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# Structure, physical properties, and molecule transport of gas, liquid, and ions within a pentablock copolymer



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## ABSTRACT

The morphology and physical properties of a pentablock copolymer (PBC) were investigated as a function of sulfonation or ion-exchange capacity (IEC). This material is comprised t-butylstyrene (tBS), hydrogenated isoprene (HI), sulfonated polystyrene (sPS), and polystyrene (PS). Thermally reversible crosslinks are created with tBS, which is dispersed within a rubbery phase of HI, sPS, and PS. A morphology change was observed upon sulfonating PBC. This created abrupt material changes such as water swelling, proton conductivity, and methanol transport at an IEC greater than one. Water, proton, and methanol transport are associated with sPS domains. Gas transport occurs mainly through more permeable HI and tBS phases that were disrupted with increasing IEC. The permeability ( $P$ ) was modeled using a lamellar morphology. Ion and methanol transport occurred via sulfonated domains. Finally, a structure–property and transport property correlation of this multi-block PBC ionomer is discussed within this paper.

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## 1. Introduction

Gas separations using polymer membranes is a pressure-driven process with applications in areas such as refineries and chemical industries [1]. Polymer membranes are gaining increasing attention for separating components from gas streams [2]. The majority of this research focuses upon exploring materials with high thermal stability and molecule permselectivity. Typically, low free volume polymers have good selectivity in contrast to porous materials. Furthermore, excellent processability offers several advantages over inorganic materials.

Polysulfones [3–6], polyimides [7], and ionomers [8,9] have been investigated for their gas separation properties. An ionomer contains ion aggregates forming a domain that strengthens polymer segment interactions leads to several unique properties. These properties include improved gas barrier resistance, enhanced mechanical properties, and greater thermal stability [8–10]. Tsujita et al. [11] investigated the sorption behavior of CO<sub>2</sub> in ethylene–methacrylic acid ionomers. It was found that ionic domains act as absorption sites for CO<sub>2</sub>, and reduce polymer mobility within the amorphous phase. Therefore, these groups enable tailoring of gas transport properties. Fan and Cornelius et al. [9,12] studied a polysulfone multiblock ionomer's physical properties and molecule

transport at a constant ion-exchange capacity that had proton conductivity comparable to Nafion. These materials had a phase-separated morphology that was dependent upon sulfonated and unsulfonated average molecular weight block lengths of 5k, 10k, and 15k g/mol. In this work, the gas permeability decreased with increasing block length, which was attributed to an observed reduction in ionomer fractional free volume FFV. Triblock copolymers poly(styrene-*b*-isobutylene-*b*-styrene) proton and methanol transport properties have been widely investigated by Elabd et al. [13–15]. These triblock ionomers had proton conductivities greater than Nafion, but they had extreme water uptakes (348 wt%) and high methanol permeability, which is not a desirable material trait [13].

One class of sulfonated ionomer is a PBC developed by Kraton LLC known as Nexar™ (Fig. 1) [16]. In this material system, solvent swelling is controlled via physical crosslinks using t-butyl polystyrene, material flexibility is due to the hydrogenated isoprene rubbery phase, and ion and liquid transports occur through the partially sulfonated polystyrene phase. This arrangement of functional blocks is unique when compared to other styrene based ionomers. Its composition provides high proton conductivity and water permeability, good mechanical properties under hydrated conditions, water uptake of less than 100 wt%, and improved swelling as compared to triblock and diblock ionomers [16,17]. Currently, only a few publications have examined its properties and material structure. Paul et al. [18] investigated its use for water desalination. In this work, water sorption and salt permeability increased with sulfonation near an IEC of 1.0. Winey et al. [19] discovered a spherical micellar morphology

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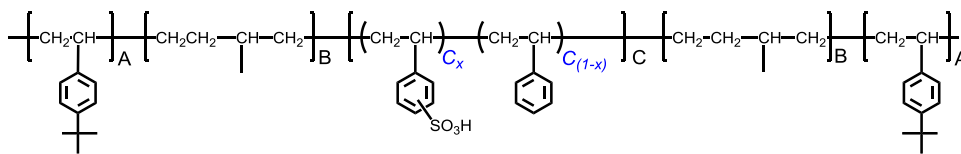


Fig. 1. PBC-XX structure with a stoichiometric ratio of  $C_x$  that is proportional to IEC.

Table 1  
PBC physical properties [23].

PBC-XX	Density (g/mL)	IEC (mEq/g)	FFV	$V_o$ (cm <sup>3</sup> /mol)	CE (kJ/mol)	Volume fraction, $\phi$ tBS-PS(sPS)-HI
PBC-0.0	0.958	0.0	0.254	103.5	122.5	0.331–0.377–0.292
PBC-1.0	1.009	1.0	0.243	108.1	156.9	0.309–0.417–0.274
PBC-1.5	1.033	1.5	0.231	111.4	177.3	0.304–0.427–0.269
PBC-2.0	1.061	2.0	0.199	114.1	199.4	0.300–0.434–0.266

in dilute PBC ionomer solutions using X-ray scattering. The film morphology transitions from discrete sulfonated domains into a disordered and bicontinuous material with increasing IEC. This structural change enabled higher water vapor transport. The results exemplify the complexity of PBC morphology and the need for more structure–property–transport studies.

In this study, sulfonated and unsulfonated PBC ionomers were examined with respect to gas, liquid, and ion transport. Gas permeation tests were performed at temperatures ranging from 30 °C to 70 °C with several gases of varying molecular sizes (CO<sub>2</sub>, O<sub>2</sub>, and CH<sub>4</sub>). Liquid and ion transport properties were studied in order to evaluate their potential application as a polymer electrolyte membrane (CH<sub>3</sub>OH and H<sup>+</sup>). The PBC materials discussed in this paper are abbreviated as PBC-XX with XX representing its IEC defined as milliequivalents (mEq) of sulfonic acid per gram of dry polymer. This work provides insights needed to further structure–property–transport correlations.

## 2. Experimental

### 2.1. Materials

Commercial PBC ionomer films were provided by Kraton Polymers LLC, Houston, TX [16], and used as received. These films were prepared on a continuous basis that produces uniform and reproducible 1 mil films using a 50/50 vol% solution of cyclohexane and heptane. The process used a hot air oven with four heated zones operating between 38 °C and 98 °C with a film uptake speed between 9 and 21 m/min to generate films within minutes. The material is comprised t-butyl polystyrene (tBS), hydrogenated isoprene (HI), polystyrene (PS), and sulfonated polystyrene (sPS) blocks (Fig. 1). PBC was supplied with a reported molecular weight is 100,000 g/mol and a polydispersity of less than 1.04.

The PBC density was calculated using its dry membrane weight divided by a known volume. Fractional Free Volume (FFV) was evaluated using a group contribution method as described by others [9,20–22]. The predicted FFV is based upon the polymer's density to calculate its specific volume  $V$ , volume occupied by polymer chains  $V_o$ , structural group van der Waals volume  $V_w$ , and total number of structural groups  $k$  within a polymer repeat unit Eq. (1) [21]. These values are summarized in Table 1.

$$\text{FFV} = 1 - \frac{1}{V} \left( 1.3 \sum_{k=1}^k (V_w)_k \right) \quad (1)$$

### 2.2. Thermal analysis

Thermal gravimetric analysis (TGA) was performed using a TGA Q500 (TA Instruments). Samples were pretreated to remove residual water by isothermal heating at 120 °C for 20 min. Conditioned samples were heated in an inert N<sub>2</sub> atmosphere from 50 °C to 700 °C using a heating rate of 10 °C/min.

### 2.3. Infrared spectroscopy

FTIR is collected with a Nicolet-iS 10 spectrophotometer with a wavenumber resolution of 4 cm<sup>-1</sup>. A spectrum is collected in the attenuated total reflectance (ATR) mode using a single bounce ZnSe crystal and an average of 16 scans.

### 2.4. Small angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed using a Rigaku S-Max 300 with a three pinhole collimation camera. The X-ray source is CuK<sub>α</sub> radiation operating at 40 kV and 44 mA. The incident X-ray beam had a wavelength of 0.154 nm with a sample-to-detector distance of 16.0 cm. The  $d$ -space for both techniques was calculated using Bragg's equation  $n\lambda = 2d \sin(\theta)$ . A series of films were stacked to provide sufficient scattering intensity.

### 2.5. Transmission electron microscopy

Transmission electron microscopy (TEM) images were collected with a FEI Tecnai Biotwin G2 Spirit Transmission Microscope using 80 kV. PBC-0.0 was stained by RuO<sub>4</sub> vapor. All PBC acid form samples were treated using a BaCl<sub>2</sub> solution to enhance electron density and contrast of sulfonated domains. Films with a nominal dimension of 0.5–1.0 mm wide by 5.0–10.0 mm long were embedded in epoxy. Sections were cut using a Diatome diamond knife and mounted on 400 mesh copper–ruthenium grid.

### 2.6. Dynamic mechanical analysis

The glass transition temperature ( $T_g$ ) of PBC ionomers was obtained using Dynamic Mechanical Analyzer Q800 (DMA, TA instruments). Membrane samples were analyzed in the tensile mode using a frequency of 1 Hz and a heating rate of 2 °C/min from –90 °C to 120 °C. The strain  $\epsilon_t$  applied was 0.01%.

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