



# Crystallite dissolution in PEO-based polymers induced by water sorption



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## ARTICLE INFO

### Article history:

Received 30 June 2016

Accepted 7 August 2016

Available online 11 August 2016

### Keywords:

Amphiphilic block copolymer

Water uptake

Water diffusion

Hierarchical polymer structure

Crystallite dissolution

## 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.

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## 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 properties [1]. 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 applications [4], including fuel cells [5] and air batteries [6–9], CO<sub>2</sub> separation [10–13], water desalination [14,15], food packaging [16,17], drug delivery [18], and biomedical implants [19]. 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 strength [20]. 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 H<sub>2</sub>O and CO<sub>2</sub> over other gases [21–23], 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 properties [24–26]. Another application in which amphiphilic BCPs are of interest is for

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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 exclusion [27], 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 dissolution [28]. 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 degraded [29]. 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  $^1\text{H}$  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 $\Omega$  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 ( $\text{H}_2\text{O}$  and  $\text{O}_2$  less than 1 ppm) at 60 °C overnight and then under vacuum at 90 °C for 12 h. Dry membranes for thermal and gravimetric experiments have average thickness of  $105 \pm 11$   $\mu\text{m}$  (PS-*b*-PEO) and  $98 \pm 17$   $\mu\text{m}$  (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 h 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].

$$X_c = \frac{\Delta H_f}{w_{EO}\Delta H_f^0} * 100\% \quad (1)$$

$\Delta H_f$  is the enthalpy of formation of the crystalline PEO phase (J/g),  $\Delta H_f^0$  is the enthalpy of formation of a perfect PEO crystal.  $\Delta H_f^0$  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  $\Delta H_f$ .

### 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

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