**Anion exchange membranes composed of a poly(2,6-dimethyl-1,4-phenylene oxide)
random copolymer functionalized with a bulky phosphonium cation**

Ye Liu,^a Bingzi Zhang,^b Corey L. Kinsinger,^a Yuan Yang,^c Soenke Seifert,^d Yushan Yan,^b
C. Mark Maupin,^a Matthew W. Liberatore,^c and Andrew M. Herring.^{a,*}

^aDepartment of Chemical and Biological Engineering, ^cDepartment of Chemistry and
Geochemistry, Colorado School of Mines, Golden, CO 80401, United States

^bDepartment of Chemical and Biomolecular Engineering, University of Delaware,
Newark, DE 19716, United States

^dX-Ray Science Division, Argonne National Laboratory, Argonne, IL 60439, United
States

^eDepartment of Chemical and Environmental Engineering, University of Toledo, Toledo,
OH 43606, United States

Corresponding author

Andrew M. Herring

Tel.: 303-854-8806

Fax: 303-273-3730

E-mail address: aherring@mines.edu

ABSTRACT

A random copolymer, tris(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP) was cast from three different solvents: dimethyl sulfoxide (DMSO), ethyl lactate, or a 41:59 vol% mixture of DMSO and ethyl lactate. Solvents were selected via analysis of the Hansen solubility parameters to vary the phase separation of the polymer in the films. An optimized mixture of DMSO and ethyl lactate chosen for film fabrication and this film was contrasted with films cast from the neat constituent solvents. Atomic force microscopy identified domains from nanometer to tens of nanometer sizes, while the light microscopy showed features on the order of micron. SAXS revealed a cation scattering peak with a d-spacing from 7 to 15 Å. Trends in conductivity and water diffusion for the membranes vary depending on the solvent from which they are cast. The mixed solvent cast membrane shows a linear Arrhenius behavior indicating fully dissociated cationic/anionic groups, and has the highest bromide conductivity of 3 mS/cm at 95% RH, 90 °C. The ethyl lactate cast membrane shows a linear Arrhenius relation in conductivity, but a Vogel-Tamman-Fulcher behavior in its water self-diffusion. While water increases bromide dissociation, water and bromide transport in these films seems to be decoupled. This is particularly true for the film cast from ethyl lactate.

Keywords: Anion exchange membrane, Hansen solubility parameter, Morphology, Ionic conductivity, Water transport

1. Introduction

Anion exchange membranes (AEMs) exhibit potential for a large variety of processes, such as mass separation (electrodialysis, filtration, water purification) [1,2], chemical synthesis (electrolysis) [3], and energy conversion and storage (fuel cells and advanced batteries) [4-6]. In all of these processes, the cationic groups attached to the polymer backbone control the transport of the anionic species [7]. However, many AEMs are not chemically stable to hydroxide, which is essential to some applications, especially under drier and hotter conditions. High hydroxide concentrations decompose the cationic groups via S_N2 , Hofmann elimination, or other degradation processes [8,9]. Therefore, durable AEMs with efficient, selective transport are desired, and so new stable cations and polymer backbones must be developed.

Recently, bulky cations have shown improved chemical stability. Zhang et al. designed a new diphenyl (3-methyl-4-methoxyphenyl) tertiary sulfonium cationic group [10]. This sulfonium cation remained stable in 1M KOD solution at 60 °C for 10 days. A 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation [11,12] demonstrated that attaching the 2,4,6-trimethoxyphenyl group to the cation improves stability. In Gu et al.'s work [13], a tris(2,4,6-trimethoxyphenyl) phosphonium functionalized polysulfone membrane survived for 48 h when immersed either in 10 M KOH at room temperature or in 1 M KOH at 60 °C. Jiang et al. [14] investigated a tris(2,4,6-trimethoxyphenyl) phosphonium functionalized bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) that maintains stability in 1 M NaOH at 60 °C for 75 h. Zha et al. [15] first reported

AEMs with a ruthenium bis(terpyridine) complex cation. This membrane exhibited excellent stability in 1 M NaOH solution at room temperature over 6 months. Promising chemical stability of these bulky cations results from the contributions of the electron donating function as well as increased steric effects from the attached side groups. It has also been recently realized that the polymer backbone stability is also a crucial factor towards durable polymers for AEM applications. In particular, residual bromide from incomplete quaternization is a site for hydroxyl attack and so should be avoided [16].

The polymer morphology, ionic nanostructure, and degree of ionic dissociation all affect transport properties in AEMs [17,18]. Solvents can alter the polymeric configuration and properties due to distinct interactions between the polymer chain and the solvent. Effects of the casting solvent on the phase behavior of the diblock [19,20] or triblock [21] copolymers is well studied. The conductivities of AEMs can also be influenced by changing solvents during the casting process. Elabd et al. [22] investigated the conductivity of sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymers applied in proton exchange membrane fuel cells. The proton conductivities of these triblock copolymers varied by 3 orders of magnitude, ranging from 1.07×10^{-2} mS/cm cast from a toluene/ethanol mixture (85/15 w/w) to 5.95 mS/cm cast from toluene. Ong et al. [23] developed a random poly(2,6-dimethyl-1,4-phenylene oxide) AEM with a hydroxide conductivity of 17 mS/cm at 60 °C in water when cast from NMP, while the conductivity of a membrane cast from a chlorobenzene/DMF mixture solvents was 8 mS/cm.

Little work has investigated the casting solvents' influence on water and ionic

transport in AEMs. In this study, we report the synthesis of a new polymer with a bulky phosphonium cation attached to a polyphenylene oxide polymer via a selective bromination method used to avoid the large amount of excess bromide present in a previously synthesized similar AEM [16]. The polymer is fully characterized by NMR, FTIR, SAXS and microscopy. By studying the random copolymer, instead of a block copolymer, the intrinsic transport properties can be examined in a system with more random phase separation and structuring. By varying the solvent used for casting, based on the solubility of each of the polymer components, the impact of polymer morphology with transport and conductivity is established. Insights into the anionic conductivity are gained from a study of the water self-diffusion coefficients from NMR measurements.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide), N-bromosuccinimide, chlorobenzene, 2,2-azobis(2-methylpropionitrile), ethanol, 1-methyl-2-pyrrolidone, tetrahydrofuran and tris(2,4,6-trimethoxyphenyl)phosphine were purchased from Sigma-Aldrich. The molecular weight of poly(2,6-dimethyl-1,4-phenylene oxide) was reported as $M_w=35000$, $M_n=16000$ (Sigma-Aldrich).

2.2. Synthesis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP)

A solution of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (6 g, 50 mmol in 60 mL chlorobenzene) was heated to 140 °C, followed by addition of *N*-bromosuccinimide (5.34

g, 30 mmol) and 2,2-azobis(2-methylpropionitrile) (0.246 g, 1.5 mmol). After mechanically stirring at 140 °C for 1 h, the reaction mixture was poured into ethanol to precipitate the product. The brominated polyphenylene oxide (BPPO) precipitate was filtered, washed with ethanol, and dried in vacuum at room temperature for 12 h.

The BPPO (3.03 g, 20 mmol) was dissolved in 1-methyl-2-pyrrolidone (NMP, 80 mL), followed by addition of tris(2,4,6-trimethoxyphenyl)phosphine (6.39 g, 12 mmol). The mixture was stirred at 80 °C for 12 h and then precipitated in tetrahydrofuran. The precipitate was filtered and thoroughly washed with excess tetrahydrofuran in order to remove unreacted tris(2,4,6-trimethoxyphenyl)phosphine.

2.3. Membrane fabrication

10 wt% PPO-TPQP was dissolved in DMSO, ethyl lactate, or a mixture of DMSO and Ethyl lactate (41:59 vol%) respectively at 60 °C for 2 h. The polymer solution was drop cast on a pre-cleaned glass substrate and heated in a vacuum oven at 80 °C for 24 h. After removal from the substrate, the membrane was soaked in DI water to completely remove the solvent.

2.4. Characterization

¹H nuclear magnetic resonance (NMR) was recorded on a JEOL 500 MHz spectrometer. The methods for Fourier transform infrared spectroscopy (FTIR), water vapor sorption and calculations of hydration numbers (λ) were reported previously [12]. The liquid water uptake mass was obtained by first weighing a vacuum dried membrane (oven at 60 °C for 48 h) and then soaking the membrane in DI water for 48 h at 60 °C,

followed by measuring the weight of the membrane quickly after removing the surface water.

In-plane and through-plane swelling were determined by dimensional changes (X and Y) from dry to liquid soaked conditions. The swelling of the membranes was calculated from Eq. (1) and Eq. (2)

$$\text{In-plane swelling} = \frac{X_w - X_d}{X_d}, \frac{Y_w - Y_d}{Y_d} \quad (1)$$

Where X_w and Y_w are width and length at wet condition; X_d and Y_d are width and length when the membrane is dry.

$$\text{Through-plane swelling} = \frac{L_w - L_d}{L_d} \quad (2)$$

Where L_w is the thickness at wet condition and L_d is the thickness when the membrane is dry.

Atomic force microscopy (AFM) images were taken in tapping mode using a Bruker Nanoscope III instrument with high-aspect ratio 225 μm cantilever tips (Nanoworld NCLR). Phase images analysis used Nanoscope 5.30r1 software and domain size quantification used Image J. Micron scale morphologies of the membranes were acquired using a Thermo Fisher Nicolet iN10 microscope. The image was collected in reflection mode.

Small angle X-ray scattering (SAXS) was performed at the Advanced Photon Source (APS), Argonne National Laboratory on beamline 12ID-B. The beam wavelength was $\lambda = 0.886 \text{ \AA}$, with an exposure time of 1 s, and an energy of $E = 14 \text{ keV}$. Two-dimensional scattering patterns were collected simultaneously with a Pilatus 2M detector. The

one-dimensional intensity versus q employed azimuth averaging from the 2D scattering pattern in the range of $0.005 \text{ \AA}^{-1} < Q < 1 \text{ \AA}^{-1}$ where $Q=4\pi\lambda^{-1} \sin(\theta)$. Experiments were carried out from 0% RH to 95% RH as well as liquid soaked conditions. For each water vapor humidity step, membranes were equilibrated for 20 to 40 minutes before scattering patterns were collected. The soaked sample was immersed in DI water at room temperature for 24 h before measurements.

Measurements of ^1H self-diffusion coefficients were carried out from pulsed-field gradient nuclear magnetic resonance (PFG NMR) as described before [12]. Membranes were cut into strips and loaded into a 5 mm NMR tube with DI water at the bottom. The open tube was then moved into a Test Equity oven set at 95% RH, 25 °C. The tube was sealed after 24 h when the membranes were fully equilibrated. Experiments were performed at 100% RH from 25 °C to 50 °C. The inversion recovery sequence, $180^\circ\text{-}\tau\text{-}90^\circ$, was used for T_1 measurement.

In-plane anionic conductivity was measured using electrochemical impedance spectroscopy (EIS) using a biologic VMP 3 multichannel potentiostat [12]. Measurements were performed from 50 °C to 90 °C under 95% RH and from 65% RH to 95% RH at 60 °C.

2.5. Structural modeling

The tris(2,4,6-trimethoxyphenyl) phosphonium cation structure was optimized by using density functional theory (DFT) at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program [24].

3. Results and discussion

3.1 PPO-TPQP synthesis and structure

Tris(2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-TPQP) was successfully synthesized by bromination of poly(2,6-dimethyl-1,4-phenylene oxide), followed by quaternization with tris(2,4,6-trimethoxyphenyl) phosphine (Fig. 1).

Fig. 1. Synthesis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

The synthesis of the intermediate BPPO was validated by ¹H NMR spectroscopy (Fig. S1(a)), the methyl and methylene protons of the brominated polymer were seen at 2.1 and 4.3 ppm, respectively. Integration of these two peaks gave the bromination level as 40%. The aromatic protons were observed ca. 6.6 ppm.

Structure of PPO-TPQP was validated by elemental analysis, ¹H NMR (Fig. 2(a)), ³¹P NMR (Fig. 2(b)), ¹³C NMR (Fig. S1(b) and FTIR (Fig. S1(c)). The elemental analysis (of the vacuum oven dried sample, 80 °C, 24 h) was in good agreement with the calculated values, Anal. Calcd (C₁₈₈H₂₀₈O₄₆P₄Br₄ 3,651): C 62.00, H 5.70, O 20.16, Br 8.75, P 3.39. Found: C 59.56, H 5.81, O 20.68, P 3.62. In the ¹H NMR (Fig. 2(a)), signals at 6.37-6.55

ppm and 6.25 ppm are assigned to aromatic protons from the PPO backbone and the phosphonium cation, respectively. The signals at 3.87 ppm and 3.59 ppm are attributed to the methoxy groups at the para- and ortho- positions. The group of peaks at 1.67-2.08 ppm indicates protons on methyl groups on the PPO backbone. In the ^{31}P NMR (Fig. 2(b)), after quaternization (top), there is no peak from the starting phosphine, -65.9 ppm (bottom), while a new phosphonium peak at 5.2-5.5 ppm is present, indicating the attachment of the bulky phosphonium cation. The FTIR spectra (Fig. S1(c)) of PPO-TPQP display peaks at 1229 cm^{-1} , which are not observed for PPO and are assigned to the C-O-C stretching from methoxyphenyl groups [25].

Fig. 2. (a) ^1H NMR of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO; (b) ^{31}P NMR, bottom, tris(2,4,6-trimethoxyphenyl) phosphine, top, the polymer after quaternization.

3.2. Solvent selection criteria

The Hansen Solubility Parameter (HSP) was used to select the solvent for polymer casting. In Hansen space, the sphere is defined by 3 Hansen parameters, which are the energy from dispersion forces, dipolar forces and hydrogen bonds between molecules. The relative energy difference (RED) shown in Eq. (3), measures the mutual compatibility between solvent and polymer. When RED is larger than 1, the solvent does not dissolve the polymer. When RED is less than 1, the polymer and solvent are compatible and predicted to be mutually soluble, the closer of RED to 0, the less energy difference between the polymer and solvent. When RED =1, the polymer will partially dissolve [26,27].

$$RED=R_a/R_0 \quad (3)$$

R_a -distance between Hansen parameters, which is calculated by Eq. (4)

R_0 -interaction radius (radius of Hansen sphere)

$$(R_a)^2=4(\delta d_s-\delta d_p)^2+(\delta p_s-\delta p_p)^2+(\delta h_s-\delta h_p)^2 \quad (4)$$

δd_s - energy from dispersion forces between solvent molecules

δd_p - energy from dispersion forces between polymer molecules

δp_s - energy from dipolar intermolecular force between solvent molecules

δp_p - energy from dipolar intermolecular force between polymer molecules

δh_s - energy from hydrogen bonds between solvent molecules

δh_p - energy from hydrogen bonds between polymer molecules

The units of all parameters are $\text{MPa}^{1/2}$.

The determination of HSPs for PPO-TPQP began with dissolving the polymer in a set of 12 different common solvents of known HSP chosen to vary δ_d , δ_p and δ_h (Table S1). Generally the polymer did not dissolve when δ_p was < 5.7 and δ_h was < 7.0 . From this HSP of 17.5, 10.7 and 11.6 were calculated for δ_d , δ_p and δ_h of PPO-TPQP and R_0 was 6.2 (Table 1). This information was used to calculate the R_a and RED for a number of solvents with appropriate cost, safety, and odor over a range of volatilities. DMSO was shown to give a RED of almost 1 (Table 1), and represented the limit of solvents that the PPO-TPQP would dissolve in. Ethyl lactate was chosen as being a good solvent for the polymer with much higher volatility than DMSO with RED = 0.7 (Table 1). The HSPiP package [28] was then used to find the ethyl lactate : DMSO ratio with the minimum RED which was at 59:41 vol% with a RED of 0.2, even closer to 0 (Table 1).

Table 1 Hansen solubility parameters, R_a , RED of casting solvents (DMSO, Ethyl lactate, Mix solvent) and PPO-TPQP

sample designation	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	R_a (MPa ^{1/2})	R_0 (MPa ^{1/2})	RED
PPO-TPQP	17.5	10.7	11.6		6.20	
DMSO	18.4	16.4	10.2	6.17		0.998
Ethyl lactate	16.0	7.6	12.5	4.38		0.709
Mix solvent	17.0	11.2	11.6	1.13		0.183

As the ethyl lactate evaporates, the solubility of the PPO-TPQP will, therefore, get worse and the more hydrophilic parts of the polymer will tend to phase separate. Hence solvent casting PPO-TPQP from DMSO, ethyl lactate, and the optimized mixture of the

two solvent should give us AEMs with differing morphologies and properties.

3.3. Morphology and water uptake

All three films were formed as visibly transparent yellow/orange materials (Figure S2). Light microscopy revealed all films to have dark circular features ranging in size from 2 – 10 μm (Fig. 3).

Fig. 3. Light microscope images of PPO-TPQP-MIX. (Scale bar is 50 μm)

Fig. 4. AFM tapping mode phase images of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c). (Scan boxes are 500 nm $\times$ 500 nm)

The influences of the 3 solvent systems on the membranes morphology at smaller scale were observed by AFM tapping mode phase images (Fig. 4). All of them have a more hydrophilic and hydrophobic phase separation at ambient conditions, where the dark regions have been shown to be the ionic aggregates and the light regions to be the

hydrophobic polymer backbone [29]. Thus, microscopies of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate suggest a hierarchical domain structure with morphology on both micron and nanometer scales.

The ionic and hydrophobic domain sizes are different for each of the three different membranes in a length scale from nanometers to tens of nanometers (Table 2). The PPO-TPQP-DMSO membrane shows larger hydrophilic ($FD = 22 \pm 12$ nm) and hydrophobic ($FD = 31 \pm 17$ nm) domains than the PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes (hydrophilic $FD = 16 \pm 8$, 15 ± 9 nm, hydrophobic $FD = 19 \pm 10$, 21 ± 12 nm, respectively), which have similar domain sizes. Clearly the DMSO in which the hydrophobic part of the polymer is more soluble created large domains while the ethyl lactate in which the more hydrophilic part is more soluble created smaller domains.

Table 2 Image J analysis of Feret diameters (FD) and standard deviations (SD) of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate

sample designation	average of FD (nm)	SD of size distribution (nm)	average of FD (nm)	SD of size distribution (nm)
	Bright domain		Dark domain	
PPO-TPQP-DMSO	31	17	22	12
PPO-TPQP-MIX	19	10	16	8
PPO-TPQP-Ethyl lactate	21	12	15	9

SAXS patterns of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes (Fig. 5), were measured from dry to 95% RH at 60 °C. No distinct

peaks were observed in the low q range of $0.005 - 0.1 \text{ \AA}^{-1}$, but in all cases, upturn was observed at $q = 0.02 \text{ \AA}^{-1}$, designating poorly organized long-range order, which is not surprising for the random PPO-TPQP copolymer. By examining the slope variation from 0 to 95% RH, the slope of the PPO-TPQP-DMSO membrane has a relative large drop from 2.9 to 2.0, while the slope for the PPO-TPQP-MIX membrane increases from 2.4 to 2.6 and the slope for the PPO-TPQP-Ethyl lactate membrane remained constant at 3.2. The large change for the PPO-TPQP-DMSO membrane is not surprising considering the film was cast from the hydrophobic DMSO. On absorbing water at 60°C the water strongly influences the polymer morphology by swelling the hydrophobic regions decreasing their symmetry. For the films cast from the mixed solvent system or the ethyl lactate which influenced the more hydrophilic domains, less changes or even no changes are observed on swelling and the symmetry of the more hydrophilic domains remains higher than for the DMSO cast film. At large q range at $0.1-1 \text{ \AA}^{-1}$, a small peak was found at a d-spacing of $7-15 \text{ \AA}$ (Fig. 5(d)-(f)) and the peak positions did not shift from dry to 95% RH. However, the size of the observed d-spacing is smaller than that of ionomer peaks in other AEMs, where $d = 10 \text{ nm} - 32 \text{ nm}$ for 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO [12] or $d = 3 \text{ nm} - 5 \text{ nm}$ for trimethyl ammonium functionalized perfluorinated material based on the 3M perfluorinated sulfonyl fluoride [30]. Because the peak does not move with changing humidity and we know that in two of the films the symmetry of the scattering objects in the more hydrophilic domains is changing, a hypothesis that the $7-15 \text{ \AA}$ feature was due

to scattering from the large phosphonium cation was tested by calculating the cation structure using the Gaussian 09 program (Fig. 6).

Fig. 5. SAXS and zoom in SAXS spectra of PPO-TPQP-MIX (Fig. 4 (a), (d)), PPO-TPQP-DMSO (Fig. 4 (b), (e)) and PPO-TPQP-Ethyl lactate (Fig. 4 (c), (f)). (Fig. 4 (a), (b), (c) $\circ$ 0% RH, $\square$ 25% RH, Δ 50% RH, ∇ 75% RH, $*$ 95% RH, $\diamond$ soaked; Fig. 4 (d), (e), (f) $\circ$ 0% RH, $*$ 95% RH)

Fig. 6. Tris(2,4,6-trimethoxyphenyl) phosphonium cation optimized at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program.

The dimensions of the cation size from different configurations are between 7-13 Å, which has excellent agreement to the d-spacing shown in SAXS spectra. This is in contrast to the polymer we studied with the bulky 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium cation [12], where the cation size obtained is in the range of 6-12 Å (Fig. S3), the d-spacing of the corresponding peaks in SAXS is between 31-62 Å and shows a definite dependence on RH. These results indicate that the peaks in the SAXS patterns, Fig. 5 (d)-(f) are attributed to the scattering between cations, whereas in the polymer with the bulky imidazolium, the peaks are due to interference between ionic aggregates, similar to the ionomer peaks observed in perfluorosulfonic acid polymers such as in Nafion[®] [31,32].

The influence of polymer morphology on water uptake is shown in Fig. 7. The PPO-TPQP-MIX membrane has the highest water uptake and hydration number

(WU=28%, $\lambda=12.8$, liquid water) while the PPO-TPQP-Ethyl lactate membrane has the smallest (WU=10%, $\lambda=4.6$, liquid water). Water uptake generally matches the swelling behavior (Fig. 8). This data is consistent with the SAXS data that shows the PPO-TPQP-Ethyl lactate cast membrane has no change on exposure to higher RH. Overall, modest water uptakes are observed in the range of 10%-28% when all the films are soaked in liquid water corresponded to an in-plane-X swelling of 4%-7%, in-plane-Y swelling of 4%-6% and a through-plane swelling of 6%-10%.

Fig. 7. Water uptake and lambda value of PPO-TPQP casted from different solvents.

(Water uptake: ■ PPO-TPQP-MIX, ◆ PPO-TPQP-DMSO, ▲ PPO-TPQP-Ethyl lactate;

Lambda: □ PPO-TPQP-MIX, ◇ PPO-TPQP-DMSO, △ PPO-TPQP-Ethyl lactate)

Fig. 8. In-plane and through-plane swellings of PPO-TPQP casted from different solvents.

3.4. Self-diffusion and ionic conductivity

To probe the molecular motions of the water in the polymer, spin-lattice (T_1) relaxation time was used to correlate morphological structures. Since T_1 probes molecule motions on a time scale of 2.5 ns ($1/\omega_0$, ω_0 is the ^1H Larmor frequency, 400 MHz in our experiment) [33], diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate are calculated as $2.13 \times 10^{-6} \text{ cm}^2/\text{s}$, $2.04 \times 10^{-6} \text{ cm}^2/\text{s}$ and $2.08 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. Therefore, from Eq. (5) the diffusion lengths [34,35] of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate are 1.03 nm, 1.01 nm and 1.02 nm, showing that all three films have the same solvated cation-anion dissociation.

$$\langle a^2 \rangle^{1/2} = \sqrt{2Dt_d} \quad (5)$$

where $\langle a^2 \rangle^{1/2}$ is the diffusion length, t_d is the diffusion time and D is the diffusion

coefficient.

Dependence of water self-diffusion coefficient upon diffusion time was recorded at 25 °C (Fig. 9) by PFGSE NMR. The PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate membranes all display restricted diffusion behavior where the self-diffusion coefficients decrease and then level off with increasing diffusion evolution time [36,37]. Restricted diffusion implies that water diffuses in a heterogeneous network, which corresponding to the phase separation as observed in the AFM and light microscope images (Fig. 3 and 4). When full geometrical restriction is achieved, the water self-diffusion coefficient (D_{∞}) of PPO-TPQP-Ethyl lactate is higher, 6.3×10^{-7} cm²/s, while those of PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate are both ca. 4.6×10^{-7} cm²/s. These values are one order of magnitude smaller than diffusion coefficients of 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized PPO (1.0×10^{-6} cm²/s) [12] and Nafion[®] 117 (5.6×10^{-6} cm²/s) [38] where ionomer peaks that swell are observed, and two order of magnitude smaller than the bulk water diffusion coefficient (2.3×10^{-5} cm²/s at 25 °C) [39].

Fig. 9. Water self-diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX, PPO-TPQP-Ethyl lactate versus the square root of the diffusion time. ($\diamond$ PPO-TPQP-DMSO, $\blacksquare$ PPO-TPQP-MIX, $\blacktriangle$ PPO-TPQP-Ethyl lactate)

The same diffusion experiments (Fig. 9) also revealed the membrane heterogeneity via a theory developed by Mitra (Eq. (6)) [40,41].

$$D = D_0 \left[1 - \frac{4}{9\sqrt{\pi}} \cdot \frac{S}{V} \cdot \sqrt{D_0 \cdot t_d} \right] \quad (6)$$

where D_0 is diffusion coefficient at $t_d=0$, and S/V is the surface-to-volume ratio of the porous material. By fitting the slope of the diffusion data from Fig. 9 into Eq. (6), evidence of morphological complexity is quantified by the critical length scale, R_c , the reciprocal of S/V and the tortuosity ($\alpha=D_0/D_\infty$) [12,42] (Table 3). R_c is on the order of hundreds of nanometers, which is larger than the domain sizes shown in AFM images and so must extend into the domains observed in the light microscope (Fig. 3). It is the same (0.39 μm) for PPO-TPQP-DMSO and PPO-TPQP-MIX, but larger for the ethyl lactate cast film (0.43 μm). The tortuosity decreases in the order PPO-TPQP-DMSO>PPO-TPQP-MIX>PPO-TPQP-Ethyl lactate with values of 4.50, 4.35

and 3.32, respectively.

Table 3 Surface/volume ratio, R_c , tortuosity and T_l of PPO-TPQP-DMSO, PPO-TPQP-MIX and

PPO-TPQP-Ethyl lactate

sample designation	S/V (μm^{-1})	R_c (μm)	Tortuosity (α)	T_l (ms)
PPO-TPQP-DMSO	2.58	0.39	4.50	596
PPO-TPQP-MIX	2.57	0.39	4.35	535
PPO-TPQP-Ethyl lactate	2.33	0.43	3.32	478

The Arrhenius plots of the water self-diffusion coefficients as a function of temperature (Fig. 10) implicate that the solvent from which the membrane was cast also impacts the mechanism of water transportation. In Fig. 10, diffusion coefficients with non-linear trends are observed for PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate. The Vogel-Tamman-Fulcher (VTF) [43] equation (Eq. (7)) is used to represent the ion transport facilitated by the movement of the cationic side chains. The results of the VTF fitting of the self-diffusion coefficients are given in Table 4. The water self-diffusion of PPO-TPQP-MIX shows a linear Arrhenius behavior (Table 5).

$$D(T) = AT^{-1/2}e^{-E_i/R(T-T_0)} \quad (7)$$

where A is a constant, R is the gas constant, E_i is the pseudo-activation energy and T_0 is the temperature at which the mobility of ions and the conductivity drop to zero.

Fig. 10. Water diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate in terms of different temperature under 100% RH. (◆ PPO-TPQP-DMSO, ■ PPO-TPQP-MIX, ▲ PPO-TPQP-Ethyl lactate)

Table 4 Parameters of VTF regression of PPO-TPQP-DMSO and PPO-TPQP-Ethyl lactate on conductivity as well as diffusion coefficients versus temperatures

sample designation	relative humidity	A	E _i (kJ/mol)	T ₀
PPO-TPQP-DMSO (D)	100%	$1.3 \pm 0.5 \times 10^{-8}$	1.6 ± 0.6	227 ± 14
PPO-TPQP-DMSO (σ)	95%	0.8 ± 0.3	2.4 ± 0.3	256 ± 4
PPO-TPQP-DMSO (σ)	80%	0.08 ± 0.03	1.2 ± 0.8	278 ± 9
PPO-TPQP-Ethyl lactate (D)	100%	$8.9 \pm 0.9 \times 10^{-9}$	1.0 ± 0.1	242 ± 6

Conductivity versus temperature of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate measured at both 95% RH and 80% RH are shown in Fig. 11. PPO-TPQP-MIX has highest conductivity of 3 mS/cm⁻¹ at 90 °C, 95% RH. A comparison to literature values for bromide conductivities reported previously is shown in Fig. S4 [44,45]. There are surprisingly few good comparative studies in the literatures. These two polymers were selected, because they are random copolymer structures with a bromide counter ion and PPO backbone, measured under water vapor, which have a true comparison to PPO-TPQP. The bromide conductivities of PPO-TPQP-MIX comparable

to and intermediate to the values from IEC of 0.9 and 1.8 mmol/g membranes with trimethyl ammonium cations at identical temperature and humidity level, indicating the bulky phosphonium cation does not negatively impact bromide transport.

Fig. 11. Bromide conductivities of PPO-TPQP-DMSO (a), PPO-TPQP-MIX (b) and PPO-TPQP-Ethyl lactate (c) as a function of temperature under 95% RH and 80% RH. (◆ 95% RH, ■ 80% RH)

Also, we noticed that plot of PPO-TPQP-MIX exhibits a linear trend, the same as small cation (imidazolium and ammonium) random copolymers (Fig. S4). The Arrhenius plot for PPO-TPQP-DMSO is curved so fit to the VTF equation (Eq. (8)) under both 95% RH and 80% RH (Table 4), similar to its water diffusion behavior in Fig. 10.

$$\sigma(T) = AT^{-1/2}e^{-E_i/R(T-T_0)} \quad (8)$$

where A is a constant proportional to the number of mobile charge carriers, R is the gas constant, E_i is the pseudo-activation energy and T_0 is the temperature at which the mobility of ions and the conductivity drop to zero. Constant A at 95% RH is ca. one order of magnitude larger than that of 80% RH since more bromide is dissociated and so

contributes more to the ionic conductivity. A thermal transition is indicated in the region of all the conductivity measurements (VTF T_0 is 50 °C lower than measured transitions). However, the plot of PPO-TPQP-Ethyl lactate displays a linear Arrhenius relation (Table 5), which is in contrast to the water self-diffusion curve trend in Fig. 10. The Arrhenius plots of PPO-TPQP-MIX indicate that the cation anion pairs are always dissociated probably because it exhibits the highest water uptake. Even so there is never enough water in these films to fully hydrate the bromide anion that typically needs 6 waters [46], where as at 95% RH, PPO-TPQP-MIX film approaches 5. Increasing the water content of the films increases the conductivity values for bromide. However increasing RH also increases the E_a for bromide transport, E_a doubles from 36 ± 5 kJ/mol at 80% RH to 70 ± 6 kJ/mol at 95% RH, whereas the water self-diffusion exhibits a E_a of 21 ± 1 kJ/mol at 100% RH indicating that water transport is decoupled from bromide transport. This seems to be consistent as we also noticed another trend for PPO-TPQP-Ethyl lactate, which has the lowest conductivity but has the highest water diffusion coefficient among the three membranes.

Table 5 Parameters of Arrhenius fit of PPO-TPQP-MIX and PPO-TPQP-DMSO on conductivity as well as diffusion coefficients versus temperatures

sample designation	relative humidity	E_a (kJ/mol)
PPO-TPQP-MIX (D)	100%	21 ± 1
PPO-TPQP-MIX (σ)	95%	70 ± 6
PPO-TPQP-MIX (σ)	80%	36 ± 5
PPO-TPQP-Ethyl lactate (σ)	95%	73 ± 4
PPO-TPQP-Ethyl lactate (σ)	80%	45 ± 8

To further illustrate this point we consider an approach where impact of ion concentration on conductivity is eliminated. A solution is performed by calculating bromide diffusion coefficients from bromide conductivities by Nernst-Einstein equation (Eq. (9)) [47], from which enable a direct comparison between the measured water self-diffusion and bromide diffusion.

$$D = RT \frac{\kappa}{cz^2F^2} \quad (9)$$

where κ is the conductivity, c is the concentration of anionic groups in the membrane, z is the ionic charge, F is the Faraday constant, R is the gas constant and T is the temperature.

Fig. S5 shows bromide diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate as a function of temperature calculated from Nernst-Einstein equation. We observe PPO-TPQP-Ethyl lactate has a conflicting behavior towards water and bromide diffusion when compared with the other two membranes. Exploring why PPO-TPQP-Ethyl lactate has such a different behavior, we study the water contributions to the diffusion process by calculating hydration number normalized conductivity. We use conductivity measured under 60% RH to 95% RH (Fig. S6) divide by hydration number under the same humidity level as shown in Fig. S7. We observed as the RH increases, conductivity/ λ ratio of PPO-TPQP-Ethyl lactate increases more slowly than that of PPO-TPQP-Ethyl lactate and PPO-TPQP-DMSO. When relative humidity is 95% RH, conductivity/ λ ratio of PPO-TPQP-Ethyl lactate is less than half of PPO-TPQP-DMSO and PPO-TPQP-MIX. These findings indicate that single water molecule in PPO-TPQP-Ethyl lactate make the smallest contribution to conductivity, in

other words, PPO-TPQP-Ethyl lactate has a weakest correlation between water and conductivity, therefore exhibit a discrepancy between water and bromide diffusion.

4. Conclusions

In this study, DMSO, Ethyl lactate and DMSO & Ethyl lactate mix solvents were selected based on Hansen solubility parameter to drop cast PPO-TPQP containing the large phosphonium cation. All three membranes have modest water uptake in the range of 10-28 wt% after being soaked in DI water at 60 °C. From SAXS measurements, the membranes' nanoscale morphology was shown to be invariant with humidity. The peak at about d-spacing of 7-15 Å was consistent with the optimized cation size calculated by DFT from the Gaussian program. The casting solvents influence on the more hydrophilic and hydrophobic domain distributions were observed by AFM. Both SAXS and AFM demonstrate a poorly organized long-range order structure in the membranes. The membrane cast from the optimized solvent mixture, PPO-TPQP-MIX, did indeed have the highest conductivity among the three membranes with 3 mS/cm at 95% RH, 90 °C, while PPO-TPQP-Ethyl lactate has highest water diffusion coefficient of $6.3 \times 10^{-7} \text{ cm}^2/\text{s}$ at 100% RH, 25 °C. The PPO-TPQP-MIX material always showed Arrhenius behavior in bromide conductivity and water diffusion. Conductivity follows PPO-TPQP-MIX > PPO-TPQP-DMSO > PPO-TPQP-Ethyl lactate which are in the same order as water uptake. However, Water diffusion coefficient follows PPO-TPQP-Ethyl lactate > PPO-TPQP-MIX $\approx$ PPO-TPQP-DMSO since PPO-TPQP-Ethyl lactate has smallest tortuosity. Furthermore, PPO-TPQP-MIX and PPO-TPQP-DMSO have similar trends in

both conductivity and water diffusion versus temperature. Yet, PPO-TPQP-Ethyl lactate shows a linear Arrhenius relation in conductivity, while exhibits a VTF non-linear in water diffusion coefficient behavior. Such a different conductivity and diffusion behavior of PPO-TPQP-Ethyl lactate is due to its strongest bromide water decoupling. First, the activation energy at 80% RH doubles to that at 95% RH indicating water molecules contribute to dissociate ionic groups instead of improving the conductivity. Second, hydration number normalized conductivity confirms PPO-TPQP-Ethyl lactate does have the weakest water/bromide transport correlation.

Acknowledgments

The authors thank the Army Research Office for support of this research under the MURI grant number #W911NF-10-1-0520. The Advanced Photon Source operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was support by the U. S. DOE under Contract No. DE-AC02-06CH11357. We also thank Dr. Steven Abbott for the HSP calculation on PPO-TPQP by using the HSPiP package.

Appendix A. Supporting information

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

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Figure Captions

Fig. 1 Synthesis of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

Fig. 2 ^1H NMR (a), ^{31}P NMR (b) of tris(2,4,6-trimethoxyphenyl) phosphonium functionalized PPO.

Fig. 3 Visible microscope images of PPO-TPQP-Ethyl lactate. (Scale bar is 50 μm)

Fig. 4 AFM tapping mode phase images of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate. (Scan boxes are 500 nm $\times$ 500 nm)

Fig. 5 Water uptake and lambda value of PPO-TPQP casted from different solvents

Fig. 6 In-plane and through-plane swellings of PPO-TPQP casted from different solvents.

Fig. 7 SAXS and WAXS spectra of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate.

Fig. 8 Tris(2,4,6-trimethoxyphenyl) phosphonium cation optimized at the B3LYP/6-311G(2d,d,p) level of theory and basis set using the Gaussian 09 program.

Fig. 9 Water self-diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX, PPO-TPQP-Ethyl lactate versus the square root of the diffusion time.

Fig. 10 Water diffusion coefficients of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate in terms of different temperature under 100% RH.

Fig. 11 Bromide conductivities of PPO-TPQP-DMSO, PPO-TPQP-MIX and PPO-TPQP-Ethyl lactate as a function of temperature under 95% RH and 80% RH

Graphical abstract