared with an ultramicrotome (Leica EM UC6) and placed on a carbon-coated copper grid. Images were obtained on a Tecnai 12 (FEI) operating at 120 keV. Most samples were stained with RuO₄ vapors before imaging to increase contrast. An additional membrane prepared from solutions containing [B3MIM][BF₄] was stained with methyl iodide (CH₃I). TEM tomography was performed for one of the samples.

Field Emission Scanning Electron Microscopy (FESEM)

Micrographs of membranes were obtained using a FEI Quanta 600 Field Emission Scanning Electron Microscope. Imaging was carried out at 5 kV with a working distance of 10 mm. The membrane samples were mounted on aluminum stubs using aluminum tape and Au coated before imaging for 45 s at 20mA.

Cryo- Field Emission Scanning Electron Microscopy:

The low temperature FESEM was performed using a FEI Nova Nano 630 SEM with a field emission electron source through the lens electron detector. A small amount of block copolymer /ILs solution mixture was placed between two rivets and was then cryo quenched by rapidly plunging into liquid nitrogen at -180°C . The sample was then transferred to a SEM cryo- stage, which was held at -115°C . Then the sample was sputter coated with 5 nm thick platinum in an argon atmosphere inside the cold chamber and high resolution FESEM images were captured. Detailed procedure reported elsewhere [32, 38].

Rheology

Rheological measurements were carried out at 25°C with AR- 1500 ES Rheometer with cone and plate fixture of diameter 25 mm and a cone angle of 1° . The rheology measurements were performed in the linear viscoelastic region. The range of shear rates used for the viscosity measurements is $10\text{-}1000\text{ s}^{-1}$. All tested solutions had 17.4 to 18 wt % copolymer. Except for solutions containing [IM][TFSI], all solutions had 3.8

wt % ionic liquid/ 31 wt% THF/ 48 wt% DMF. In the case of [IM][TFSI] and [HMIM][HSO₄] the copolymer was dissolved in 1.2 wt % IL/ 32 wt% THF/ 49 wt% DMF. Larger [IM][TFSI] concentration led to gelation. Larger concentration of [HMIM][HSO₄] led to phase separation.

Water Flux Measurement

Pure water fluxes of membranes were measured using a stirred Amicon dead-end ultrafiltration cell at 1 bar. The membranes for flux measurements were prepared on a nonwoven polyester support. Effective membrane area was 5 cm². Deionized water was used for water flux measurements.

Results and Discussion

Membrane preparation

Different types of ILs shown in Scheme 1 were added as an additive/cosolvent to guide the assembly of PS-*b*-P4VP copolymers in THF/DMF solutions. When used as casting solutions for the manufacture of membranes by phase inversion in water baths, no regular pore structures were observed with the 188,000-*b*-64,000 g/mol PS-*b*-P4VP without addition of ILs. The ILs evaluated so far strongly interact with the copolymer, but are not capable to dissolve PS-*b*-P4VP with Mw.188,000-*b*-64,000 g/mol as single solvent. Gelation or phase separation was observed in some cases even at IL concentrations higher than used here. On the other hand we observe that even small amounts of ILs with different chemical structures can be very useful to tune the membrane morphology. The block copolymer solutions were cast on glass plates and allowed to evaporate in different time periods before immersion in water. The incipient

membrane on the glass plate was immersed in water. During this process solvent-water exchange occurs, the solvent and ILs migrate from the block copolymer solution to the water bath. Water penetrates the solution, leading to an unstable thermodynamic condition. The introduction of water abruptly decreases the solvent quality and kinetically traps the order previously achieved in solution, leading to the formation of smaller regular pores at the membrane top layer. Microphase separation proceeds in deeper layers. The phase with lower concentration of copolymer leads to pore formation with increasing size across the membrane. An asymmetric structure is finally observed. The combination of a more classical phase separation mechanism and copolymer self-assembly has been discussed in previous publications without the presence of ionic liquids [30-34].

(Scheme 1)

The addition of ionic liquids affected the final membrane morphology. Being soluble in water, the IL is washed out. No IL residue was detected by FTIR spectroscopy after washing with water for 3-4 times repeatedly during 24 h and dried.

Membrane Morphology

We used protic ([IM][TFSI], [HMIM][HSO₄]) and aprotic ([B4MPy][BF₄], [B3MPy][TFMS], [EMIM][BF₄], [B3MIM][BF₄]) ionic liquids as additives. Figure 1 shows membranes prepared with various concentrations of the aprotic [B4MPy][BF₄]. Figure 1a is the control, PS-*b*-P4VP membrane manufactured from solutions in DMF/THF without ionic liquid. Although Peinemann et al [29] reported isoporous membranes obtained from

PS-*b*-P4VP in DMF/THF an analogous ordered structure could not be obtained with other copolymer molecular weights investigated by our group, including the 188,000-*b*-64,000 copolymer used in this work. As the IL concentration increases from 1.8 wt% to 5.1 wt% (Figure 2 b-d) the morphology changes. Solutions containing 3.8 wt% IL have an optimized pore structure (Figure 1c). With further IL concentration increase to 5.1% the pores become elongated; 1.8 wt % IL facilitates the micelle self-assembly but was not enough to induce the needed order. This indicates that the concentration of [B4MPy][BF₄] contents plays a vital role in the final membrane morphology.

We have earlier explained the formation of block copolymer membranes from PS-*b*-P4VP solutions in selective solvents (THF/DMF) with complexing salts (Cu²⁺). It starts with the copolymer micellization with an inner core of PS block and P4VP block as corona, which strongly interacts with the dissolved cation [31]. A supramolecular assembly of block copolymer micelles is responsible for the final membrane morphology in the top layer of the membranes. In this work the IL also preferentially interacts with the pyridine blocks. The polar [B4MPy][BF₄] solvates the basic nitrogen atoms of pyridine, keeping the micelles formed in solution intact in a hexagonal arrangement, which leads to the ordered membrane pore structure.

(Figure 1)

(Figure 2)

To study the effect of evaporation time during the membrane formation, the membranes were prepared with 3.8 wt % [B4MPy][BF₄] with various evaporation times ranging from 0 s to 60 s respectively. The resulting FESEM images are shown in Figure 2. The most regular pores were obtained with 20-30 s (Fig. 2b) evaporation time. Longer evaporation led to heterogeneous morphology.

(Figure 3)

Similarly to [B4MPy][BF₄], we tested ILs with a different substituted pyridinium, [B3MPy][TFMS] and different imidazolium functionalizations as cation, [EMIM][BF₄], [B3MIM][BF₄], all aprotics. The comparison for two concentrations (1.8 and 3.8 wt %) can be seen also in Figure 3. When 3.8 wt% was added, all ILs referred in Figure 3 led to ordered pores tending to hexagonal pore geometry. The image for [B3MIM][BF₄] shows slightly better order (Figure 3b). [EMIM][BF₄] led to larger pores (Figure 3a). The most evident difference could be seen in Fig. 3c with addition of 1.8 wt% [B3MPy][TFMS], which has a different anion than the other ILs in Figure 3. While BF₄⁻ is completely symmetric, TFMS is an asymmetric anion. Also the cation, B3MPy, is less symmetric than B4MPy.

(Figure 4)

This shows that all the above aprotic ILs having both the pyridinium and imidazolium cation group favor the formation of hexagonal pores during the membrane preparation if the IL concentration is high enough. However when the protic ionic liquids, [IM][TFSI] and [HMIM][HSO₄], were added to the block copolymer solution, only lamellar

morphologies were observed, for all investigated IL concentrations (0.6-1.2 wt %) as seen in Figure 4 (a-d). Solutions of poly(styrene-block-2-vinylpyridine) copolymer in [IM][TFSI] have been reported to have lamellar geometry, when studied by small-angle X-ray scattering (SAXS) [14, 19, 20]. A large change in the domain spacing upon addition of a small amount of ionic liquid has been detected. [IM][TFSI] selectively solvates the PVP block. The imidazolium group interacts with PVP and protonates it, promoting strong interactions between protonated 2VP moieties and the TFSI anion. It is clear that the [IM] [TFSI] IL behaves both as a solvent and salt. [HMIM][HSO₄], another protic IL, led also to a lamellar morphology (Figure 4d) similar to [IM][TFSI]. The interactions in the case of protic ionic liquids were strong enough to promote macroscopic phase separation ([HMIM][HSO₄]) at high IL concentration. For all other ILs both the imidazolium group and the pyridinium groups are non protic, apparently with weaker interaction with the P4VP blocks.

To get further insight into the effect of ILs on final membrane morphological details, we investigated the block copolymer /ILs solutions by cryo scanning electron microscopy. Figure 5 shows the cryo FESEM images of block copolymer solutions in DMF/THF, containing different ILs. We have previously demonstrated how micelles self-assemble in solution prior to immersion in water [20] for membrane formation. The cryo FESEM image of the solutions clearly depicts the spherical micelle formation and their ordering pattern in the solution state. Figure 5 shows a very well ordered pattern of micelles for the ([B4MPy] [BF₄])/ block copolymer solution, which directs the final membrane morphology into the hexagonal ordered porous structure shown in Figure 2. In the case

of ([IM][TFSI])/ block copolymer solutions the spherical micelles form strings, which leads to a lamellar morphology after the phase inversion in water as in Figure 4.

(Figure 5)

(Figure 6)

Membrane cross sections were microtomed and imaged using TEM, the cross sectional TEM images of all ILs/ block copolymer membranes are shown in Figure 6. For [IM][TFSI], lamellar or cylindrical arrangements are clearly seen but the general order is smaller. The best order is seen by TEM for [B3MIM][BF4]. However cylindrical or lamellar structures are observed apparently parallel to the membrane surface. This would not be consistent with the regular pores imaged in Figure 3b. We performed therefore the TEM tomography shown in Figure 7. By tilting the membrane slice, we see that they are rather worm-like with an arrangement, which leads to the pore formation on the surface. This morphology can be also well correlated to the order observed in solution, imaged by cryo microscopy and shown in Figure 5. The membrane has high water flux, as shown in Table 1, again demonstrating high porosity. RuO₄ increases the contrast and it is known to stain both PS and P4VP [39, 40]. By taking into account that P4VP is the shorter block (PS 188,000 g/mol, P4VP 64,000 g/mol) the darker regions in Figure 6 should correspond to P4VP. For [B3MIM][BF4] the TEM was repeated, staining with CH₃I, which preferentially stains only P4VP. A higher

magnification of the CH_3I stained image is shown in Figure 6, revealing areas with brighter PS cores surrounded by darker P4VP coronas. The micelles assemble into strings with cores partially merged into the cylindrical or worm-like structures seen also with RuO_4 staining.

(Figure 7)

The morphological analysis proves that ILs chemical structure, particularly its capability of forming hydrogen bonds or protonating pyridine, and the added concentration play important roles in the self-assembly and membrane formation.

A simplistic approach would be the estimation of solubility parameters, in analogy to organic solvents. For instance for $[\text{B3MIM}][\text{BF}_4]$ a solubility parameter of $16.2 \text{ cal}^{0.5} \text{ cm}^{-1.5}$ has been estimated by Swiderski et al. [41], placed between water $23.4 \text{ cal}^{0.5} \text{ cm}^{-1.5}$ and THF $9.1 \text{ cal}^{0.5} \text{ cm}^{-1.5}$. However the solubility parameter alone might be oversimplified, since it does not take into consideration strong directional interactions such as coulombic, hydrogen-bonding and π - π interactions, which are important for ionic liquids and can contribute to structure-forming solvation and self-assembly. Protic IL can even protonate pyridine. The anions can influence in different extents. BF_4 anion is known to have strong hydrogen bond acceptor ability, low polarizability and has the highest symmetry of all IL anions investigated here.

Rheology of block copolymer solution

In order to better understand the effect of the IL on the final membrane morphology, the rheological behavior of IL/ block copolymer solutions was investigated.

The rheology of ionic liquids like [B3MIM][BF₄] or [B3MIM][Cl] in DMF solutions (without copolymer) was investigated by Wang et al. [42] and by Attri et al. [43]. Negative excess molar volumes have been detected for [B3MIM][BF₄], suggesting that effective packing and attractive interactions are present. DMF has resonance structures characterized by a negative pole in the oxygen atom, which make it a very good hydrogen bond acceptor. Hydrogen bond can be formed with the alkyl chain IL cation. Furthermore ion-dipole interactions between DMF and the [B3MIM][BF₄] ions are also possible. Depending on the IL concentration the hydrogen bonds between [B3MIM][BF₄] and DMF becomes less relevant. At high [B3MIM][BF₄] concentration self-association through hydrogen bonding or ion-ion interaction can also take place.

Pyridine is also a good hydrogen bond acceptor and strongly interacts with hydrogen bond-forming IL cations, particularly those with protic character. Figure 8 shows how the viscosity of 17.4 wt % PS-*b*-P4VP copolymer solutions in 31 wt% THF and 48 wt% DMF changes with addition of 3.8 wt% ionic liquids and with shear rate. The effect of different ILs is compared. Except for [HMIM][HSO₄], the addition of IL increases the viscosity at low shear rates. Turbidity was observed for solutions with [HMIM][HSO₄] in this concentration range, indicating that phase separation takes place, explaining the low viscosity. All solutions had a shear-thinning behavior. For the block copolymer sample without IL, an accentuated viscosity decay occurs already below 20 s⁻¹ and becomes practically constant until 200 s⁻¹, passing through an almost Newtonian regime, probably corresponding to the flow of disconnected spherical micelles. The viscosity at low shear

rate is highly influenced by the soft interaction between micelle coronas. Higher viscosity values in the presence of IL indicate that the ILs improves the linking between the crew cut micelles, which are formed in DMF/THF. The shear thinning at higher shear rate values might be more related to micelle deformation and alignment under stress.

Higher viscosity than solutions without IL indicates a stronger connectivity between micelles, favored by stronger interaction between IL and pyridine.

Among solutions containing aprotic ILs, the largest viscosity was measured with addition of [B3MIM][BF₄]. At high shear rates the viscosity difference between solutions containing aprotic ILs is small. A clear difference was observed when measuring the storage and loss moduli as a function of angular frequency or oscillation strain (Figure 9). Particularly the storage moduli of solutions with [B3MIM][BF₄] and [B3MPy][TFMS] are more than 10-fold larger than that of solutions with [EMIM][BF₄] or [B4MPy][BF₄]. Figure 10 shows analogous curves for storage and loss moduli of solutions without ILs or with protic ILs. The storage modulus for solutions without IL is similar to that with [B4MPy][BF₄]. For all systems shown in Figure 9 and for the system without IL the storage modulus was larger than the loss modulus, at least in angular frequencies up to 200 rad s⁻¹, indicating high elastic contribution. For [B3MIM][BF₄] and [B3MPy][TFMS] the storage modulus remain larger than the loss in all investigated angular frequency range, indicating a strong elastic contribution and a stable tridimensional micelle network.

We recently reported [34] a rheological investigation proposing how curves of storage and loss moduli could be correlated to intermicellar connectivity. High storage modulus values are related to strongly connected micelles, forming a gel-like tridimensional network, similar to what is observed for solutions with [B3MIM][BF₄] and [B3MPy][TFMS]. At high angular frequency, the micelle network disrupts and the micelles align to the shear direction, reducing the storage modulus to values similar to or smaller than the loss modulus. The gel behaves then like a fluid.

(Figure 8)

(Figure 9)

(Figure 10)

Solutions with protic ionic liquids with similar concentrations have much lower storage moduli (<20 Pa). The storage modulus decreases even more with angular frequency and becomes smaller than the loss modulus between 3 and 10 rad s⁻¹. For these systems turbidity started to be observed at this IL concentration. This is an indication of macrophase separation. Homogeneous membranes could be prepared only with solutions containing up to 1.2 wt % IL. Solutions with 1.2 wt % [IM][TFSI] had storage modulus close to 100 Pa at low angular frequency range, higher than the 3.8 wt% solution. The strong interaction between [IM][TFSI] and the copolymer probably might lead to aggregation and further to phase separation. Phase separation with a copolymer concentrated phase dispersed in a diluted phase (rich in solvents) would explain the low

storage moduli. Hoarfros et al [44, 45] reported that [IM][TFSI] highly protonates the P2VP block when the PS-*b*-P2VP mixed with [IM][TFSI]. A strong interaction is expected to take place also with the P4VP block in this work, since P4VP is also basic in nature and susceptible to protonation. If the [IM][TFSI] concentration is low aggregation is moderate. The micelles assembly in strings, worm-like or lamellar structures in solution, as shown in cryo images depicted in Figure 5. With immersion in water the lamella morphology is kinetically trapped giving rise to the membranes shown in Figure 4.

The protic ionic liquid [HMIM][HSO₄] also led to membranes with lamellar structures, with strong protonation of pyridine groups in the copolymer as in the case of [IM][TFSI]. The loss modulus becomes higher than the storage one already at 3 rad s⁻¹ angular frequency, as shown in Figure 10, indicating a liquid-like behavior. Probably the addition of [HMIM][HSO₄] led also to the formation of micelle aggregates, which flow under conditions close to complete phase separation.

In order to understand the reasons for exceptionally high values of viscosity and storage modulus for solutions with aprotic [B3MIM][BF₄] we take into consideration previous investigations reported for [B3MIM][BF₄] and pyridine single molecules targeting extraction application. Beside hydrogen bonds, coulombic interactions, charge distribution and steric factors are also relevant. Both cations and anions have to be taken in account. Lü et al. [46] investigated the interactions between 1-butyl-3-methylimidazolium tetrafluoroborate ([B3MIM]⁺), [BF₄]⁻ and pyridine in pyridine/hexane solutions by means of computational analysis using density functional calculations. They considered π (imidazolium) – π (pyridine) interactions with the 2 rings parallel to

each other, hydrogen bonds between [B3MIM] [BF₄]-pyridine and partial charge transfer, analyzing the maximum electron density (NBO, natural bond orbital analysis) of [B3MIM]⁺, [BF₄]⁻, pyridine as isolated unities and as interactive [B3MIM]⁺ [BF₄]⁻-pyridine system. They found out that for [B3MIM]⁺ and pyridine rings σ -bonds are formed through overlap of five hybridization orbitals of carbon and nitrogen atoms and delocalized bonds are formed through overlap of the p-orbitals perpendicular to the rings. They calculated the extent of electron delocalization from donors to acceptors as 15.40 kcal/mol in [B3MIM][BF₄]-pyridine. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are directly related to ionization potential and electron affinity respectively. The LUMO indicates the capability of a ligand to accept electrons from a donor. For [B3MIM][BF₄] HOMO was estimated to be that of occupied p orbitals of F atoms in [BF₄]⁻ and the LUMO was estimated to be the π^* orbitals of imidazolium ring. The HOMO of [B3MIM][BF₄]-pyridine is mainly that of pyridine ring, while the LUMO is that of delocalized orbitals of imidazolium ring. They demonstrate that there is no π - π interaction between imidazolium ring and pyridine ring. Pyridine N $\cdots$ H hydrogen bonds are on the other hand very important for the strong interactions between [B3MIM][BF₄] and pyridine. There are nine possible hydrogen bonds for [B3MIM] [BF₄]-pyridine. The short estimated distances between fluorine and hydrogen atoms indicate also strong H bonds, which involve the anion [BF₄]⁻ as link between pyridine and the ionic liquid cation. The estimated interaction energy reported for [B3MIM] [BF₄]-pyridine was 75.9 kJ/mol. The discussion proposed by Lü et al. [46] could be extended to our case to explain the interactions between the pyridine groups of the P4VP copolymer block with [B3MIM] [BF₄], guiding morphology and part of the

rheological behavior. Anantharaj and Banerjee [47] used mainly HOMO-LUMO energies and the corresponding energy gaps to understand the interaction and availability of ionic liquids to form complexes. Large HOMO-LUMO energy gap implies high stability, being less prone to charge transfer when forming complexes. High IL HOMO indicates willingness in interacting for instance with the external pyridine ring.

Hunt [48] used density functional theory to compare viscosities between [B3MIM]-based compounds and their analog 1-butyl-2,3-dimethyl-imidazolium [BDMIM]-based ionic liquids (not used in our work), which has an additional methyl group and even higher viscosity. She found out that comparisons between molecular orbitals and differences in electronic densities were not enough and steric factors had to be taken into consideration. ILs usually form a number of stable conformers, frustrating crystal packing, with larger anions forming a larger number of stable ion-pair structures. This characteristic is less pronounced with compact anions like [BF₄]. On the other hand, analogously to the arguments used by Hunt [48] for comparing [B3MIM] and [BDMIM], the large butyl substitution in the imidazole ring might reduce ion pair configurational variation, sterically hampering rotation, at least compared to [EMIM][BF₄], the ethyl-substituted analog and maybe also compared to other ionic liquids. Fewer stable conformers are possible if rotation is low, leading to lower entropy and a more regular arrangement of ions. This might also facilitate the alkyl chain association, increase viscosity and favor the order observed by TEM in Figures 6 and 7. Beside the specific interactions discussed above and the steric factors, the tetrahedral symmetry of BF₄⁻ favors the tridimensional intermicelle network connectivity, more than other anions used in this work, which are asymmetric and less compact.

Water flux measurements

Table 1 reports the water flux of membranes prepared with different casting solutions. Water flux measurements were carried out using an Amicon cell at 1 bar N₂ feed pressure. All the membranes have high water flux, ranging from 450 to 1800 L m⁻² h⁻¹ bar⁻¹. IL/ block copolymer membranes having hexagonal pores structure have higher water flux than block copolymer membranes prepared without IL. The [IM] [TFSI]/block copolymer membrane with lamellar structure and low porosity, as shown in Figure 4, has low water flux compared to other membranes and a molecular weight cut-off of 50 kg/mol with more than 95 % retention of 150 kg/mol polyethylene glycol (PEG). Membranes prepared without IL rejected 55 wt% of the same molecular weight PEG; membranes with other ILs rejected 61-66 wt% 150 kg/mol PEG.

Table 1 Water flux and structure arrangements of membranes prepared from PS-*b*-P4VP Solutions with various ILs

Ionic Liquids	Membrane morphology	Water flux (L m ⁻² h ⁻¹ bar ⁻¹)
No IL	Random spherical, low porosity	1110
[B4MPy][BF ₄]	Spherical, hexagonal, highly porous	1300
[B3MPy][TFMS]	Spherical hexagonal, highly porous	1600
[EMIM][BF ₄]	Spherical hexagonal, highly porous	1120
[B3MIM][BF ₄]	Spherical hexagonal, highly porous	1800
[IM][TFSI]	Lamella	450
[HMIM][HSO ₄]	Lamella	550

Conclusion

We demonstrate the use of ionic liquids for the self-assembly of block copolymers and their application for the manufacture of membrane with tuned porous nanostructured morphology. Both substituted pyridinium and imidazolium-based ILs induce hexagonal cylindrical porous morphology. The highly protic ILs preferentially solvate P4VP blocks and direct the micelle ordering during the membrane formation, forming lamellar structure. The morphology in solution was imaged by cryo scanning electron microscopy. The solution viscosity, storage and loss moduli were measured for PS-*b*-P4VP solutions containing different protic and aprotic ionic liquids. [B3MIM][BF₄] solutions had the largest viscosity. Beside the interaction between imidazolium, BF₄ and pyridine the high viscosity was explained by taking in account steric effects. High water flux of these membranes reflects the high porosity. Particularly high order was observed for solutions with [B4MPy][BF₄] by cryo microscopy, leading to porous membranes with hexagonal pore distribution. The [B4MPy][BF₄] solution had a strong gel-like behavior. Low water flux was observed for membranes prepared from protic

[IM][TFSI]/block copolymer solutions, which have a lamellar structure with strong connection between lamellae.

Acknowledgements:

This work was sponsored by King Abdullah University of Science and Technology (KAUST). The research activities are partially integrated in the Competitive Research Grant program (CRG2).

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Figure Captions

Scheme 1. Chemical structures of the aprotics ([B3MIM][BF₄], [EMIM][BF₄], [B4MPy][BF₄], [B3MPy][TFMS]) and protic ([IM][TFSI], [HMIM][HSO₄]) ILs used for membrane preparation.

Figure 1. Membranes prepared from (a) 18 wt% PS-*b*-P4VP solutions in 32 wt% THF/ 50 wt% DMF; (b) 18 % PS-*b*-P4VP solutions in 1.8 wt% [B4MPy][BF₄]/ 31 wt% THF/ 49 wt% DMF; (c) 17.4 wt % PS-*b*-P4VP solutions in 3.8 wt% [B4MPy][BF₄]/ 31 wt% THF/ 48 wt% DMF; (d) 17.4 wt % PS-*b*-P4VP solutions in 5.1 wt% [B4MPy][BF₄]/ 30 wt % THF/ 47 wt % DMF. The evaporation time was 20 s.

Figure 2. Membranes from 17.4 wt % PS-*b*-P4VP solutions in 31 wt% THF/ 48. wt% DMF with 3.8 wt % [B4MPy][BF₄], prepared with different evaporation times: (a) 0s, (b) 30s, and (c) 60s.

Figure 3. Membranes from 17.8 wt% PS-*b*-P4VP solutions in 31 wt% THF/ 49 wt% DMF with 1.8 or 3.8 wt % IL. Aprotic ionic liquids: (a) [EMIM][BF₄], (b) [B3MIM][BF₄] and (c) [B3MPy][TFMS]. The evaporation time was 10s.

Figure 4. Membranes prepared from 17.8 wt% PS-*b*-P4VP solutions in 32 wt% THF/ 49 wt% DMF and (a) 0.6 wt%, (b) 0.8 wt%, (c) 1.2 wt% [IM][TFSI] or (d) 1.2 wt% [HMIM][HSO₄]. The evaporation time was 10s.

Figure 5. Cryo FESEM images of 17.4 wt% PS-*b*-P4VP solutions in 31 wt% THF/ 48 wt% DMF with 3.8 wt % [B4MPy][BF₄], [EMIM][BF₄], [B3MPy][TFMS], [B3MIM][BF₄];

17.8 wt % PS-*b*-P4VP solution in 32 wt% THF/ 49 wt% DMF with 1.2 wt % [IM][TFSI].

Figure 6. TEM cross section images of membranes prepared from 17.4 wt% PS-*b*-P4VP solutions in 31 wt% THF/ 48 wt% DMF with 3.8 wt % [B4MPy][BF₄], [EMIM][BF₄], [B3MPy][TFMS], [B3MIM][BF₄]; 17.8 wt % PS-*b*-P4VP solution in 32 wt% THF/ 49 wt% DMF with 1.2 wt % [IM][TFSI]. All stained with RuO₄, except for [B3MIM][BF₄], which was stained both by RuO₄ (top) and CH₃I (bottom).

Figure 7. TEM tomography (different tilting angles) of membranes prepared from 17.4 wt% PS-*b*-P4VP solutions in 31 wt% THF/ 48 wt% DMF with 3.8 wt % [B3MIM][BF₄].

Figure 8. Plots of viscosity vs shear rate for 17.4 wt % PS-*b*-P4VP copolymer solutions in 31 wt% THF, 48 wt% DMF, containing 3.8 wt % aprotic ionic liquids, [B4MPy][BF₄], [EMIM][BF₄], [B3MPy][TFMS] or [B3MIM][BF₄]; and protic ionic liquids [IM][TFSI] or [HMIM][HSO₄].

Figure 9. Plots of (■) storage and (□) loss moduli vs angular frequency for 17.4 wt % PS-*b*-P4VP copolymer solutions in 31 wt% THF/ 48 wt% DMF, containing 3.8 wt % aprotic ionic liquids, [B4MPy][BF₄], [EMIM][BF₄], [B3MIM][BF₄] and [B3MPy][TFMS].

Figure 10. Plots of storage and loss moduli vs angular frequency for 17.4 wt % PS-*b*-P4VP solutions in 31 wt% THF/ 48 wt% DMF containing 3.8 wt % protic ionic liquids [IM][TFSI], [HMIM][HSO₄]; analogous PS-*b*-P4VP solution without ionic liquid.

Highlights:

- Ionic liquid complexation guiding asymmetric block copolymer membranes morphology
- Final membrane morphology matching self-assembly in solution imaged by cryo microscopy
- Correlation between protic/aprotic ionic liquids and morphology
- Transmission electron tomography membrane characterization

Accepted manuscript

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10