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Highways for water molecules: Interplay between nanostructure and water vapor transport in block copolymer membranes

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Abstract

Water vapor removal is a crucial process for several industries (*e.g.*, air conditioning systems, flue gas dehydration, compressed air drying *etc.*). An effective dehumidification has the potential to drastically reduce the energy consumption and the overall cost of a process stream. Membranes with high water permeance and selectivity are promising candidates to achieve an energy-efficient water removal. We propose self-assembled membranes with interconnected and ordered hydrophilic domains that act as extremely fast water transport highways (water channels). We used a commercial amphiphilic pentablock copolymer (NexarTM), which has the ability to form long-range, self-ordering nanoscale morphologies with rigid end-blocks and a

flexible molecular network where polar and non-polar solvents regulated the final morphologies of the membranes are systematically investigated. Our results demonstrate how well-defined periodic morphology allow for molecular level control in effective removal of water vapor. The membranes with ordered hydrophilic nanochannels present a 6-fold improvement in water vapor permeability and a 14-fold increase in water vapor/N₂ selectivity compared to Nexar™ membranes with disordered domains.

Molecular dynamics stimulations are carried out on the self-assembly behavior of block copolymer solution in different solvents. In addition, sorption and desorption kinetics studies for Nexar™ films were correlated to the different morphologies imaged by transmission electron, atomic force and environmental scanning electron microscopy.

Graphical Abstract:

Block copolymer membranes with ordered and disordered nanostructure showing highways for water molecules.

Keywords: Pentablock copolymer, self-assembly, water vapor transport, water vapor/N₂ selectivity.

1. Introduction

The removal of water vapors from humid streams is an important and energy-intensive process (e.g., dehydration of flue gas, natural gas, and drying of compressed air) [1-4]. The presence of water vapor in gaseous streams is not always desirable and can pose problems for the transport through pipelines, where water can cause corrosion and create catastrophic blockage through methane ice formation. Other applications in which the control of the water vapor presence in the environment is critical include moisture control in buildings (*i.e.*, air-conditioning), aviation and space flight as well as the storage of fruit and vegetables [5, 6]. According to a US Department of Energy (D.O.E) report, building cooling systems consume a significant part of the total primary energy consumption in US and a major part of this energy is utilized in air dehumidification before the HVAC (heating, ventilation and air conditioning) system [7]. The majority of the current space cooling is provided by the vapor compression systems. Such systems use a lot of energy for condensing water vapor to eliminate moisture before cooling [8, 9]. Other sorption based technologies used currently include desiccant dehumidifiers, gas dryers, and other porous materials like zeolites and metal organic frameworks (MOFs). However, several issues associated with the desired level of dehumidification and the improved energy efficiency needed for the regeneration of these materials limit their use in large scale applications [10]. A more efficient process should have high water vapor permeability and selectivity in the presence of different components, while working at low partial pressures of water. The water vapor removal using membranes is attractive due to its low energy cost and ease of operation.

Various organic, inorganic and mixed matrix membranes have been explored in dehumidification applications like flue gas dehydration, compressed air drying, dehydration of

organic compounds, and dehumidification before the HVAC systems [3, 11-17]. Polymeric membranes manufactured from both rubbery and glassy polymers have high water vapor permeability and selectivity for vapors [3, 4, 15, 18-22]. The fundamentals of gas and vapor transport are described by Matteucci *et al.* [23] and will not be discussed here. But generally the gas permeability through dense polymer films is a function of the product of diffusion and solubility of the permeating species. Water molecules permeate preferentially through most polymers and the typical trade-off between permeability and selectivity is not observed. Instead the water vapor selectivity increases simultaneously with its permeability. The reason is the dominance of the solubility term [20].

For different applications like ventilation and air conditioning operating at low temperature, a stable performance can be achieved using polymeric membranes [8, 22, 24]. Mixed matrix membranes (MMMs) can overcome neat polymeric membranes if the right filler-polymer combination is used. Fillers used in the past include MOFs, graphene oxide, silica nanoparticles, titania nanoparticles, *etc.* [11, 12, 16, 25, 26]. Major limitations restricting the use of MMMs for large-scale industrial applications are filler agglomeration and polymer-filler incompatibility. Another approach to improve the membrane performance is to modify the morphology of the polymeric membranes and for this block copolymers are particularly interesting.

Block copolymers are extensively studied because of their ability to self-assemble into nanoscale morphologies upon microphase separation [27]. The chemical incorporation of sulfonic acid group along the polymer backbone is particularly beneficial, when water and/or other polar gas molecules diffuse through this type of polymers. Nexar™, commercially available sulfonated pentablock copolymers, are an interesting class of block copolymers that maintain a good balance between mechanical properties and membrane performance [28-30]. Nexar™ with a high degree of sulfonation maintains its mechanical integrity in the hydrated state because of the

glassy end blocks [29, 31-34]. The middle sulfonated block can create water-selective channels, while the two end blocks (*tert*-butyl styrene and ethylene-*co*-propylene) provide good mechanical stability and chain flexibility, respectively (Fig. 1) [33].

Fig. 1. Chemical structure of the pentablock copolymer Nexar™.

Due to the Nexar™ advantageous properties, it has been widely explored for various applications like water treatment [35-37], desalination [31, 32, 38, 39], pervaporation [40], gas separation [41, 42], fuel cell [43], organic photovoltaics [44] and sensors [45, 46]. Various studies have explored solvent-templating approaches to tune the morphology of the sulfonated block copolymer [33, 47-49]. A particular spatial distribution of ions can be achieved by varying morphology and periodicity of the block copolymers [41, 49-51]. Despite the good performance of Nexar™ in various fields, questions concerning the correlation of performance with the nanostructure of the film and transport kinetics remain unanswered.

Herein, we show how the internal nanostructure of Nexar™ membranes plays a crucial role in an efficient water vapor transport and water vapor/N₂ selectivity. We demonstrate that the water vapor sorption of the membranes is fundamentally different for different morphologies. We imaged the films at different humidity in an environmental scanning electron microscopy (ESEM), and used atomic force microscopy (AFM) and transmission electron microscopy (TEM) to image the fine structure of the dry membranes. Additionally, we used molecular

dynamics (MD) simulations to identify the transport mechanism and studied the sorption and desorption kinetics of the different nanostructures.

2. Experimental

2.1. Materials

Commercial sulfonated pentablock copolymer (Nexar™ MD9200) was kindly provided by Kraton Polymers (Houston, TX) in the form of films. According to the manufacturer, the Ion Exchange Capacity (IEC) of the polymer is 2.0 meq/g. Tetrahydrofuran (THF) and isopropanol (IPA) were obtained from Fisher Scientific (UK), and toluene was received from Honeywell. These solvents were used as received. Lead acetate trihydrate (ACS reagent grade) was provided by MP Biomedicals, LLC (France).

2.2. Fabrication of membranes

The chemical structure of the Nexar™ polymer used (52 mol% degree of sulfonation) is shown in Fig. 1. The equilibrium morphology of a block copolymer is mainly guided by the interaction between blocks and the molar ratios between them. The equilibrium is however usually reached only after long processes of temperature annealing. When films are cast from solution, the morphology is highly affected by the chosen solvents. We compare in this work films obtained by casting from 3 different solvents or solvent mixtures. We fabricated a film with disordered spherical micelles, one with interconnected hydrophilic nanochannels and compared them with an as-received Nexar™ film, systematically studying their performance for water transport in relation with their nanostructure. Briefly, we fabricated the membranes by casting a 2 wt% polymer solution in two different solvents based on the differences in their polarity. Firstly, tetrahydrofuran (THF) was used as a solvent and in the second case, a mixture of toluene (85wt. %) and isopropanol (IPA) was used to dissolve the polymer. The dielectric constants of these

solvents are: THF 7.58, toluene 2.38, IPA 19.92. In case of the toluene/IPA mixture the minor component IPA evaporates much faster during film formation due to its higher volatility. Hence, the less polar toluene governs the block copolymer self-assembly.

A slow evaporation rate was ensured in order to avoid macrophase separation by covering the pans with a glass cover. The resultant films were subjected to vacuum for 24 hr at room temperature to remove further traces of solvent and finally 50 μm thick dried films were obtained as confirmed by TGA given in Fig. S1, Supporting Information. We also investigated the use of more concentrated solutions to prepare the films. However, 3 wt% solutions showed an undesirable macrophase separation during the drying process. Nexar™ films as received from the manufacturer (prepared using cyclohexane) were also examined for comparison.

2.3. Membrane Characterization

The resulting membrane morphologies were characterized using TEM and AFM. The TEM images were obtained using a FEI Titan 80-300 CT operating at 300 kV. For TEM analysis, membranes were embedded in a low viscosity epoxy (Agar R1165) and sectioned with a Leica EM UC6 ultramicrotome to get thin sections (~ 80 nm thick) of the dried membranes. To enhance the contrast, the membrane samples were stained by immersing the films into a saturated lead acetate solution and exploiting the ion exchange potential of pentablock copolymer by replacing the H^+ ions on the sulfonated styrene middle block units with heavy metal ions followed by vacuum drying for 12 h.

The removal of residual solvent was confirmed by thermogravimetric analysis (TGA) using TA Instruments (Q5000IR) under Nitrogen flow. A ramp rate of 15 $^{\circ}\text{C}/\text{min}$ was used to raise the temperature till 100 $^{\circ}\text{C}$. Finally the temperature was maintained at 100 $^{\circ}\text{C}$ for 240 minutes to observe the residual solvent.

The swelling of the membrane was imaged by environmental scanning electron microscopy (ESEM) using FEI Quanta 600. The cross-sections were prepared after immersing the membranes in liquid nitrogen for 2 minutes. The humidity was changed inside the chamber and images were recorded after saturating for 5 minutes at a certain humidity.

AFM images were captured with a Veeco Dimension Icon SPM using a resonance frequency in the range of 76 to 263 kHz under tapping mode. The scan size to record the AFM image was kept at $1\ \mu\text{m} \times 1\ \mu\text{m}$.

The amount of bound and free water content was calculated using differential scanning calorimetry (DSC) using Q2000, TA Instruments, USA. The wet membrane sample was sealed in an aluminum pan and the analysis was performed in the temperature range of -20 to $+20^\circ\text{C}$ with a scanning rate of $10^\circ\text{C min}^{-1}$ under N_2 environment.

The water vapor sorption experiments were conducted under different humidity at 25°C using a gravimetric sorption balance method on a VTI-SA sorption analyzer from TA instruments, USA. Once the mass uptake reached to a desired humidity, it was equilibrated for at least 3 hours. Thick membrane samples were selected for sorption experiments to avoid any error during analysis ($78\ \mu\text{m}$ for Nexar-THF and $55\ \mu\text{m}$ for Nexar-Tol/IPA). The membrane samples were dried inside the sorption analyzer at 100°C to achieve a constant weight prior to the sorption measurement. Sorption measurements were recorded from 0 to 95% relative humidity and desorption measurements were also recorded over the entire range. In order to measure the mass uptake at 100% relative humidity, dry membrane samples were placed in the liquid water for 24 h. The excess water was wiped quickly from the surface before its measurement.

2.4. Performance of the membranes

2.4.1 Gas permeation study

Pure gas permeance was obtained using a constant volume/variable pressure test method. Single gas permeance through the membranes was calculated according to the Eq. 1.

$$J = \frac{V \times 22.4}{R \times T \times A \times t} \ln \left(\frac{P_f - P_0}{P_f - P_{p(t)}} \right) \quad (1)$$

Where V is the permeate volume, R is the ideal gas constant ($\text{m}^3 \text{ bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature (K), A is the membrane area (m^2) and t is time (s), p_f and p_o , are pressures at feed side and $p_{p(t)}$ is permeate pressure (bar).

The experimental setup for conducting mixed humid gas experiments is shown in Fig. S2, Supporting Information. The system is based on the constant pressure/variable volume method. Temperature and humidity of the humid stream is determined by humidity transmitter (Probe type 334, Vaisala Oyj, Finland).

2.4.2 Water vapor transport measurement

The membranes were tested for water vapor transport using a modified permeability cup test method reported earlier by our group. The details of this procedure can be found elsewhere [11, 12]. The water vapor permeance was calculated by Eq. 2.

$$WVTR_m = \frac{dm}{dt} \times [A \times P_{sat} \times (R_1 - R_2)]^{-1} \quad (2)$$

Where A is area of the membrane, P_{sat} is the saturated vapor pressure at the test temperature, R_1 and R_2 are the relative humidity at the source and the vapor sink. The water vapor permeance for the actual driving force is calculated using Eq. 3 by considering a correction factor for apparent and actual driving force [7].

$$WVTR_c = WVTR_m \left[\frac{p_0 - p_2}{p_1 - p_2} \right] \quad (3)$$

Where p_l is the water vapor partial pressure beneath the surface of membrane.

2.5. Computational details

Employing the Forcite module of Materials Studio (version 8.0) with the COMPASS force field, MD simulations are carried out at 298 K for Nexar-THF and Nexar-Tol/IPA mixtures as well as for mixtures of the resulting polymer structures with water molecules. The investigated mixtures are created by the amorphous cell module, using 5 repeat units of Nexar™ with 2700 THF molecules for Nexar-THF, 5 repeat units of Nexar™ with 1895 toluene and 335 IPA molecules for Nexar-Tol/IPA, and the obtained structures of the polymer with numbers of water molecules that give rise to specified relative humidities in the range from 10% to 100%. For equilibration (100 ps) the isothermal-isobaric ensemble and for production (900 ps) the isothermal-isopyknic ensemble is used, in each case with a time step of 1 fs. The Andersen and Berendsen methods are employed for temperature and pressure control, respectively. Long range Coulombic interactions are taken into account by means of the Ewald sum method and non-bonded energies are calculated with a cut-off distance of 9.5 Å.

3. Results and discussions

3.1. Nanostructure of the Membranes

Fig. 2. (a, d) TEM, (b, e) AFM images and (c, f) water droplets formation of (a-c) Nexar-Tol/IPA and (d-f) Nexar-THF membranes, respectively.

Fig. 2(a, d) shows the morphology of the membranes cast from a mixture of solvents and THF, respectively. The membranes cast from a mixture of toluene and IPA (Nexar-Tol/IPA) have rather disordered spherical lead-stained sulfonated cores embedded in an unstained matrix composed of both the hydrophobic blocks (Fig. 2a). The AFM image of the membrane surface (Fig. 2b) shows globular structures. This morphology is similar to the as-received commercial pentablock copolymer which is prepared by solvent-casting from cyclohexane or a mixture of cyclohexane with other solvents [33, 50]. In 2012, Choi *et al.* reported different film morphologies of sulfonated pentablock copolymers as function of the volume fraction of the sulfonated polystyrene block. The films were cast from cyclohexane/heptane and a higher sulfonation led to a structure of interconnected hydrophilic microdomains. They reported a significant increase in the water vapor transport rate with increasing ion exchange capacity [33].

Griffin *et al.* reported similar structures, when films were prepared from solutions with low content of polar solvents [48]. Mineart *et al.* published a detailed study on the morphology change of Nexar films, when solvents of different polarities were used. With THF as solvent they found continuous ion rich pathways in the prepared film [51]. We observed the same self-assembled structure (Nexar-THF) when the pentablock copolymer film is prepared using THF as a solvent (Fig. 2d). The AFM image of the film surface (Fig. 2e) indicates the presence of lamellae or laid parallel cylinders. The phase periodicity is $L = 57 \text{ nm} (\pm 4)$. The TEM cross sectional image shows hexagonally packed nonionic non-stained cores. Each spherical core has a dimension of ca. 40 nm. This excludes the lamellar morphology and support the cylindrical one. Previous investigation on Nexar™ pentablock copolymers using THF as solvent reported a mixture of lamellar and cylindrical morphology [49, 52]. Lamellar morphology was favored under long annealing with THF vapor [49]. Since these are non-equilibrium morphologies, they are highly dependent on the method of preparation, including polymer concentration, time and temperature of solvent evaporation. Fig. 2d shows a very clear microphase separation between the hydrophobic and hydrophilic blocks. In the Nexar-Tol/IPA films, the hydrophilic cores seem to be partially isolated, surrounded by the hydrophobic coronas. The water vapor transport would depend on random percolation of partially merged micelles. A completely different arrangement is observed for Nexar-THF with dramatic consequences for the transport properties. While the cylinder cores are hydrophobic, the coronas clearly assemble, forming hydrophilic nanochannels, which serve as highways for an exceptionally fast water vapor transport.

3.2. Water vapor sorption and diffusivity measurements

Fig. 3. (a) Water vapor sorption isotherm of Nexar™, Nexar-Tol/IPA and Nexar-THF membranes; sorption kinetics for (b) Nexar-THF membrane and (c) Nexar-Tol/IPA membrane; (d-i) desorption kinetics for (d-f) Nexar-Tol/IPA and (g-i) Nexar-THF measured at 40, 50 and 60 °C, respectively.

Fig. 3a shows the water vapor sorption and desorption isotherms measured at 25°C for both membranes along with as received samples for comparison. All the three membranes depict an increase in water uptake with the increase in relative humidity. They follow the same trend as the number of hydrogen bonds estimated by MD simulation. This water uptake is similar to dual-mode sorption isotherms, which is characteristic of glassy polymers. Desorption isotherms show

small hysteresis at high water vapor activities due to slow volume relaxation of the hydrophilic clusters in response to the change in relative humidity [53]. The majority of the water is absorbed in the sulfonated block rather than in the hydrophobic blocks [31]. As observed by TEM and AFM, the Nexar-Tol/IPA membranes have a spherical disordered morphology, which is similar to that of commercial Nexar™ membranes. Therefore, the sorption isotherm for both are very similar [37]. The sorption isotherm of Nexar-THF membranes yields 62% water uptake which is higher than for the other ones. This confirms the role of the hydrophilic nanochannels in Nexar-THF membranes as pathways to transfer water molecules without any hurdle. This ultimately improves the water uptake which increases steeply with the increase of relative humidity, due to membrane swelling at high humidity levels. However, in the case of the disordered nanostructure, the water molecules are blocked by the hydrophobic outer blocks, constituting a large part of the pentablock copolymer. To reaffirm this, the membranes were imaged using ESEM, where their swelling could be monitored directly as a function of humidity. The ESEM image for the Nexar-Tol/IPA membrane (Fig. 4a and 4b) shows 24% increase in the membrane thickness when the relative humidity was raised from 10% to 100%. This is mainly attributed to the swelling of the sulfonated block. On the other hand, there was 53% increase in thickness of Nexar-THF membrane with the same increase of relative humidity shown in Fig. 4c and 4d. This two-fold larger thickness increase is possible due to the open-ended, and interconnected channels of sulfonated block. The water droplets formed on the surface of membranes as the vapor pressure increased during ESEM imaging (Fig. 2 c, f). The membrane reinstated to its dried thickness with the decrease in vapor pressure and the water droplets vanished from the membrane surface.

Fig. 4. ESEM micrograph of Nexar-Tol/IPA (a, b) and Nexar-THF membranes (c, d) measured at 10% RH (a, c), and 100% RH (b, d), respectively.

The data described above is a strong qualitative indication of the possibility of faster water transport in the self-assembled Nexar-THF membranes. The sorption kinetics provides the quantitative confirmation. We consider here the water sorption as being a result of one-dimensional, isothermal penetrant diffusion into a thin slab of polymer. Using Fick's second law, along with the appropriate initial and boundary conditions we obtain [54]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left\{ -D(2n+1)^2 \pi^2 \frac{t}{l^2} \right\} \quad (4)$$

For early time analysis when $\frac{M_t}{M_\infty} \leq 0.6$ the equation can be expressed as:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (5)$$

Fig. 3(b-c) presents the diffusion kinetics for both membranes measured at 25°C under 90% RH using the complete solution (Eq. 4). The inset images correspond to the kinetics measured by early time analysis (Eq. 5). The diffusion coefficients (D) calculated in this way are summarized in Table 1.

Table 1. Diffusion coefficients for sorption kinetics measured at 25 °C.

Membrane	R ²	D by early time analysis (cm ² /s)	D by complete solution (cm ² /s)
Nexar-Tol/IPA	0.9813	8.34×10^{-10}	6.47×10^{-10}
Nexar-THF	0.9518	1.79×10^{-9}	1.23×10^{-9}

The diffusion coefficient is higher for the Nexar-THF membrane than that for Nexar-Tol/IPA membrane with disordered micelles. Both early time analysis and complete solution resulted a 2-fold increase in water diffusion coefficient for the self-assembled Nexar-THF membranes. This corroborates our findings about the role of the hydrophilic channels acting as highways for fast vapor transport. The data described above give rise to the following question: Is the release of water vapor (desorption) faster for membranes with ordered nanostructure (Nexar-THF)? We addressed this question, by studying the deswelling kinetics under different temperatures, using the Fick's law expressed in Eq. 4 and Eq. 5.

Deswelling isotherms show that the deswelling rate is faster with the increase of temperature. The deswelling kinetics measured by Eq. 4 shows two different regions for water desorption. In the first region the deswelling kinetics is fast and is attributable to the free water release. At a fixed temperature, the water desorption kinetics is faster for the Nexar-Tol/IPA membrane than for the Nexar-THF membrane, as demonstrated by the Fick's law (Fig. 3d-i). This apparently would raise a serious contradiction to the diffusion coefficient measured in sorption experiments. To better understand this, we studied the state of the water molecules (bound water and free water) in the membranes, by calorimetry. The swelling and water mobility are mainly governed by the free water content in the membranes (see Text S1, Fig. S3, Supporting Information) [55]. The bound water content in both membranes is similar, due to the equal number of sulfonic acid groups. However, the Nexar-Tol/IPA membrane has 1.25% free water whereas the cylindrically self-assembled Nexar-THF membrane shows a content of free water nine times higher (*i.e.*, 11%). Therefore it takes more time for water desorption in the case of Nexar-THF than Nexar-Tol/IPA membrane. At 40 °C, Nexar-Tol/IPA required 160 seconds and Nexar-THF required 270 seconds to desorb the free water present in the membranes (Fig. 3d,g) with almost similar diffusion coefficients, (Table S1, supporting information). At higher temperature of 60 °C, Nexar-Tol/IPA required 48 seconds as compared to 106 seconds for Nexar-THF (Fig. 3f, i). This increase in time for Nexar-THF is based on the high free water content present in the Nexar-THF membranes.

The Flory-Huggins theory and Hansen solubility (δ) parameters, separated in dispersive (δ_d), polar (δ_p) and hydrogen-bond (δ_H) contributions, are normally used to predict or understand the predominant non-equilibrium morphology of block copolymer films cast from solution (Eq. 6). The δ values for the blocks used here, THF, IPA, toluene and cyclohexane are shown in Table 2. The interaction between blocks and solvents is analyzed based on how close the δ contribution

values are. If the interaction distance, R , is small, the solvent (S) tends to be a better solvent for the specific block (B):

$$R = \left[4(\delta_{DB} - \delta_{DS})^2 + (\delta_{PB} - \delta_{PS})^2 + (\delta_{HB} - \delta_{HS})^2 \right]^{1/2} \quad (6)$$

Table 2. Hansen solubility parameters for the investigated copolymer blocks and solvents [48, 56].

Block and solvents	Hansen Solubility Parameters		
	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})
Poly(<i>tert</i> -butyl styrene)	17.3	1.8	1.7
Poly(hydrogenated isoprene)	16.2	1.1	2.1
Poly (styrene- <i>co</i> -styrene sulfonate 52%)	20.2	9.1	13.1
Toluene	18	1.4	2
Isopropanol	15.8	6.1	16.4
Tetrahydrofuran	16.8	5.7	8
Cyclohexane	16.8	0	0.2

Higher R corresponds also to a high Flory-Huggins parameter between block and solvents and therefore to a less thermodynamically favored mixing. In this way it is clear that THF is a better solvent for the sulfonated blocks than for the hydrophobic ones, while a toluene or cyclohexane rich mixture would be a better solvent for the hydrophobic blocks. This difference guides which block would be more prone to become a micelle or cylinder core in solution, avoiding the exposure to a solvent with unfavorable interaction. In a general consideration, the δ values would give a rough indication of which morphology would be favored or at least which block would form the core with different solvent mixtures.

3.3. MD simulations for block copolymer membranes

The Flory-Huggins theory and the solubility parameters explained above have limitations, particularly for systems with strong charges or electrostatic interactions. This is clearly the case for polymers with sulfonated blocks. Complementary methods to fully understand or predict different conformations in solution, which would lead to different film morphologies, therefore become relevant. Here, we used MD simulations to explain the morphological changes in the presence of different solvents. Snapshots from simulations of Nexar-THF and Nexar-Tol/IPA are shown in Fig. 5(a, c) and Fig. 5(b, d), respectively. The hydrophobic and hydrophilic blocks of Nexar™ result in different conformations for the different solvents. Immersed in THF the hydrophobic blocks of the polymer tend to be located at its center and the hydrophilic blocks ($-\text{SO}_3\text{H}$) at its edges, interacting strongly with polar THF through hydrogen bonds. In addition, we observe π - π interactions between the aromatic rings of the polymer. The simulated conformation agrees with the fact that in our TEM images the hydrophilic blocks assembled outside hydrophobic cylinders. The entanglement with corona chains of other cylinders results in the formation of hydrophilic channels, which we refer to as highways for transport of water vapor molecules. Immersed in Tol/IPA the hydrophobic blocks of the polymer develop π - π and H- π interactions with non-polar toluene and the hydrophilic blocks interact through hydrogen bonds with polar IPA. This leads to the disordered nanostructure of the resulting membrane as observed in Fig. 2a. Thus, in both solvents, electrostatic (hydrogen bonds) as well as van der Waals (π - π and H- π) interactions are critical for the structure formation, which is key for the fabrication of polymeric membranes.

Fig. 5. Cubic simulation cell, nanostructure conformation, and network of hydrogen bonds for (a, c, e) Nexar-THF and (b, d, f) Nexar-Tol/IPA.

We used then MD simulations to explain the differences in water permeation and sorption/desorption of membranes with different morphology by exposing the polymer in the obtained Nexar-THF and Nexar-Tol/IPA conformations to water, using different relative humidity levels. Snapshots for 100% relative humidity are shown in Fig. 5(e, f). It turns out that immediately a network of hydrogen bonds is formed that involves the hydrophilic blocks and

water molecules. The total number of hydrogen bonds grows for increasing relative humidity (Fig. S4, Supporting Information), in agreement with the experimental sorption results.

3.4. Water vapor permeation and selectivity

The water vapor permeability was measured for the membranes containing both the cylindrical nanochannels and the disordered micellar nanostructure. The membranes with disordered nanostructure (Nexar-Tol/IPA) yield a vapor permeability of 85 ± 11 kBarrer measured using the modified permeability cup method [11, 12]. This water vapor permeability is close to that of the received commercial Nexar™ membranes (89 ± 8 kBarrer) due to similar morphologies [33]. They have also similar morphologies. These are very high values, compared to other available materials. However, the water vapor permeability of the Nexar-THF membrane with nanochannels is 554 ± 29 kBarrer—more than six times higher than the value for Nexar-Tol/IPA. The very high water vapor permeability is attributable exclusively to the morphological difference of the membranes. The interconnected hydrophilic blocks in the reverse micelles form vapor rich channels which act as highways for transporting water molecules. Other researchers have also observed similar increase in permeability of polar molecules when transferring from discrete nanostructures to a highly ordered nanostructure for other sulfonated polymers [41]. An interesting observation is that the N_2 gas permeability varies in the opposite way with the membrane morphology, since the transport is probably favored through the flexible hydrophobic phases. The dry N_2 gas permeability for Nexar-THF was 0.36 Barrer and for Nexar-Tol/IPA we determined 0.78 Barrer. This yields a very high ideal water vapor/ N_2 selectivity of 1.10×10^5 for Nexar-Tol/IPA and 1.5×10^6 for Nexar-THF. However, the humid N_2 gas permeability increased to 3.60 Barrer for Nexar-Tol/IPA and 1.31 Barrer for Nexar-THF. This increase in humid gas permeability due to the membrane swelling decreases the selectivity as compared to single gas

experiments. Taking the nitrogen permeability under wet condition, the water vapor/nitrogen selectivity for Nexar-Tol/IPA is 2.4×10^4 and 4.2×10^5 for Nexar-THF membranes.

The results shown in Fig. 6 and Table S2, Supporting Information describe the very high water vapor/ N_2 selectivity of the Nexar-THF membrane, compared to the Nexar-Tol/IPA and to other available polymeric membranes, including the mixed matrix ones.

Fig. 6. Comparison of water vapor permeability and water vapor/ N_2 selectivity with other reported membranes in the literature.

4. Conclusions

Our results unequivocally signify the distinctions between self-assembled, highly ordered and disordered morphologies as a decisive factor to obtain high-performance dehumidification membranes. TEM images revealed a highly ordered ion-rich nanochannel morphology when the membrane was cast with THF in solutions. AFM images of the Nexar-THF membrane surface also affirmed the highly ordered self-assembled cylindrical nanostructure. We suggest that these nanochannels act as highways for the transport of water vapor with increase up to 6-fold

permeability and an order of magnitude in water vapor/N₂ selectivity was observed compared to membranes with disordered morphology. The sorption kinetics show that the time for water uptake is shorter in the case of membranes with cylindrical nanochannels compared to the disordered ones whereas deswelling kinetics is slow for the nanochannel membranes due to presence of high free water.

The solvent influence on the morphology was explained by MD simulations showing interaction of polar THF with the hydrophilic block of Nexar™ through hydrogen bonding and π - π interactions between the planar aromatic rings of the pentablock copolymer. MD simulations for the obtained copolymers in contact with water point to an interaction between the sulfonic acid groups and water molecules. Our findings provide a framework for future studies on potential practical applications of this polymer especially with periodic mesoscale self-assembly.

Supporting Information

Supplementary data associated with this article can be found in the online version of article.

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Highlights

- The Nexar nanoscale morphology was optimized for maximum water permeance.
- The water vapor permeance of commercial Nexar films could be increased by 500%.
- The water vapor selectivity could be increased 14 fold by optimizing the morphology.
- Performance enhancement is explained using molecular dynamics simulations.