Water and salt transport properties of zwitterionic polymers film

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ABSTRACT

Two series of crosslinked zwitterionic polymer films were synthesized via UV-photopolymerization of aqueous solution, and the films were prepared using sulfobetaine methacrylate (SBMA) or carboxybetaine methacrylate (CBMA) as the zwitterionic co-monomer and poly(ethylene glycol) diacrylate (PEGDA) as the crosslinker. The water and salt transport properties of the obtained polysulfobetaine methacrylate (PSBMA) and polycarboxybetaine methacrylate (PCBMA) films were studied using permeation and kinetic desorption methods with crosslinked poly(ethylene glycol) acrylate (PEGA) films as a control. Zwitterionic films absorb more water and are more permeable to both water and salt than PEGA films as a result of interactions between the zwitterions, water molecules, and salt ions. The transport properties of PSBMA and PCSMA depend similarly on crosslinking density, and high water and salt permeability correlates with high water uptake. However, the relationship between salt permeability and salt concentration differed between PSBMA and PCBMA. PSBMA behaves like a charged film, and its salt permeability increases with salt concentration while PCBMA shows the opposite trend. Transport properties for both materials are consistent with a trade-off between water permeability and water/salt selectivity. Zwitterionic films exhibit high permeability/low selectivity among polymers reported in the literature. This result suggests that they could be useful as coating materials for membrane fouling control where the anti-fouling properties of the zwitterionic material is more important than water/salt selectivity.

1. Introduction

Dense polymer films have been widely used in diverse membrane applications for water scarcity alleviation and alternative energy development. These applications include reverse osmosis (RO), forward osmosis (FO), electrodialysis (EDI), pressure retarded osmosis (PRO), reverse electrodialysis (RED) and fuel cells [1–3]. The ion/salt transport properties of these polymer films play a key role determining the separation performance and energy productivity of these applications [3]. The performance of current polymeric materials must be improved to enhance the performance of water purification and energy technologies, and there is an urgent need to better understand fundamental water and salt transport properties of dense polymeric films.

Zwitterions contain both a positively and a negatively charged moiety on the same pendant group, while maintaining overall charge neutrality [4]. Zwitterionic polymers have received growing attention as a new generation of anti-biofouling desalination materials due to favorable resistance to protein adsorption and bacteria attachment [4–8]. Chang et al. used interfacial polymerization followed by immobilization of zwitterions by crosslinking to prepare an antifouling NF membrane [4]. Zwitterionic monomers were also directly used in interfacial polymerization to prepare a novel zwitterionic NF membrane [7]. Membrane performance and/or antifouling properties were improved considerably due to the incorporation of zwitterionic moieties in the membrane. However, even as zwitterionic polymers are promising materials for use as antifouling coating layers on membrane surfaces or are of interest as desalting layers of thin film composite membranes, the salt transport properties of zwitterionic polymers are not well understood.

Generally, water and salt transport in non-porous polymers can be described by solution-diffusion theory [9–13]. Polymer structure has a strong impact on the water uptake of the material [2,14–18], which subsequently can influence strongly water and salt sorption, diffusion and permeation properties. In addition, many polymers used as membranes for desalination and energy applications have ionizable or charged functional groups on the polymer backbone [2,13,19]. Therefore, it is important to evaluate the impact of charge on transport properties in these films. Charged and uncharged polymers exhibit very different salt and water sorption and diffusion properties [13]. Uncharged polymers, swollen with water and not containing functional groups that can ionize, exhibit water and salt transport properties that follow a

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simple partitioning mechanism [11,13–16]. Conversely, charged polymers containing fixed charge groups, which are covalently connected to the polymer backbone and can ionize when the polymer is swollen with water [20], exhibit different ion sorption and diffusion behavior compared to that of uncharged polymers [3,13,20–22]. Ion sorption in an uncharged polymer proceeds by a simple partitioning mechanism and its dependence of ion diffusion properties on salt concentration in the external solution is mainly related to osmotic de-swelling. On the other hand, ion sorption in a charged polymer proceeds by both ion exchange and simple partitioning mechanisms and ion diffusion is strongly influenced by electrostatic interactions.

Zwitterionic polymer films have a high charge density of both positive and negative charge groups but are overall charge neutral, so it is not clear whether the water and salt transport properties of zwitterionic polymers are similar to charged or uncharged polymers. To study the impact of zwitterionic groups on water and salt transport properties, we synthesized UV crosslinked films containing sulfobetaine and carboxybetaine groups crosslinked with poly (ethylene glycol) diacrylate (PEGDA) and characterized their salt transport properties. A crosslinked poly(ethylene glycol) acrylate (PEGA) film was prepared and used as a control membrane. The structures of the two zwitterionic co-monomers (sulfobetaine methacrylate, SBMA, and carboxybetaine methacrylate, CBMA) and the neutral co-monomer, poly(ethylene glycol) acrylate (PEGA), are shown in scheme 1. Two zwitterionic polymers, poly (sulfobetaine methacrylate) (PSBMA) and poly(carboxybetaine methacrylate) (PCBMA), and a neutral polymer, poly(ethylene glycol) acrylate (PEGA), were obtained using UV photopolymerization where the crosslinking density of the polymers was tuned by controlling the ratio of co-monomer to PEGDA.

2. Experimental

2.1. Materials and reagents

The photoinitiator 1-hydroxycyclohexyl phenyl ketone (HPK), crosslinker PEGDA (Mn=700, n=13), co-monomer PEGA (Mn=380, n=7) and co-monomer SBMA were obtained from Sigma–Aldrich and used as received. The co-monomer CBMA was synthesized according to the method reported in the literature [23] and the purity of the product was confirmed using ^{1}H NMR (Fig. S1 in Supporting Information). De-ionized (DI) water was obtained from a Millipore MilliQ system (18.2 MΩ cm, 1.2 ppb TOC, pH=6.9). All the other chemicals and reagents were used as received without any purification.

2.2. Film synthesis

Polymer films were prepared by UV induced polymerization of a mixture of zwitterionic monomers, PEGDA crosslinker, HPK photoinitiator and 60 wt% DI water. The pre-polymerization
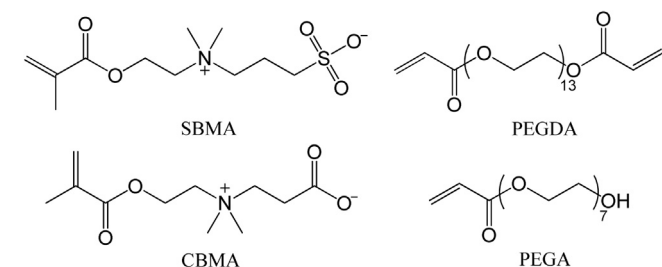
Scheme 1. Chemical structures of the co-monomers and crosslinker used in the UV crosslinked polymer films.

solution was mixed in an amber glass jar for one hour to completely mix the monomers, crosslinker, and initiator while minimizing exposure to light. Next, DI water was added (60 wt%), and the solution was stirred for an additional hour. N_2 was bubbled through the solution for 10 min prior to polymerization to remove dissolved oxygen. The pre-polymerization solutions with monomer contents of 0, 10, 20, 30, 40, and 50 mol% (molar ratio of co-monomer to PEGDA) were cast between two quartz plates where polytetrafluoroethylene sheets were used as spacers to control the separation between the quartz plates and, thus, the polymer film thickness. The reaction mixture was cured under 312 nm UV radiation for 60 s to produce solid, transparent, crosslinked polymer films. The thickness of the films was measured using a micrometer. The films are designated as PEGAX, PSBMAX and PCBMAX, where X indicates the molar composition of co-monomers in the polymerization mixture.

2.3. Hydrogel film characterization

The surface of each dried polymer film was chemically characterized using ATR-FTIR (Bruker TENSOR37, USA). A ZnS crystal with a 45° angle of incidence was used. The Zeta potential of the films was measured as a function of pH using an Anton-Paar SurPASS Electrokinetic Analyzer with clamping cell apparatus (Anton-Paar GmbH, Austria). All measurements were conducted in an electrolyte solution containing 10 mmol L^{-1} KCl. The pH was varied from 3 to 10, and the temperature was maintained at 298 K. The data were analyzed using the Fairbrother–Mastin algorithm.

2.4. Density and water uptake measurement

The dry film density was measured by Archimedes' principle using an analytical balance (CP 214, Ohaus, USA) with an Ohaus density determination kit. Film density (ρ_p) was calculated as [15,16]

$$\rho_P = \frac{M_A}{M_A - M_L}\rho_0 \tag{1}$$

where M_A is the film mass measured in air, M_L is the film mass measured in a non-solvent (hexane, ρ=0.659 g cm^{-3} at 298 K) that does not cause the polymer to swell, and ρ_0 is the density of the non-solvent. Samples were dried overnight under vacuum conditions and at room temperature prior to performing the density measurement.

Equilibrium water uptake at room temperature was determined gravimetrically. Samples were equilibrated in DI water, and the mass of the wet polymer, m_{wet}, was measured after wiping surface water off of the film. Next, the film was dried under vacuum until a constant dry mass, m_{dry}, was obtained and measured. Water uptake was calculated as [15]

$$\text{Water uptake} = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{2}$$

Assuming volume additivity applies in the cross-linked PEDGA and zwitterionic polymers, the masses measured during the water uptake experiment can be used to determine the volume fraction of water in the fully hydrated film, V_{H_2O}, and the volume fraction of water is often taken as a measure of K_w, which is the water partition coefficient, or water solubility in the polymer [13,24]:

$$V_{H_2O} = \frac{\frac{m_{wet} - m_{dry}}{\rho_{H_2O}}}{\frac{m_{wet} - m_{dry}}{\rho_{H_2O}} + \frac{m_{dry}}{\rho_P}} = K_w \tag{3}$$

where ρ_{H_2O} is the density of water (taken as 1.0 g cm^{-3}).