Crystallite Dissolution in PEO-Based Polymers Induced by Water Sorption

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ABSTRACT

Poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) is a model hierarchically nanostructured polymer that contains PEO crystallites within microphase segregated block copolymer morphology. In order to investigate dynamics in this hierarchically nanostructured polymer, water was used as a selective, interacting probe molecule. First, the equilibrium effect of water sorption on the polymer structure was examined. Then, the coupled dynamics of structural changes and water diffusion were studied. At moderate water activity, crystallite dissolution caused water diffusion to appear non-Fickian (determined by Fourier Transform infrared – attenuated total reflectance spectroscopy). PEO deliquescence was so extreme at high water activity that dynamics could not be measured in a homopolymer control. In the block copolymer at unity water activity, a second stage of water sorption occurred that was attributed to relaxation of the glassy PS phase. Water desorption was ten times faster than sorption. Desorption is thought to be less hindered by tortuosity resulting from PEO crystallites. These results are of interest for a wide-range of applications including batteries and fuel cells, water desalination, food packaging, and biomedical implants.

1. Introduction

Water-containing polymers present complex systems that contain at least one hydrogen bonding component (water) and a component whose long-chain physics can only be accurately expressed statistically (polymer). This richness of interactions and significant entropic effects can lead to nonlinear sorption behavior. Furthermore, a range of dynamic time-scales can be present that include polymer relaxation, reactions, and water diffusion that can result in unexpected transport properties¹. Studies of the complex behavior of water sorption and diffusion in polymers have been on-going for decades. This is due to interesting behavior and the practical importance for applications such as biological processes, food packaging, protective coatings, and water purification^{2,3}.

Water sorption and diffusion in amphiphilic block copolymers (BCPs) are of interest for a wide range of applications⁴, including fuel cells⁵ and air batteries⁶⁻⁹, CO₂ separation¹⁰⁻¹³, water desalination^{14,15}, food packaging^{16,17}, drug delivery¹⁸, and biomedical implants¹⁹. Proton exchange membrane fuel cells and air batteries rely on a solid polymer electrolyte to separate the electrodes and conduct ions. In amphiphilic BCPs, the hydrophilic block provides ion conduction and the hydrophobic block provides mechanical strength²⁰. The ionic conductivity of fuel cells is intimately tied to water transport such that high water flux is desirable. On the other hand, the lithium electrode of lithium-air batteries is degraded by water, *ergo* the polymer electrolyte membrane should be impermeable to water. Or at least, it is necessary to determine the extent to which feed oxygen must be dehydrated in order to prevent water sorption into the polymer electrolyte. Polar polymers like poly(ethylene oxide) (PEO) are of interest for gas dehydration and separation due to selective solubility for H₂O and CO₂ over other gases²¹⁻²³, but a glassy (or crystalline) hydrophobic block is needed to make robust films that can withstand pressure gradients. The presence of water in polymer membranes is known to affect gas separation properties²⁴⁻²⁶. Another application in which amphiphilic BCPs are of interest is for membrane-based desalination, which requires high water flux while maintaining high salt rejection. Charged hydrophilic polymers tend to have high water flux and can reject ions based on Donnan exclusion²⁷, but a hydrophobic block is needed to prevent dissolution of the polymer membrane. Finally, BCPs have been used to control the degradation rate of degradable polymer for biomedical implants, in which water sorption enables polymer hydrolysis and subsequent dissolution²⁸. Clearly, fundamental understanding of sorption and transport of water in amphiphilic BCP membranes is important for a wide range of applications.

PEO is a polymer with amazing properties, such as an upper critical solution temperature in water, the ability to complex salts and charged polymers, and an ability to be mechanically degraded²⁹. Dilute solutions of high M_w PEO in water display significant friction reduction (Toms effect), which is of

engineering interest for pumping water and for coating ship hulls ²⁹. At higher concentrations, the solution displays some elastic character, siphoning out of an open beaker ²⁹. Block copolymers containing PEO are also of significant interest, for example as emulsifiers ³⁰⁻³². Despite the extensive work on PEO polymers in solutions and emulsions, the other limit, water sorption in neat PEO polymers, has received little attention, with only a few reports of water sorption in homopolymer PEO ³³ or low- M_w PEO-containing block copolymers ^{4, 34-36}. In all these studies, the PEO was amorphous. Reported properties of PEO vary widely due in large part to the variety of synthetic techniques with which the polymer can be synthesized and to the wide range of molecular weights that have been studied. In addition, the thermal stability of PEO appears to be strongly dependent on the presence of solvent, oxygen, and catalytic contaminants (such as residual synthesis reagents) ³⁷⁻³⁹. Interestingly, copolymers containing PEO have been reported to be more stable ⁶.

Poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) is an amphiphilic BCP consisting of hydrophilic blocks of PEO and hydrophobic blocks of PS. In high molecular weight lamellar PS-*b*-PEO, such as that studied in this work, the PEO crystallizes within the block copolymer structure. At room temperature, PS-*b*-PEO is a hierarchically structured material comprising semicrystalline hydrophilic domains within a glassy hydrophobic matrix. It can be synthesized with controlled living polymerization providing a material with well-defined molecular weight and controlled morphology. The properties of PS and PEO are well known so that the effects of BCP structure and water interactions can be better understood from experimental results. Due to interesting structure and practical usefulness, PS-*b*-PEO is a particularly interesting amphiphilic BCP in which to examine transport through heterogeneous media ⁴⁰. It has been discovered that small molecule transport in structured polymers often results in non-Fickian transport ^{41, 42}. In fact, small molecule transport has been used as a probe to better understand the structure and dynamics of semicrystalline block copolymers ^{6, 41, 43}. We asked the question, how does a semicrystalline amphiphilic BCP respond to being swollen by a selective solvent, such as water, that will interact with the semicrystalline phase? Furthermore, how does the polymer response affect water sorption and diffusion? A comprehensive study has been conducted to examine the effect of water activity on PEO crystallinity, and how the PEO crystallinity in turn affects water sorption and diffusion.

2. Experimental

2.1. Materials

Poly(styrene-*block*-ethylene oxide) copolymer (PS-*b*-PEO) and poly(ethylene oxide) (PEO) were prepared using anionic polymerization ^{44, 45}. The PS-*b*-PEO copolymer comprises a polystyrene block (M_n = 133 kg/mol, M_w = 145 kg/mol) and a PEO block (M_n = 114 kg/mol). The polydispersity index (PDI) of

the BCP is 1.11 as measured by gel permeation chromatography (Viscotek GPCmax with dimethylformamide solvent and 0.05 wt% LiBr). The PEO volume fraction is 0.42 as measured via ^1H Nuclear Magnetic Resonance and calculated using the density of each block at 25 °C ⁴⁶. The PEO homopolymer has an M_n of 143 kg/mol and a PDI of 2.3. Potassium acetate, sodium bromide, sodium chloride, and potassium nitrate were used as received (Sigma Aldrich). The aforementioned salts were used to prepare saturated aqueous salt solutions with corresponding water activities of 0.22, 0.56, 0.75, and 0.93. Deionized (DI) water from a Milli-Q water purification system was used throughout this study (resistivity of 18.2 M Ω ·cm).

2.2. Membrane preparation

PS-*b*-PEO and PEO were dissolved in *n*-methyl-2-pyrrolidone and cast onto nickel foil (for thermal and gravimetric experiments) or directly onto an attenuated total reflectance (ATR) crystal for Fourier Transform infrared spectroscopy (FTIR) experiments. Membranes were dried in an argon environment (H_2O and O_2 less than 1 ppm) at 60 °C overnight and then under vacuum at 90 °C for 12 hours. Dry membranes for thermal and gravimetric experiments have average thickness of 105 ± 11 μm (PS-*b*-PEO) and 98 ± 17 μm (PEO). The thicknesses of dry membranes for FTIR-ATR experiments are reported in Table S1. Specific sample thickness (rather than average of multiple samples) was used for analysis of each diffusion experiment.

2.3. Thermal property measurements

The thermal properties of PS-*b*-PEO and PEO membranes were measured using differential scanning calorimetry (DSC, TA Q100 with RCS event control). The effect of water vapor on the thermal properties of PS-*b*-PEO and PEO were studied by first equilibrating samples in a relative-humidity-controlled glove box. Equilibrated samples weighing between 2 and 7 mg were sealed in gas-tight DSC pans (Perkin Elmer) under controlled relative humidity. Dry samples were sealed in pans directly in argon environment without exposure to air. DSC scans were conducted between 5 °C and 140 °C at a scan rate of 5 °C/min. The temperature at each limit was maintained for 1 hour before the next heating or cooling step. The heating and cooling cycle was repeated 3 total times for each sample. The melting temperature of PEO (T_m) was measured as a function of water activity. The degree of crystallinity (X_c) was evaluated by measuring the area under the melting endotherm in the first heating scan using equation 1 ⁴⁷.

$$X_c = \frac{\Delta H_f}{w_{EO} \Delta H_f^o} * 100\% \quad (1)$$

ΔH_f is the enthalpy of formation of the crystalline PEO phase (J/g), ΔH_f^o is the enthalpy of formation of a perfect PEO crystal. ΔH_f^o was taken as 196.9 J/g as reported by other researchers with PEO of similar molecular weight^{6, 48-54}. w_{EO} is the weight fraction of PEO in the BCP ($w_{EO} = 0.46$) or PEO homopolymer ($w_{EO} = 1$). The reported error is based on three repeated DSC measurements of ΔH_f .

2.4. Small-Angle X-ray Scattering (SAXS).

To determine the effect of water content on the BCP morphology, small-angle X-ray scattering (SAXS) was conducted at beamline 12-ID-B at Argonne National Laboratory. PS-*b*-PEO membranes were equilibrated at different water activities and sealed in aluminum laminated pouches (MTI). The sample-to-detector distance for all measurements was 4 m. The 2-D SAXS images were azimuthally averaged to produce one-dimensional profiles of intensity, I , versus wave vector, $q = 4\pi \sin(\theta)/\lambda_{X\text{-ray}}$, where $\lambda_{X\text{-ray}}$ is the X-ray wavelength and θ is the Bragg angle. The X-ray wavelength was 0.0886 nm.

2.5. Gravimetric sorption

Sorption and desorption of water vapor were measured gravimetrically on 0.2 ± 0.05 g of PS-*b*-PEO and PEO membranes. The polymer samples were placed in a humidity-controlled glove box (ultrasonic humidification system, ETS). The membrane weight at each equilibrated humidity was measured (Metler Toledo, MS204S). All measurements were taken at ambient temperature (24 ± 1 °C) and controlled relative humidity ranging from 0 – 95 % relative humidity (RH). The equilibrium water uptake, W_T (g_{H2O}/g_{polymer}), at a given relative humidity was evaluated as follows:

$$W_T = \frac{W_{wet} - W_{dry}}{W_{dry}} \quad (2)$$

where W_{wet} is the weight of the membrane at a given relative humidity. W_{dry} is the weight of the dry membrane at 0 % RH (in an argon environment). At each relative humidity, two sorption and two desorption measurements were taken on three PS-*b*-PEO membranes and three PEO membranes, and average values are reported.

2.6. Time-resolved FTIR–ATR spectroscopy

Experiments were conducted with 45° multi-reflection germanium and zinc selenide ATR crystals (Specac) in an FTIR spectrometer with a mercury-cadmium-telluride (MCT) detector (Perkin Elmer, Frontier). The membrane-coated ATR crystal, salt solution, and vapor flow path were maintained at 30 °C with a water bath. All spectra were the result of 32 scans, collected at 4 cm⁻¹ resolution in the range of 4000 to 650 cm⁻¹. Time-resolved data were collected at intervals of 12 ± 1 seconds. The final spectra were used to determine equilibrium absorbance values at the humidities of interest.

Water diffusion was measured using OH stretching (3500 cm⁻¹). Polymer swelling was monitored using the COC stretch of PEO (1107 and 1114 cm⁻¹), the CH₂ stretch of PEO (2900 cm⁻¹), and the CH₂ stretch of PS (2924 cm⁻¹). Analysis of PEO swelling was not attempted in experiments on a ZnSe ATR crystal, because the COC stretching absorbance saturated the detector. For such analysis, experiments on a Ge ATR crystal were used. Water diffusion measurements were not sensitive to crystal type. Dissolution of PEO crystallites was tracked with the CH₂ vibration specific to PEO crystallites (843 cm⁻¹).

To measure the diffusion coefficient of water in each membrane the O-H stretching band was integrated from 3647 – 3117 cm⁻¹ at each time point and the integrated absorbance plotted versus time. Details of the FTIR-ATR data analysis can be found elsewhere^{1, 55-57}. The one-dimensional solution to Fick's Law with boundary conditions denoted in Figure 1 can be related to absorbance by integrating according to the Beer–Lambert Law.

$$\frac{A - A_o}{A_{eq} - A_o} = 1 - \frac{8}{\pi d_p \left[1 - \exp\left(-\frac{2l}{d_p}\right) \right]} \times \sum_{n=0}^{\infty} \frac{1}{2n+1} \left[\frac{\exp(-f^2 D_{eff} t) \left[f \exp\left(-\frac{2l}{d_p}\right) + (-1)^n \frac{2}{d_p} \right]}{\left(\frac{2}{d_p}\right)^2 + f^2} \right] \quad (3)$$

$$\text{where } f = \frac{(2n+1)\pi}{2l} \quad (4)$$

A is the integrated infrared absorbance at time t , A_o is the initial absorbance, and A_{eq} is the final equilibrium absorbance. For a thick membrane, where the ratio of membrane thickness (l) to the depth of penetration (d_p) is much greater than 10 (as was the case in this study), absorbance can be approximated as occurring at the polymer/ATR crystal interface ($z = 0$). This yields a simplified solution,¹

$$\frac{A - A_o}{A_{eq} - A_o} = \frac{C - C_o}{C_{eff} - C_o} = 1 - \frac{4}{\pi} \times \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp(-D_{eff} f^2 t). \quad (5)$$

The effective diffusion coefficient (D_{eff}) of water in PEO and PS-*b*-PEO is used as the only adjustable parameter to regress the model to the time-resolved data. At least three membranes were used for diffusion experiments at each relative humidity condition.

3. Results

3.1. Thermal properties

The thermal properties are presented in Figure 2(a) as a function of water activity. The melting behavior of the PEO phase of PS-*b*-PEO and of the PEO homopolymer was investigated at different water activities and are shown in Figure 2(a). There is a small increase in T_m from the dry state in argon to that at 5 %RH in air, possibly due to desorption of argon. Above 0.05 water activity, the melting temperature for both PS-*b*-PEO and PEO decreases with increasing water activity. The BCP has a lower T_m ($67 \pm 1^\circ\text{C}$) than the homopolymer ($70 \pm 2^\circ\text{C}$) at 0.05 water activity. This is due to confinement within the BCP morphology⁵⁸⁻⁶⁰. Both polymers follow a similar trend of slight decrease of T_m up to a water activity of 0.56. From 0.05 to 0.56, the T_m of both PS-*b*-PEO and PEO decreases by only 6% (4 °C). At a water activity of 0.75, both polymers have approximately the same T_m . This could suggest either that the PEO crystal lamellae, which were larger at low water activity, have been partially dissolved and are similar in size to those of PS-*b*-PEO, or that the slightly higher water uptake by PEO (reported below) causes a more significant colligative effect. At still higher water activity (e.g. 0.85), T_m decreases significantly. Based on experiments and analysis presented below, this is due to crystallite dissolution. From 0.05 to 0.85, the decrease in T_m is approximately 30% for PS-*b*-PEO and 21% for PEO. See Tables S2 and S3 in supporting information. We do not have an explanation for why the T_m of PEO is so much higher than that of PS-*b*-PEO at 0.85 water activity. This is nearing the conditions (≥ 90 %RH) at which PEO completely loses mechanical integrity and becomes deliquescent. So, it could be due to error in the measurement. On the other hand, one could surmise that the significant swelling of the PEO at 0.85 water activity might lead to chain-orientation-induced crystallization with higher T_m . This hypothesis is supported by the fact the PEO has significantly higher crystallinity than PS-*b*-PEO at 0.85 water activity (as shown in Figure 2b).

The degree (mass fraction) of PEO crystallinity (X_c) is shown in Figure 2(b) as a function of water activity. The dashed lines indicate the minimum PS-*b*-PEO crystallinity and maximum PEO crystallinity due to uncertainty in the literature values of ΔH_f° . Similar to T_m , X_c decreases with increasing water activity. At all water activities, X_c of the BCP is less than that of the homopolymer. Since this is the case even in the dry state, it is attributed to the BCP morphology, i.e. a smaller fraction of the PEO component can crystallize in the BCP, which has been shown to be due to confinement⁵⁸. There is a surprisingly large decrease in X_c from the dry membranes in argon to that at 5 %RH in air. It is unclear whether this is due to

argon desorption or strongly adsorbed water molecules ⁶¹. From 0.05 to 0.95 water activity, X_c of PS-*b*-PEO decreases by 49% (Table S3), and X_c of PEO decreases by 38% (Table S2). Not only does the loss of crystallinity profoundly affect the mechanical properties ⁶², but it also has an influence on water uptake and diffusion as described below.

3.2. Polymer structure

The effect of water on the morphology of the BCP was investigated with SAXS for humidity controlled samples, shown in Figure 3 as a Kratky plot (i.e., Lorentz corrected). The dry polymer scattering is indicative of a lamellar morphology showing primary, tertiary, and quinary peaks. Absence of secondary and quaternary peaks has been observed in symmetric BCPs ⁶³. In the SAXS profiles, several effects are apparent with increasing relative humidity. The intensities of the BCP scattering peaks decrease with increasing water content. This could be due to contrast matching between the PS phase and the PEO + water phase. The scattering length density, B_i , for X-rays can be calculated using⁶⁴

$$B_i = \frac{r_e \sum_j Z_j}{v_{mon}}, \quad (6)$$

where r_e is the classical radius of an electron ($2.82 \times 10^{-6} \text{ nm}$ ⁶⁵), Z_j is the number of electrons in a monomer of volume v_{mon} . The monomer volume was calculated using the specific volume, V_i , at 25 °C and molar mass, M_i , of each component:

$$v_{mon} = \frac{\hat{V}_i M_i}{N_A}, \quad (7)$$

where N_A is Avogadro's number. The constants used for each component are reported in Table 1. B_i of the water + PEO phase was then calculated as a simple volume fraction weighted average of the respective B_i 's. It makes little difference whether semicrystalline (or amorphous) PEO is used in this calculation, a water content of 98.5 (or 97) vol% would be required to reduce the electron density of the PEO phase to that of the PS phase. This is approximately three times the highest water content measured in this study (38 vol% at 95 %RH). If compression of the PS phase (due to PEO swelling) is considered, then contrast matching is possible. At 11% compression, $\hat{V}_{PS}$ is $0.8701 \text{ cm}^3/\text{g}$ and B_{PS} is $1.05 \times 10^{-3} \text{ nm}^{-2}$, the same as semicrystalline PEO with 38 vol% water. The loss of scattering due to the BCP morphology could also be due to a loss of BCP order, caused by water compatibilizing PEO and PS. However, this interpretation is at odds with DSC results, in which the BCP T_g tracks that of homopolymer PS.

In addition to the decrease in BCP scattering intensity, the primary and tertiary peaks shift to lower q , indicating that the domain spacing is increasing due to water swelling. The domain spacing was calculated using Braggs Law from both the primary scattering wave vector, q^* , and from the tertiary scattering peak, $3q^*$. q^* was determined from a Gaussian regression to the data. The $3q^*$ peak had much less noise than q^* and did not require a Gaussian regression. The average domain spacing calculated from q^* and $3q^*$ is reported in Table 2. The value of q^* at 5 %RH is 145 nm. At the highest humidities (85 and 95 % RH), the scattering peaks were too weak to reliably determine a domain spacing and are therefore not reported.

In the magnified inset of Figure 3, a high- q shoulder is apparent on the quinary peak as well as a broad peak at 0.545 nm^{-1} in the dry BCP. These peaks correspond to the PEO crystallite long spacing (i.e., crystal lamellae center-to-center distance or fold length) ⁶⁶. The samples were not isothermally crystallized, but rather cooled to room temperature after drying. Therefore, the PEO crystals formed at deep undercooling. Coupled with the high molecular weight, nonintegral folding is expected and the broad crystal lamella peak with 11.5 nm spacing agrees well with a wide range of PEO molecular weights reported in literature for nonintegral, rapid, metastable PEO folding ^{67,68}. This is to be expected based on the fact that crystal lamellar spacing is dictated by the critical nucleus size ⁶⁹. The shoulder that is only present in dry PEO, has a spacing of 22 nm, which has been observed in poly(butadiene)-PEO and PS-PEO BCPs crystallized at room temperature ^{66, 70}. It is roughly twice the major crystal peak and might be caused by the mutual rearrangement of adjacent crystals ⁷¹. PEO crystallization has also been carefully studied in low molecular weight PS-PEO ⁷² and PEO-PPO-PEO BCPs ⁷³. The 11.5 nm crystal lamellar spacing of the broad peak in our SAXS data agrees reasonably well with these BCP references. At moderate humidity (56 and 75 %RH) the broad peak shifts to slightly lower q (0.48 nm^{-1} , i.e., the crystal lamellar spacing increasing to 13 nm) and becomes significantly more intense. Clearly water is swelling the amorphous interlamellar PEO, which one might expect to be necessary for crystallite dissolution. Crystal lamellae swelling by water has been observed in polyacrylonitrile ⁷⁴ and crystallite dissolution by water has been observed in polyvinylalcohol ⁷⁵. Since we know from thermal measurements that the crystallinity does not increase, we infer from the increased intensity of the crystal scattering peak that water increases the contrast between PEO crystallites and amorphous regions. The scattering length density of water ($B_{\text{water}} = 0.94 \times 10^{-3} \text{ nm}^{-2}$) is significantly less than that of PEO crystals ($B_{\text{PEOc}} = 1.18 \times 10^{-3} \text{ nm}^{-2}$, estimated based on semicrystalline PEO X_c being $0.6 \text{ g}_{\text{crystal}}/\text{g}_{\text{total}}$). In other words, water decreases the electron density of the amorphous PEO where it is preferentially sorbing. An extreme example of this effect is in starch, where crystal/amorphous contrast is not possible without water sorption ⁷⁶. At yet higher humidity, significant dissolution of PEO crystallites occurs and the broad peak disappears. At this time, we do not have an explanation for the lack of a PEO crystallite peak at 22 %RH other than to say that it appears to be an outlier. We point the reader to interesting

reports of non-monotonic properties of PEO with increasing hydration^{77, 78} and with increasing crystallization temperature⁶⁷. It is worth noting that the increase in intensity of the broad crystal lamellae peak could be due to improved packing of the PEO lamellae from a transition in the supermolecular structure⁷⁹ or from a crystal-crystal transition^{80, 81}, either of which could be induced by water uptake.

3.3. Water uptake

The water sorption isotherms of PS-*b*-PEO and PEO membranes are shown in Figure 4 along with several results from literature. Water uptake values from sorption and from desorption experiments were not statistically different. Only sorption results are shown for clarity. At most water activities, the amount of water vapor sorbed in PEO is nearly twice as high as that in PS-*b*-PEO. This can be explained by the weight fraction of PEO in the PS-*b*-PEO membrane, which is 0.46. Although water molecules can occupy free voids within the amorphous polystyrene phase⁸², the total amount of water sorbed into PS films is small compared to that in PEO. Day et al. report water sorption of 0.048% by weight in PS at 0.70 water activity⁸². In other words, the water content in the PEO phase of PS-*b*-PEO is similar to that in the PEO homopolymer.

Below a water activity of 0.56, PS-*b*-PEO and PEO membranes absorb less than 0.01 g_{H2O}/g_{polymer}, and the water uptake has a roughly linear dependence on water activity. The literature results show similar behavior (Figure S1), especially considering the fact that the PEO molecular weight in the homopolymers and BCPs range from 1,000 g/mol to 200,000 g/mol. Such behavior is typical of rubbery polymers, such as PEO, which is well above its T_g . In fact, a linear regression yields the Henry's Law coefficient (k_D) or the partition coefficient (K) if the water vapor concentration is used rather than partial pressure. For PEO, $k_D = 41$ mol/L bar and $K = 1000$. For PS-*b*-PEO, $k_D = 28$ mol/L bar and $K = 700$. Note the lower slope for the BCP attributable to the presence of the glassy, hydrophobic PS phase.

Above a water activity of 0.56, the water content is a much stronger function of water activity, and the agreement among the various reports is poorer. A roughly exponential sorption isotherm is widely observed for more condensable gases and vapors in rubbery polymers, such as PEO⁸³. This behavior is often modeled with a modified Flory-Huggins equation^{84, 85}. This model does not fit our data well unless the PEO-water interaction parameter, χ , is taken to be a function of polymer volume fraction, which is explained by theory for PEO⁸⁶. At low water activity (and low water volume fraction or high polymer volume fraction) χ is roughly constant for both PEO and PS-*b*-PEO at a value of 3.2 ± 0.4 . As the water content in the membrane increases significantly (above an activity of 0.56), χ decreases with a quadratic dependence on polymer volume fraction to a value of 1.2 in PEO and 1.3 in PS-*b*-PEO at a water activity of 0.9. Note that both polymers have similar polymer volume fractions at this activity (0.85 for PEO and 0.86 for PS-*b*-PEO). Remarkably, despite the similar polymer volume fractions, at a water activity of 0.9, PEO is a gel while

PS-*b*-PEO is a tough solid. These values of χ agree well with literature⁸⁷, and they demonstrate that the PEO-water interactions become more favorable with increasing water activity. Based on the similarity between PS-*b*-PEO and PEO sorption isotherms, it seems that loss of PEO crystallinity in the polymers is closely linked to water sorption above a water activity of 0.56. Data above a water activity of 0.9 may not be reliable for homopolymer PEO due to it becoming deliquescent. Even though the PEO was of high molecular weight with highly entangled chains, it became a soft gel with no mechanical strength at high relative humidity. Similar behavior was reported for low molecular weight PEO membrane by Singh *et al*³⁵. The authors observe a sharp upturn in sorption around 0.75 water activity, and surmise that PEO/water interactions overcome crystallite restraints and lead to dissolution.

Water uptake in PS-*b*-PEO and PEO membranes was also measured using FTIR-ATR spectroscopy. The FTIR-ATR spectra of the polymers equilibrated at different water activities are shown in Figure 5a for PS-*b*-PEO and in Figure 5b for PEO between 3800 and 2600 cm⁻¹. With increasing water activity, the IR absorbance due to water O-H stretching (3647 - 3117 cm⁻¹) increases in both polymers. A calibration of the integrated O-H stretching absorbance versus membrane water concentration (from gravimetric measurements) is shown in Figure S2. The decrease in the value of d_p with increasing humidity was insignificant, changing by only 3% over the entire range of humidities studied. The polymer CH₂ stretching absorbance (3000 - 2750 cm⁻¹) in Figure 5 decreases with increasing water activity. This indicates that the polymer is being swollen by water. This effect is particularly noticeable at the highest humidities (93 and 100 % RH). It is interesting to note that in Figure 5a, the decrease in PEO CH₂ stretching (2900 cm⁻¹) is much more significant than the decrease of PS CH₂ stretching (2924 cm⁻¹). This intuitively makes sense; the water preferentially swells the hydrophilic rubbery PEO but swells the hydrophobic glassy PS much less. Hydrated amorphous PEO is significantly less dense and mechanically weaker than dry semicrystalline PEO.

3.4. Water diffusion

Time-resolved FTIR-ATR spectroscopy has been used to examine water diffusion as well as polymer swelling and PEO crystallite dissolution in PS-*b*-PEO and PEO membranes. Figure 6 shows the time-resolved infrared spectra of a selected diffusion experiment: water diffusion through an initially dry PS-*b*-PEO membrane with an equilibrating water activity of 1.00. The infrared bands of interest are listed in Table 3. None of the peaks of interest overlap, except the aliphatic CH₂ vibrations of PEO and PS. However, even the CH₂ vibrations are sufficiently resolved to analyze qualitatively.

In Figure 6, the initial spectrum of the dry membrane is orange. In the OH region there is a very weak signal from the hydroxyl chain ends of PEO. The signals from all polymer peaks are most intense in the

dry spectrum. As water molecules diffuse across the membrane and reach the polymer/ATR interface, the OH stretching absorbance (due to water) increases and the polymer peaks decrease. For example, the low wavenumber region (800 - 1200 cm^{-1}) in Figure 6 shows the COC stretching of the PEO backbone and the CH_2 rocking of the PEO crystals decreasing with time. The final, equilibrium spectrum is blue. Similar to the behavior at equilibrium (Figure 5a), the CH_2 absorbance of PEO (2900 cm^{-1}) decreases dramatically with time, whereas that of PS (2924 cm^{-1}) has little change. This suggests that the PEO domains of the BCP swell to a large extent, but that the macroscopic swelling of the BCP is less significant. Dissolution of PEO crystals and compression of the PS phase allows this to occur. It is important to mention that, due to phase error, there is some negative absorbance in the infrared spectra. Such errors have been reported by Miljković *et al*⁸⁸ to be a consequence of dispersive and reflective line shape contributions in asymmetric interferograms, which translates into negative absorbance after Fourier transformation. The negative signals did not interfere with any of the bands of interest.

Water diffusion has been investigated quantitatively by integrating the OH peak from 3117 to 3647 cm^{-1} and plotting the integrated absorbance versus time. This result is presented in Figure 7. The integrated absorbance is initialized by the dry value and normalized by the difference between the equilibrium value and the dry value $[(A-A_o)/(A_{eq}-A_o)]$. Four representative experiments at water activities of 0.56, 0.75, 0.93, and 1.0 are shown for PS-*b*-PEO (Figure 7 a-d). Two representative experiments at water activities of 0.56 and 0.75 are shown for PEO (Figure 7 e-f). Experiments on PEO at water activities of 0.93 and 1.0 were not reproducible (due to loss of mechanical integrity) and are therefore not reported. For both polymers, no water signal was detected with FTIR-ATR at an activity of 0.22.

The best-fit diffusion model (equation 5) is presented as a solid line in each pane of Figure 7. The apparent diffusion coefficients (D_{eff}) from the regressions are reported in Figure 7. The averages and standard deviations of repeated diffusion experiments are reported in Table 4. Water transport at 56 %RH is anomalous in both polymers. This is apparent in the deviation between the time-resolved FTIR-ATR data and the Fickian model in Figures 7a and 7e. Water transport appears non-Fickian also at 75 %RH in the block copolymer (Figure 7b), but appears Fickian in the homopolymer (Figure 7f). At 93 %RH, water diffusion in PS-*b*-PEO appears Fickian (Figure 7c). At 100 %RH (Figure 7d), the data has a distinctly different anomalous shape, which is reminiscent of two-stage diffusion behavior. The first stage has a diffusion coefficient of $5.0 \times 10^{-8} \text{ cm}^2/\text{s}$, similar to results at other water activities. The second stage is slower with an apparent diffusion coefficient of $9.8 \times 10^{-9} \text{ cm}^2/\text{s}$. As shown in Table 4, despite the deviations from Fickian behavior and excluding the second stage at 100 %RH, the apparent diffusion coefficient of water in PEO and PS-*b*-PEO during sorption is within the same order of magnitude for all humidities with an average value of $(6 \pm 3) \times 10^{-8} \text{ cm}^2/\text{s}$.

Spectroscopic evidence of PEO crystallite dissolution at different water activities is presented in Figure 8 where the absorbance of the CH₂ vibration of PEO crystallites is shown from 870 – 820 cm⁻¹. Characteristic experiments of water vapor at 56 %RH diffusing into dry PS-*b*-PEO (Figure 8a) and PEO (Figure 8e) show very little change in the CH₂ vibration of the PEO crystallites. This corroborates the sorption and DSC results, which show only small changes up to 56 %RH. At 75 %RH, the diffusion of water in PS-*b*-PEO (Figure 8b) and PEO (Figure 8f) causes more significant decrease of the PEO crystallite peak. Crystallite dissolution appears to be more significant in PEO than in PS-*b*-PEO. The time-resolved integrated absorbance of these peaks (Figure S3) shows that crystallite dissolution is slower in PEO (almost 3000 s to reach equilibrium) than in PS-*b*-PEO (only 1000 s to reach equilibrium). Differences in the rate of crystallite dissolution between PEO and PS-*b*-PEO could be due to differences in crystallite size/surface area, crystal lamellae orientation⁸⁹, and supermolecular structure⁷⁹. At 93 %RH (Figure 8c) and 100 %RH (Figure 8d) the diffusion of water in PS-*b*-PEO causes the PEO crystallite absorbance to decrease by about half. At these conditions a large fraction of the PEO crystallites are dissolved, and at 100 %RH significant swelling occurs. Interestingly, in both Figure 8c and Figure 8d, the crystallite absorbance goes through a minimum, recovering a noticeable amount of absorbance in the final approach to equilibrium (see supporting information Figure S3 for time-resolved curves of the integrated absorbance). We suspect that interplay between internal stress and crystallinity is taking place. The rapid crystallite dissolution and swelling of the PEO phase occurs with little change in the PS phase, suggesting that the PS phase is withstanding some compression. Slow relaxation of these compressive forces is presumably mediated by PS relaxation and allows for macroscopic swelling of the PS-*b*-PEO membrane. Such relaxation allows for the large, slow second diffusion stage in the 100 %RH experiment and apparently some swelling-induced recrystallization⁹⁰.

The COC stretching vibrations of the polymer between 1170 and 1000 cm⁻¹ are shown in supporting information Figure S4. This peak changes both with a change in crystallinity and with PEO swelling. With increasing humidity, the primary COC stretching peak at 1111 cm⁻¹ broadens and decreases in intensity. The time-resolved curves of the COC vibration, embodying both crystallite dissolution and swelling, are shown in Figure S5. The time-resolved changes of the CH₂ vibration of PEO crystallites (Figure S3) and of the COC vibration (Figure S5) are quite similar, further supporting the assertion that PEO swelling is primarily due to crystallite dissolution.

4. Discussion

Regarding water sorption in the membranes, we should distinguish this work from previous reports on water vapor sorption and permeation in PEO-based block copolymers that include poly(amide-6-*b*-

ethylene oxide) (AKA PEBAX[®]) and poly(butylene terephthalate-*b*-ethylene oxide) (PBT-*b*-PEO)^{91, 92}. In these previous studies, the molecular weight of the PEO block was on the order of 1000 g/mol, such that the PEO T_m was below room temperature. Unfortunately, the block copolymer morphology was not reported. However, equilibrium sorption and diffusion were reported. In those studies, the water sorption isotherms were able to be regressed to the Flory-Huggins equation, albeit with a concentration dependent interaction parameter (χ)⁹¹. χ was negative (as expected for attractive interactions), but became less negative with increasing water activity. Some thermodynamic arguments could be made to explain this trend, but the configurational entropy of the polymer should not be neglected. In contrast, χ values for PEO-water interaction determined in aqueous solution were found to be positive and increase with increasing polymer concentration to a value of 1.24 at a polymer volume fraction of 0.9⁸⁷. Aqueous solutions of PS-*b*-PEO reported similar results⁹³. When we determined χ from either our sorption isotherms or from melting point depression⁹⁴, the apparent χ was found to be positive (between 1 and 5). Note that caution is needed when determining χ from melting point depression, because the penetrant can decrease crystallite size (due to dissolution)⁹⁵. Smaller crystallites have higher surface energy (i.e. are less stable), and melt at lower T_m ⁹⁶. The apparent χ from our results agree well with the solution studies, which was unexpected based on the fact that crystallite dissolution is occurring in our samples during water sorption.

The mechanism of crystallite dissolution is congruous with all of our experimental results. The large increase of equilibrium sorption at high water activity can be attributed to crystallite dissolution, which has the following effects: 1) amorphous PEO is less dense than crystalline PEO allowing for greater water uptake, and 2) it decreases the mechanical strength of the PEO phase allowing for more polymer swelling. The apparent non-Fickian water diffusion is due to crystallite dissolution. Water molecules participating in crystallite dissolution can be considered immobilized during the dissolution process. The fact that crystallite dissolution is affecting water diffusion during sorption experiments is driven home by Figure 9, which shows that water desorption from water activity of 1.00 to dry ($D_{eff} = (2 \pm 1) \times 10^{-7} \text{ cm}^2/\text{s}$) is ten times faster than the first stage of water sorption from dry to water activity of 1.00. During desorption, crystallite dissolution is not occurring and fewer crystallites are present so that water diffusion is less tortuous. During desorption, there is also not a polymer relaxation constraint⁹⁷. During sorption however, more crystallites are initially present leading to more tortuous diffusion. The second stage of sorption from water activity 0 to 1.00, coincides with slow PS relaxation. The glassy PS phase allows the block copolymer to resist larger swelling pressure than can the semicrystalline rubbery PEO homopolymer. Apparent non-Fickian diffusion is known to be caused by polymer relaxation⁹⁸⁻¹⁰⁰ and even penetrant reaction^{1, 56}, but in PEO and PS-*b*-PEO the non-Fickian behavior during sorption appears to be due to crystallite dissolution. We are aware of

only one other report of PEO crystallite dissolution by water sorption inferred from gravimetric measurements on exceptionally small samples ¹⁰¹. Our results are in agreement with this report.

The chemical reaction presented below represents similar behavior observed from the experiment as water (W) diffuses into the membrane and PEO crystallites (P_c) dissolve to form amorphous PEO (P_a).

Strongly adsorbed water on PEO crystals ($P_c \cdot W$) has been observed previously ⁶¹. We neglect macroscopic swelling of the membrane, which we consider a reasonable approximation at water activities less than 1. In other words, the sorbed water fills the existing free volume of amorphous polymer and the free volume created by crystallite dissolution. The two-step reaction forming a crystal–water complex ($P_c \cdot W$) and consequent dissolution of PEO crystallites is considered irreversible ($k_i \gg k_{-i}$).

A mathematical description of the above chemical reaction involves that of coupled dynamics of water diffusion and crystallite dissolution. Neglecting convection and assuming a concentration-independent diffusion coefficient, the governing equations can be written in one dimension as:

$$\frac{\partial C_w}{\partial t} = D \frac{\partial^2 C_w}{\partial z^2} - k_1 C_w C_c + k_2 C_{cw} \quad (7)$$

$$\frac{dC_c}{dt} = -k_1 C_w C_c \quad (8)$$

$$\frac{dC_{cw}}{dt} = k_1 C_w C_c - k_2 C_{cw} \quad (9)$$

where C_w is the water concentration in the membrane, C_c is the concentration of accessible PEO crystals, and C_{cw} is the concentration of PEO crystal–water complexes. For simplicity, the above equations were nondimensionalized using the following:

$$\theta_w = \frac{C_w}{C_w^f}, \tau = \frac{D_{eff} t}{L^2}, \eta = \frac{z}{L}, \alpha = \frac{k_1 L^2 C_c^o}{D_{eff}}, \gamma = \frac{k_2}{k_1 C_w^f}, \lambda = \frac{C_w^f}{C_c^o}, \theta_c = \frac{C_c}{C_c^o}, \theta_{cw} = \frac{C_{cw}}{C_c^o}.$$

Water concentration is normalized by the final water concentration in the membrane, C_w^f . Time is

normalized by the diffusion time, $\frac{L^2}{D_{eff}}$. Position is normalized by the membrane thickness, L . The

Damköhler number, α , is the ratio of the reaction rate to the rate of mass diffusion. A modified equilibrium rate constant, γ , is the ratio of the second and first reaction rate constants normalized to final water concentration. Nondimensionalization requires λ , the ratio of final water concentration to initial accessible crystal concentration. Finally, the accessible crystal concentration and water-crystal complex concentration are normalized to the initial accessible crystal concentration, C_c^o . The governing equations in dimensionless form are as follows:

$$\frac{\partial \theta_w}{\partial \tau} = \frac{\partial^2 \theta_w}{\partial \eta^2} - \alpha \theta_w \theta_c + \gamma \alpha \theta_{cw} \quad (10)$$

$$\frac{d \theta_c}{d \tau} = -\lambda \alpha \theta_w \theta_c \quad (11)$$

$$\frac{d \theta_{cw}}{d \tau} = \lambda \alpha \theta_w \theta_c - \lambda \gamma \alpha \theta_{cw} \quad (12)$$

At the free surface of the membrane ($z = L$), the polymer is in equilibrium with the water vapor such that $C_w(t, L) = C_w^f$ or $\theta_w(\tau, 1) = 1$ (for sorption). At the membrane-crystal interface ($z = 0$) an impermeable boundary is present such that $\frac{dC_w}{dz}(t, 0) = 0$ or $\frac{d\theta}{d\eta}(\tau, 0) = 0$. For a sorption experiment the membrane is initially dry, $C_w(0, z) = 0$ or $\theta(0, \eta) = 0$. With these initial and boundary conditions, the governing equations (10-12) can be solved numerically, for example using an explicit forward time, centered space (FTCS) algorithm. The space domain was divided into 100 node points, and each experimental time step was divided into 10,000 node points. A parametric study was conducted to better understand the effect of crystallite dissolution on water transport. The numerical solution presented in Figure 10 (a-c) shows the effect of (i) the Damkohler number (α) and (ii) the equilibrium water concentration in the polymer normalized to the initial accessible PEO crystal concentration (λ). For all cases presented here, we consider the rate constant of reaction 1 as much greater than that of reaction 2 ($k_1 \gg k_2$ and $\gamma = 0.001$).

In Figure 10 (a), $\lambda = 0.1$; this is a typical experimental condition for 56 %RH. When $\alpha \sim 1$, the rate at which water is immobilized by PEO crystals is similar to the rate at which water diffuses into the membrane, and apparent non-Fickian behavior results, which is similar to that observed experimentally in Figure 7 (a & e). Although we do not spectroscopically detect significant crystal dissolution at 56 %RH, this does not preclude reaction 1 from immobilizing a significant fraction of water. When $\alpha \ll 1$ the dissolution kinetics

are much slower than diffusion and apparent Fickian behavior is observed. This explains why the slower dissolution of crystallites in PEO results in apparent Fickian behavior at 75 %RH (Figure 7 (f)), while the faster dissolution of crystallites in PS-*b*-PEO maintains $\alpha \sim 1$ at 75 %RH (Figure 7 (b)). When $\alpha \gg 1$ the dissolution of PEO crystals is much faster than diffusion and a prolonged time lag is apparent as water is rapidly immobilized by reaction with the crystallites followed by an overshoot resulting from water being freed after crystal dissolution is complete. This type of behavior was not observed experimentally, but could be realized with a much thicker membrane. In Figure 10 (b) with $\lambda = 1$ the effect of α on water transport is similar but with smaller departures from apparent Fickian behavior. In Figure 10 (c) the final concentration of water in membrane is larger ($\lambda = 10$) and apparent Fickian behavior is observed for all α . This agrees with our results at high water activity, where the final water concentration is large and water transport appears Fickian (Figure 7 (c) and first stage of 7 (d)). In order to capture the second stage of diffusion in PS-*b*-PEO observed at 100 %RH, a polymer relaxation component would need to be incorporated into the model as well as accounting for volumetric swelling. Quantitative analyses of these results are forthcoming in a subsequent publication.

5. Conclusions

Water dissolves PEO crystals, which leads to a large upturn in water uptake at high humidity. At 56 %RH, water immobilization by PEO crystals has a similar rate to water diffusion in both PEO and PS-*b*-PEO resulting in non-Fickian diffusion behavior. As humidity is increased to 75 %RH, crystallite dissolution occurs more slowly in PEO than in PS-*b*-PEO most likely due to constrained crystals in PS-*b*-PEO being less stable. Since the rate of crystal dissolution in homopolymer PEO is significantly slower than that of water diffusion, transport appears Fickian. At yet higher humidity (93 %RH), the final water concentration in PS-*b*-PEO is high enough that transport appears Fickian regardless of the rate limiting transport mechanism. The loss of mechanical integrity prevented experiments on PEO above 90 %RH, but experiments on PS-*b*-PEO at 100 %RH found that the extent of crystallite dissolution is so large that significant swelling results in two-stage diffusion. The first stage of diffusion is similar to that observed at 93 %RH. The second stage of diffusion is slower, mediated by PS relaxation of internal swelling stress. Water diffusion during desorption was found to be an order of magnitude more rapid than during sorption. The BCP morphology constrains PEO crystallite size and allows for use over a broad range of conditions by mitigating crystallite dissolution with mechanical strength from the glassy PS phase. This work reports coupled crystallite dissolution and water transport in PEO-based polymers, which are of interest for energy, water, and food.

ASSOCIATED CONTENT

Supporting Information. Figures, tables, and text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Values for X-ray scattering length density calculations.

Component	$\hat{V}_i$ (cm ³ /g)	M_i (g/mol)	Z_i	B_i (10 ⁻³ nm ⁻²)	$\hat{V}_i$ reference
PEO (amorphous)	0.8945	44.05	24	1.03	46
PEO (semicrystalline)	0.8285	44.05	24	1.12	46
PS	0.9658	104.15	56	0.95	46
Water	1.0	18.02	10	0.94	102

Table 2. Domain spacing of PS-*b*-PEO membrane at different water activity.

% RH	d (nm)
5	145 ± 2.9
22	150 ± 1.3
56	150 ± 1.3
75	158 ± 0.3

Table 3. Infrared band assignments.

IR Band Maximum (cm ⁻¹)	Vibration Type	Component	Reference
843	CH ₂ rocking	PEO crystalline	103
1107	ν_s (COC)	PEO	104
1114	ν_a (COC)	PEO	104, 105
2900	ν (CH ₂)	PEO	106
2924	ν (CH ₂)	PS	107
3550	ν_s (OH) and ν_a (OH)	H ₂ O	108

ν_s = Symmetric stretching mode, ν_a = Asymmetric stretching mode

Table 4. Apparent diffusion coefficients of water in PEO and PS-*b*-PEO membranes.

Water activity	Diffusion coefficient ($\times 10^{-7}$ cm ² /s)		Transport Behavior	
	PEO	PS- <i>b</i> -PEO	PEO	PS- <i>b</i> -PEO
0.56	0.37 ± 0.27	1.55 ± 0.18	Non-Fickian	Non-Fickian
0.75	0.39 ± 0.23	0.91 ± 0.58	Fickian	Non-Fickian
0.93	Deliquescence	0.33 ± 0.10	N.A.	Fickian
1	Deliquescence	⁽¹⁾ 0.33 ± 0.10 ⁽²⁾ 0.10 ± 0.02	N.A.	Two stages

⁽¹⁾ first stage, ⁽²⁾ second stage

Figures

Figure 1. Schematic of a polymer membrane on an impermeable ATR crystal at $z = 0$ and with controlled humidity at $z = L$.

Figure 2. (a) Effect of sorbed water on the thermal properties of PS-*b*-PEO and PEO membranes.

Figure 2. (b) Degree of crystallinity versus water activity, calculated from DSC data.

Figure 3. One-dimensional SAXS profiles of PS-*b*-PEO membranes equilibrated at different water activities.

Figure 4. Water uptake in PS-*b*-PEO and PEO membranes as a function of water activity. The inset shows an expanded section of the isotherms from 0 to 0.6 water activity.

Figure 5. Equilibrated FTIR-ATR spectra at different water activities showing the O-H stretching and CH₂ stretching region for (a) PS-*b*-PEO and (b) PEO.

Figure 6. Time-resolved FTIR-ATR spectra of water diffusion into a dry PS-*b*-PEO membrane. The final spectrum (blue) of the polymer equilibrated at a water activity of 1.00 was collected at 25,000 s. Arrows represent absorbance increase or decrease with time. Wavenumber axis is broken from 1750 to 2500 cm⁻¹.

Figure 7. Normalized, integrated O-H stretching absorbance (○) of water in PS-*b*-PEO membranes at 30 °C for equilibrating water activities of a) 0.56, b) 0.75, c) 0.93, d) 1.00 and PEO membrane: e) 0.56 and f) 0.75. The curves are regressions of the Fickian diffusion model.

Figure 8. Time-resolved FTIR-ATR spectra showing variation of the PEO crystalline band in the range from 820 to 870 cm^{-1} during the process of water diffusion into PS-*b*-PEO membrane at different activities of water vapor: a) 0.56, b) 0.75, c) 0.93, d) 1.00; and into PEO membrane at different activities of water vapor: e) 0.56 and f) 0.75.

Figure 9. Water sorption/desorption in dry/hydrated PS-*b*-PEO membrane to/from 100 %RH at 30 °C.

Figure 10. Parametric study of the diffusion – crystallite dissolution model, where three values of the Damköhler number, α , are shown in each panel and lambda, λ , is varied between panels.

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