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## Free volume characterization of sulfonated styrenic pentablock copolymers using positron annihilation lifetime spectroscopy

Geoffrey M. Geise<sup>a</sup>, Cara M. Doherty<sup>b</sup>, Anita J. Hill<sup>b,c</sup>, Benny D. Freeman<sup>a,\*</sup>, Donald R. Paul<sup>a</sup><sup>a</sup> Department of Chemical Engineering, Texas Materials Institute and the Center for Energy and Environmental Resources, The University of Texas at Austin, 10100 Burnet Road, Building 133 – CEER, Austin, TX 78758, USA<sup>b</sup> CSIRO Materials Science and Engineering, Private Bag 33, South Clayton MDC, Clayton VIC 3169, Australia<sup>c</sup> CSIRO Process Science and Engineering, Private Bag 33, South Clayton MDC, Clayton VIC 3169, Australia

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## ABSTRACT

A series of sulfonated styrenic pentablock copolymers was characterized using positron annihilation lifetime spectroscopy (PALS). *Ortho*-positronium (*o*-Ps) lifetime was measured as a function of the polymer's degree of sulfonation and the environment in which the polymer was equilibrated. Samples ranged from an un-sulfonated styrenic pentablock copolymer to one with an ion exchange capacity (IEC) of 2.0 meq/g(dry polymer), and the samples were equilibrated in either air having 50% relative humidity, de-ionized (DI) water, or 2000 mg L<sup>-1</sup> aqueous NaCl solution environments. The *o*-Ps lifetime, and thus, the average free volume element size, decreased as the polymer's degree of sulfonation increased and as the amount of water sorbed into the polymer increased, similar to reported decreases in *o*-Ps lifetime accompanying increased water sorption in uncharged cross-linked poly(ethylene glycol) hydrogels. The *o*-Ps lifetimes of the DI water equilibrated acid counter-ion form polymers were quite similar to those of the salt solution equilibrated sodium counter-ion form polymers, suggesting that the PALS data are not particularly sensitive to the counter-ion form of these hydrated polymers. Previously reported water and salt permeability data in polymers were correlated with the PALS data. Correlating water and salt permeability with free volume data, estimated using *o*-Ps lifetime, was complicated by the micro-phase separated nature of the block copolymers. The water permeability of polymers whose hydrophilic micro-domains are believed to be well connected correlated with free volume data, based on *o*-Ps lifetime. Salt permeability, however, did not correlate with free volume data estimated from *o*-Ps lifetime, according to free volume theory. In general, contributions of the hydrophobic micro-domain free volume to the PALS measurement frustrate the correlation of water and salt transport properties with PALS parameters in a manner that is not observed in other sulfonated and uncharged polymers.

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## 1. Introduction

Water and ion transport through dense, non-porous polymers is critical for several membrane-based applications that could address critical worldwide demand for purified water and energy [1–11]. These membrane based technologies, which include reverse osmosis (RO) [4,7], forward osmosis (FO) [12,13], electro-dialysis (ED) [14,15], reverse electro-dialysis (RED) [3,16,17], and membrane assisted capacitive de-ionization (MCDI) [18,19], all rely on polymer membranes to control rates of water and/or ion transport. The fundamental influence of polymer structure, at the molecular level, on water and ion transport must be

understood to rationally tailor new polymer membranes with water and ion transport properties optimized for specific applications [1,11].

Sulfonated polymers are being explored as membrane materials for many of the applications listed above [1,2,14,20]. In applications such as RO and FO, sulfonated polymers may offer an advantage over traditional polyamide-based thin-film composite membranes because sulfonated polymers resist degradation by the chlorine-containing disinfectants widely used in water treatment processes [21–23]. These chlorine tolerant polymers, if used as water treatment membranes, could simplify desalination processes by eliminating at least the need for de-chlorination steps that are commonly used in RO processes to protect the RO membranes from the deleterious effects of exposure to aqueous chlorine [1,21]. Sulfonated polymers are also key components in potential field-driven technologies, such as ED, RED, and MCDI, because they are cation exchange membranes (CEMs), which

\* Corresponding author. Tel.: +1 512 232 2803; fax: +1 512 232 2807.

E-mail addresses: [freeman@austin.utexas.edu](mailto:freeman@austin.utexas.edu), [freeman@che.utexas.edu](mailto:freeman@che.utexas.edu) (B.D. Freeman).

along with anion exchange membranes (AEMs), are critical to the operation of such processes [14,17,19,24,25].

Sulfonated polymers based on polymer backbones such as poly(styrene) [26–28], poly(sulfone) [21–23,29–33], and poly(2,6-dimethyl phenylene oxide) [34] have been studied for water treatment applications. Most of these materials are random copolymers of sulfonated and unsulfonated monomers. Recently, sulfonated block copolymers have gained interest because the micro-phase separated morphology in such polymers can provide an additional means to optimize water and ion transport properties [2,35,36]. Nexar™ polymers, commercialized by Kraton Performance Polymers Inc. (Houston, TX), are one such example, and the general structure of this sulfonated styrenic pentablock copolymer (sPBC) is shown as Fig. 1 [26–28,37]. Micro-phase separation into hydrophilic micro-domains composed primarily of a partially sulfonated styrenic middle block and hydrophobic micro-domains composed primarily of *t*-butyl styrene and hydrogenated isoprene blocks has been reported in these materials [38–40]. This micro-phase separation influences water and ion transport properties [36,38,39].

In non-porous polymers, such as these sPBC materials, water and salt transport is commonly understood to be highly sensitive to free volume (i.e., interstitial molecular-scale voids within the polymer that are not occupied by the polymer chains themselves and are available to assist in transport of penetrants through the polymer), since molecular diffusion of water and ions through the swollen polymer matrix is the rate limiting step of the transport process [29,41–46]. Free volume theory is often used to correlate small molecule transport properties in a variety of non-porous polymers [29,45,47–53]. Water and salt permeability [36], sorption [54], and diffusion [55] coefficient data for the sPBC polymers have been reported previously. This study reports free volume data and discusses relationships between water and salt transport properties and free volume of sPBC polymers.

According to free volume theory, the diffusion coefficient of a penetrant,  $D_i$ , where  $i$  could represent water (subscript  $w$ ), salt (subscript  $s$ ), or some other penetrant, is related to the polymer's fractional free volume, FFV, as follows [56]:

$$D_i = a_i \exp\left[-\frac{b_i}{\text{FFV}}\right] \quad (1)$$

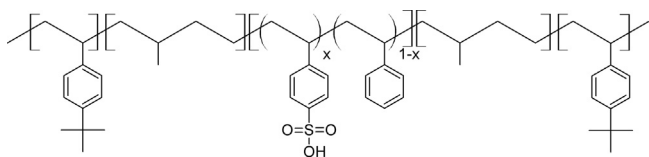


Fig. 1. Chemical structure of the sulfonated styrenic pentablock copolymer (sPBC).

where  $a_i$  and  $b_i$  are adjustable constants. High free volume polymers tend to have large diffusion coefficients according to Eq. (1). Additionally, the constant  $b_i$  increases with increasing penetrant size, so larger penetrants have smaller diffusion coefficients compared to smaller penetrants [29,45].

Positron annihilation lifetime spectroscopy (PALS) is used to characterize free volume in polymers [46,57–60], and PALS-based free volume data have been successfully correlated with transport properties of polymeric materials for both gas and liquid separations [29,45,46,51,52,57,61–71]. The PALS technique, illustrated in Fig. 2, measures the lifetime and intensity of positron species that form and annihilate in a polymer matrix when the polymer is exposed to a positron source, which is often  $^{22}\text{NaCl}$  [57]. *Ortho*-positronium (*o*-Ps), a parallel spin complex of a positron and an electron, forms in low electron density regions of the polymer, such as free volume elements (cf., Fig. 2), and the *o*-Ps lifetime and intensity are often associated with the size and concentration, respectively, of free volume elements in a polymer [57,58,72].

Traditionally, *o*-Ps has been used to probe free volume in polymers. In addition to *o*-Ps, *para*-positronium (*p*-Ps) and free positrons annihilate within a polymer sample [46,57,73]. The *p*-Ps lifetime and intensity do not provide information about the free volume of the polymer and will not be discussed further [46,57]. Recently, the free positron lifetime has been related to the size of free volume elements in a variety of materials, but the free positron intensity has not been shown to correlate with free volume [70,71]. Therefore, in this work, the free positron PALS components will not be used to estimate free volume.

The *o*-Ps lifetime,  $\tau_3$ , is typically related to the average radius of a free volume element,  $r$ , which is assumed to be spherical, by the Tao–Eldrup model:

$$\tau_3 = \frac{1}{2} \left( 1 - \frac{r}{r + \Delta r} + \frac{1}{2\pi} \sin \left[ 2\pi \frac{r}{r + \Delta r} \right] \right)^{-1} \quad (2)$$

where  $\tau_3$  is the *o*-Ps lifetime (in nanoseconds), and  $\Delta r$  is the empirical electron layer thickness, which is taken to be 1.66 Å [57,74,75]. Larger  $\tau_3$  values correspond to larger free volume elements because *o*-Ps is capable of existing in larger free volume elements for longer periods of time before annihilation [46,57,66,72,76]. The spherical approximation used to model the relationship between *o*-Ps lifetime and free volume cavity radius can be rationalized by considering that the PALS technique probes the effective, or macroscopically averaged, free volume of a material [46]. Therefore, individual discrete free volume elements, which presumably exist as a distribution of sizes and shapes within the polymer, can be described by a combination of many spherical free volume elements of varying size, and the experimentally measured *o*-Ps lifetime is representative of the average of these sizes [46]. The *o*-Ps intensity,  $I_3$ , represents the fraction of

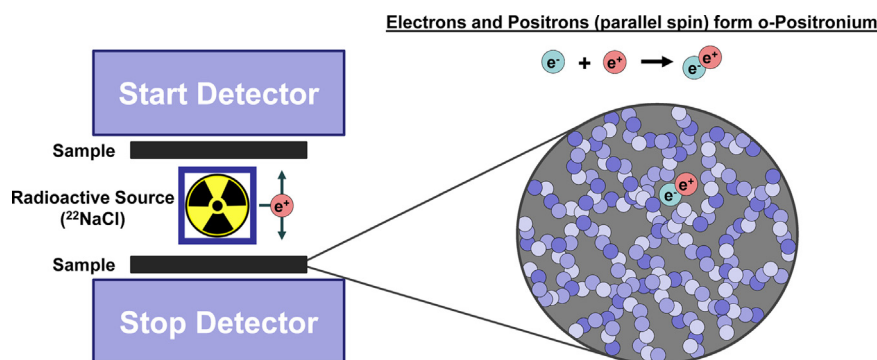


Fig. 2. Positron annihilation lifetime spectroscopy (PALS) is performed by placing a sample around a radioactive source and counting the positron formation (start) and annihilation (stop) events that occur within the material. An electron and positron (with parallel spin-states) can combine to form *ortho*-positronium (*o*-Ps), and *o*-Ps can exist for timescales of the order of nanoseconds in electron deficient regions of a polymer (i.e., free volume elements) [57].

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