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Study of gas permeabilities through polystyrene-*block*-poly(ethylene oxide) copolymers

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ABSTRACT

Pure gas permeability through a polystyrene-*b*-poly(ethylene oxide) block copolymer (SEO) membrane was measured between 20 and 80 °C. The membrane comprised alternating polystyrene (PS) and poly(ethylene oxide) (PEO) lamellae; the average center-to-center distance between adjacent PS lamellae was 96 nm. Among the different gases considered, carbon dioxide showed the highest permeability, with values up to 200 Barrer, followed by helium, oxygen, methane and nitrogen. Gas permeability appeared to be controlled by condensability of the gas, molecular size, and molecular interactions. The melting of poly(ethylene oxide) (PEO) domains, which occurred between 40 and 60 °C, caused deviation from Arrhenius behavior. A simple model that accounts for transport through a composite composed of semi-crystalline PEO lamellae and amorphous PS lamellae was developed. Model results and experimental data agreed fairly well considering the simplicity of the approach. The model can readily be used to predict pure gas permeabilities of SEO copolymers with arbitrary morphologies and crystallinity. The crystalline PEO volume fractions inferred from the permeation data are within 15% of those determined by differential scanning calorimetry.

1. Introduction

Copolymers have been the subject of intensive studies in recent years due to the possibility of controlling material properties by covalently bonding different monomers. This eliminates miscibility problems that are encountered when chemically dissimilar polymers are blended [1]. Block copolymers are of particular interest due to the possibility of decoupling different properties, e.g. ionic conductivity and shear modulus or fluid permeability [2,3]. Immiscibility of the blocks results in self-assembly of nanoscale morphologies that can be modeled by self-consistent field theory and studied experimentally using techniques such as light, neutron, and X-ray scattering, atomic force microscopy, and electron microscopy [4–9]. Block copolymers offer almost unlimited possibilities for designing new materials for a variety of applications such as gas separation, fuel cells, batteries, toughening of brittle polymers, templates for mesoporous silica, and nanolithography [2,10–19].

Transport of gases through poly(ethylene oxide) (PEO) has been studied extensively by Lin and Freeman [20]. The polar nature of the ether group leads to unusual separation properties, such as high CO_2 solubility and selectivity toward olefins relative to paraffins. Experiments and modeling suggest that these properties result from weak interactions between quadrupolar gas molecules, such as CO_2, and the polar ether group in PEO [21–25]. Amorphous PEO is a liquid-like polymer at room temperature and thus measurements of permeability of gases through it are very challenging. The low melting point of PEO and the poor mechanical properties of semicrystalline PEO limit its usage in gas separation applications. This is in contrast to other mechanically robust, semicrystalline polymers, such as polyethylene, that have been extensively studied [26,27]. The high permeability and selectivity of PEO toward CO_2 has thus been exploited by either blending or crosslinking [28–31]. Another approach that has received considerable attention is the use of multi-block copolymers, containing soft PEO segments and a variety of hard segments, including polyimide, polyamide, and poly(butylene terephthalate) [32–34]. These membranes exhibit excellent CO_2/N_2 and CO_2/H_2 selectivity without compromising permeability, and chemical, mechanical and thermal stability. PEO-containing membranes are thus ideally suited for gas separation and CO_2 recovery [35].

An emerging application for PEO-containing block copolymers is their potential use as solid electrolytes in lithium batteries [2,36,37]. A battery chemistry that is gaining increasing attention is the lithium-air cell with a lithium metal anode and an oxygen

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cathode. Such a cell must have a solid electrolyte; liquid electrolytes will evaporate through the cathode. The performance of such a cell is compromised by the permeation of gaseous species that are present in the air such as CO_2 [37]. Quantifying the permeability of CO_2 and O_2 through PEO-containing block copolymers is thus important also for this application.

This work is a study of pure gas permeability through poly(styrene-*b*-ethylene oxide) (SEO) copolymers. The mechanical integrity of the membrane is due to the glassy polystyrene block (glass transition temperature, T_g, is approximately 100 °C). This enables measurement of gas permeabilities at temperatures ranging from 20 to 80 °C, i.e., below and above the melting temperature of PEO. In closely related work, Patel and Spontak studied gas diffusion in an SEO copolymer membrane [38]. Both the experimental and theoretical work presented here is similar in spirit to that presented in Ref. [38]. The main advance in the present paper is the development of an analytical expression for the permeation of pure gases through lamellar SEO copolymers as a function of the block copolymer composition and the degree of crystallinity of the PEO microphase. We rely heavily on the classic works of Sax and Ottino [39] and Lin and Freeman [20]. Expressions for other block copolymer morphologies can readily be developed using the present analysis.

2. Materials and experimental

A poly(styrene-*block*-ethylene oxide), SEO, copolymer was synthesized via living anionic polymerization, using *sec*-butyl lithium as the initiator and P4 *tert*-butylphosphazene base as the catalyst for ethylene oxide polymerization, as described elsewhere [40,41]. The number-averaged molecular weight of the polystyrene (PS) block and the polydispersity index (PDI) of both the PS block and the SEO diblock copolymer were measured with gel permeation chromatography (GPC; Fig. S1 in Supplementary Information) using dimethylformamide (DMF, Aldrich) as carrier solvent in a Viscotek OmniSEC separations module and triple-detector system calibrated using PS standards. The volume fraction of each block was determined using ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Living diblock SEO chains were coupled with dibromo-*o*-xylene (Aldrich) [42]. GPC results (Fig. S1) indicate that 16% of the diblock chains were coupled. All experiments were conducted on the coupled polymer. The polymer was purified by precipitation and isolated by freeze drying. The dry polymer was dissolved in *n*-methyl pyrolidone (EMD Millipore) at 9 wt%. The solution was cast with a doctor blade and dried under vacuum at 90 °C.

The structure of the polymer was determined by small-angle X-ray scattering (SAXS). Samples for SAXS experiments were prepared by pressing the polymer into sample holders with a 0.15 mm thick spacer and sealing in a custom-designed airtight sample holder with Kapton windows. Measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The X-ray wavelength was 1.24 Å, and sample to detector distance was 4.4 m. Samples were mounted on a custom-built temperature stage and annealed at 120 °C before taking measurements. A silver behenate sample was used as a standard, and data were reduced using the Nika program for Igor Pro available from Jan Ilavsky. The azimuthally averaged scattering intensity, *I*, is reported as a function of the scattering vector q ($q=4\pi\ \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident beam). The domain spacing, *d*, is defined as $d=2\pi/q_{max}$, where q_{max} is the magnitude of the scattering vector q at the most intense peak. The value $q*$ is defined as the magnitude of the scattering vector associated with the (100) plane of a given morphology.

The crystallinity in the sample was studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC6 instrument. DSC runs were performed under nitrogen with a heating rate of 5 °C/min, from approximately 10 °C up to 120 °C.

Permeation tests of pure gases (at 0% R.H.) through the SEO block copolymer membranes were carried out in a closed-volume manometric apparatus described elsewhere [43], at temperatures ranging from 20 to 80 °C. Permeability, *P*, was calculated from the rate of pressure (p_1) increase in a known downstream volume (V) at constant temperature (T) using the ideal gas law. Given a nearly constant pressure difference (Δp) across the membrane, *P* can be written as:

$$P=\left(\frac{dp_1}{dt}\right)_{t\to\infty}\frac{Vl}{RTA\Delta p} \tag{1}$$

where l is membrane thickness, A is membrane area, and R is the universal gas constant. All measurements were repeated at least twice. Deviations between measurements were in the 5–10% range due mainly to the uncertainty in the film thickness. The thickness of each SEO membrane was measured at 10 different points using a Mitutoyo digital micrometer with a resolution of 1 μm.

3. Results

3.1. Structural characterization

The number-averaged molecular weight of the PS block is 75 kg/mol. The PDI of the PS block and the SEO diblock copolymer was found to be less than or equal to 1.05. The weight fraction of PEO (ω_{EO}) was calculated from the H^1 NMR data and is 0.50. Using the density of each polymer at 80 °C, 1.09 g/cm^3 for PEO and 1.03 g/cm^3 for PS [44], the volume fraction of PEO (ϕ_{EO}) in the SEO triblock copolymer is 0.49.

Fig. 1 shows *I* vs. *q* obtained from SAXS experiments on the SEO triblock copolymer. Integer spacing of the characteristic scattering peaks in Fig. 1 is indicative of lamellar morphology, which is expected from a symmetric block copolymer with $\phi_{EO}=0.49$. The primary scattering peak occurs at $q=q_{max}=0.066\ \text{nm}^{-1}$. This implies that the center-to-center distance between adjacent PEO

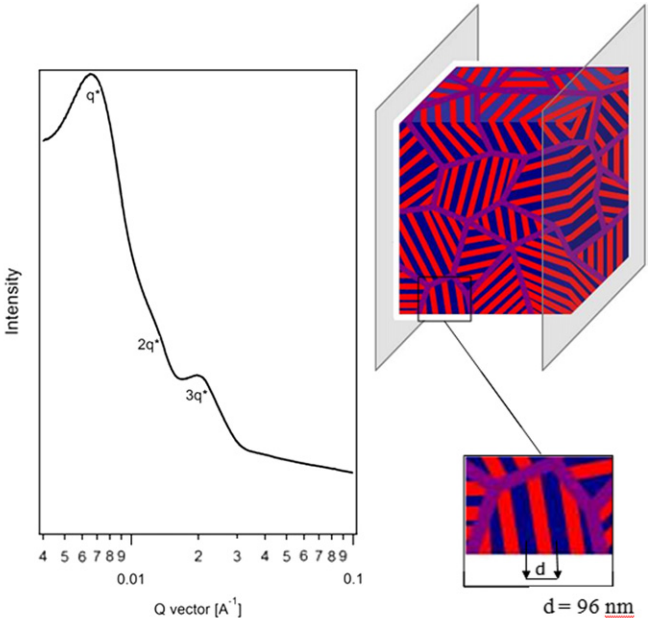

Fig. 1. One-dimensional SAXS profile of SEO and schematic illustration of the block-copolymer morphology.