



Increasing salt size selectivity in low water content polymers via polymer backbone dynamics

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ABSTRACT

Two low water content copolymers, rubbery 2-hydroxyethyl acrylate-co-ethyl acrylate (HEA-co-EA) and glassy 2-hydroxyethyl methacrylate-co-methyl methacrylate (HEMA-co-MMA), were crosslinked with poly(ethylene glycol) diacrylate and studied to investigate the influence of polymer backbone segmental dynamics on salt transport size selectivity. These copolymers were chosen for chemical similarity and because HEA-co-EA is rubbery while HEMA-co-MMA is glassy at room temperature. Thermal analysis indicated that the copolymers are relatively homogeneous as a single glass transition temperature was observed for each material. The copolymers were prepared to have low water content (approximately 8% by mass) similar to the reported water content of many commercially available desalination membrane polymers. At low water content, most of the water in the polymer is expected to interact either with the polymer backbone or sorbed ions, suggesting that the influence of backbone segmental dynamics on the transport properties of these low water content materials may be different from the situation in more highly hydrated polymers. Salt sorption similarly increased with water content for the two copolymers due to their chemical similarity. Size selectivity was quantified as ratios of the salt permeability and diffusion coefficients to the corresponding values for a reference salt, and salt size was quantified using the salt diffusivity in bulk aqueous solution at infinite dilution to take into account both ion size and hydration properties. At comparable water content, the salt permeability and diffusion coefficients of the rigid HEMA-co-MMA copolymer decreased to a greater extent as a function of salt size compared to the more flexible HEA-co-EA copolymer. These results suggest that more rigid polymer backbones may drive increases in size-based permeation and diffusion selectivity when polymer water content is sufficiently low.

1. Introduction

Membrane-based desalination is poised to address growing water shortages around the world by providing efficient desalination and improved access to clean water [1–7]. While the technology has been used for several decades, current state of the art polyamide reverse osmosis (RO) membranes are susceptible to oxidative degradation via chlorine-containing compounds that are often used to disinfect water and prevent membrane biofouling, and advanced chlorine-tolerant desalination membrane materials are needed [1,4,5,8–11]. Such materials will likely contain different chemical functionality compared to the current state of the art membranes [4,5,8]. Few structure-property relationships are available to guide the development of chemically stable membrane polymers that offer water and salt transport properties comparable to the current state of the art membranes. Critical to developing such materials is the ability to prepare highly size selective hydrated polymers, and structure-property guidance is needed to inform this aspect of molecular-level polymer design [4,12–15].

Water and ion transport in desalination membrane materials is often discussed in terms of sorption and diffusivity properties that define the thermodynamic and kinetic, respectively, contributions to membrane transport properties [4,5,9,16]. Several studies have probed the thermodynamic influences of water and ion sorption on permeability properties [4,17–20]. Fewer studies, however, have considered structure-property relationships for enhancing the size selectivity, via a diffusion-based mechanism, of membranes for desalination applications.

Commercially successful desalination membranes generally have been based on either polyamide or cellulose acetate chemistry [9], and membrane polymers that offer high salt rejection often sorb relatively little water compared to more highly hydrated ion exchange materials and hydrogels [21–23]. As a result, ions diffusing through a low water content polymer matrix may be more likely to interact with the polymer backbone compared to a more highly hydrated polymer. This situation suggests that polymer backbone rigidity in low water content polymers may influence the size selectivity of salt transport by analogy to reports

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of increased size selectivity in rigid compared to flexible backbone gas separation membrane polymers [24]. The influence of polymer backbone segmental dynamics on the size selectivity properties of low water content polymers is not generally understood.

Water molecule dynamics are often considered to govern ion transport properties in more highly hydrated materials, such as Nafion® (a perfluorosulfonic acid polymer that absorbs around 30% water by volume, depending on how the membrane prepared [25]) and other fuel cell and ion exchange membrane materials [4,5,26–30]. Transport is often considered to be facilitated by free or bulk water in these highly hydrated polymers [26–28,31]. In low water content polymers, however, little if any ‘free’ or ‘bulk’ water exists in stark contrast to many ion exchange membranes [26,32–34]. This situation suggests that polymer segmental dynamics may influence transport to a greater extent when the polymer water content is low.

To investigate this question, we studied the salt size selectivity of a flexible, acrylate-based copolymer and a rigid, methacrylate-based copolymer. The copolymers were compared at equivalent water content, as the extent of water sorption can influence strongly the transport properties of hydrated polymers [35]. The chemical structures of the two copolymers considered are very similar, and this choice was made in an effort to keep the thermodynamic interactions between salt and the polymer as similar as possible. The salt permeability, sorption, and diffusivity properties of the copolymers were characterized using salts that were effectively different sizes, as quantified by the salt diffusivity at infinite dilution in aqueous solution. The rigid, low water content copolymer ultimately was more size selective compared to the flexible, low water content copolymer suggesting that polymer segmental dynamics may be important for achieving size selectivity in low water content polymers.

2. Experimental methods

2.1. Materials

Two copolymers were prepared for this study. The first was an acrylate-based copolymer of 2-hydroxyethyl acrylate (HEA, 96%, Sigma-Aldrich, St. Louis, MO) and ethyl acrylate (EA, 99%, Sigma-Aldrich, St. Louis, MO); a 30:70 (by mass) HEA:EA mixture of the co-monomers was crosslinked with 3% (by mass) poly(ethylene glycol diacrylate) (PEGDA, average $M_n = 250$ g/mol, Sigma-Aldrich, St. Louis, MO). The second was a methacrylate-based copolymer of 2-hydroxyethyl methacrylate (HEMA, 97%, Sigma-Aldrich, St. Louis, MO) and methyl methacrylate (MMA, 99%, Sigma-Aldrich, St. Louis, MO); a 25:75 (by mass) HEMA:MMA mixture of the co-monomers was crosslinked with 3% (by mass) PEGDA. The structures of the co-monomers and the crosslinker are shown in Table 1. The compositions of the copolymers were selected such that the resulting polymers had similar equilibrium water content.

The crosslinked HEA-co-EA and HEMA-co-MMA copolymers (Fig. 1) were prepared via UV-initiated free radical polymerization. The initiator, 1-hydroxycyclohexyl phenyl ketone (99%, Sigma-Aldrich, St. Louis, MO), was mixed, for 10 min, with the co-monomers and crosslinker to form a homogeneous pre-polymerization solution, and 1% and 0.5% (by mass) initiator was used for HEMA-co-MMA and HEA-co-EA, respectively. The pre-polymerization solution then was sonicated for 15 min in an ultrasonic bath. To form films, the solution was confined between a quartz plate and a glass plate that were separated by spacers (to control the eventual thickness of the film) and was cured using $120 \mu\text{J}/\text{cm}^2$ 254 nm UV light. The exposure was 120 s for HEA-co-EA and 500 s for HEMA-co-MMA. The thickness of the resulting transparent films ranged from 50 to 200 μm , and after curing, these films were soaked promptly in de-ionized (DI) water (18.2 M Ω cm, 1.2 ppb total organic carbon) to hydrate the copolymers and to extract any water soluble unreacted co-monomers. The films were stored in DI water until use.

2.2. Methods

2.2.1. Water uptake

Samples were cut from larger pieces of polymer film and were equilibrated in either DI water or aqueous solutions of 0.5 mol/L lithium chloride, sodium chloride, or potassium chloride. After equilibration, the sample was removed from the DI water or salt solution, the surface was dried quickly with a laboratory wipe, and the wet mass of the sample, m_{wet} , was measured. Then, the sample was dried under vacuum at room temperature for 48 h. After drying, the sample was removed from the drying oven and the dry mass of the sample, m_{dry} , was measured immediately. Water uptake, w_u , was calculated as:

$$w_u = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

Using the measured water uptake, the volume fraction of water sorbed in the polymer, ϕ_w^m , was calculated, assuming volume additivity [40,41], as:

$$\phi_w^m = \frac{w_u}{w_u + \rho_w/\rho_p} \quad (2)$$

where ρ_w is the density of water (1.0 g/cm³ [42]), and ρ_p is the density of the dry polymer. The dry polymer density was measured (after drying the samples for the water uptake measurement) via an Archimedes’ principle method where sample mass measurements were made in air and in an auxiliary liquid [43]. The dry polymer density was calculated as:

$$\rho_p = \frac{m_{air}}{m_{air} - m_{aux}}(\rho_{aux} - \rho_{air}) + \rho_{air} \quad (3)$$

where m_{air} is mass of sample in air, m_{aux} is mass of sample in auxiliary liquid, ρ_{aux} is auxiliary liquid density, and ρ_{air} is air density. Cyclohexane, which is a nonpolar solvent that is commonly used to determine the dry density of hydrophilic polymers, was used as the auxiliary solvent [44–46], and the value of ρ_{aux} was evaluated at the measurement temperature using reported cyclohexane density data as a function of temperature [42,47].

The water sorption coefficient, K_w , is defined as the ratio of water concentration in the polymer, C_w^m , to that in the bulk external solution, C_w [48,49]:

$$K_w = \frac{C_w^m}{C_w} \quad (4)$$

The units of K_w are [g(water)/cm³(hydrated polymer)]/[g(water)/cm³(solution)], and K_w is related to the volume fraction of water in the polymer, ϕ_w^m , as [45]:

$$K_w = \frac{\phi_w^m M_w}{C_w V_w} \quad (5)$$

where M_w is the molecular weight of water (18 g/mol) and V_w is the molar volume of water at ambient conditions (18 cm³/mol [50]). For dilute salt solutions or DI water, C_w is approximately equivalent to the density of pure water, ρ_w , which was taken as 1 g/cm³ [45]. As a result, the water sorption coefficient is approximately equal to the volume fraction of water sorbed in the polymer (i.e. $K_w \cong \phi_w^m$).

2.2.2. Thermal characterization

Differential scanning calorimetry (DSC, TA Instruments Q1000) was used to characterize the glass transition temperature (T_g) of the hydrated HEA-co-EA and HEMA-co-MMA copolymers. DI water equilibrated polymer samples, with masses ranging from 5 to 10 mg, were sealed in hermetic aluminum sample pans to keep the samples hydrated throughout the measurement. The samples were initially heated to 150 °C, quenched to –80 °C, and subsequently scanned twice between –80 °C and 150 °C at a heating rate of 10 °C/min under a nitrogen purge flow. The glass transition temperature was determined as the

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