INFLUENCE OF POLYMER BACKBONE RIGIDITY ON WATER AND SALT TRANSPORT PROPERTIES OF LOW WATER CONTENT MEMBRANE POLYMERS FOR DESALINATION

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Providing sustainable supplies of purified water and energy is a critical global challenge for the future, and polymer membranes will play a key role in addressing these clear and pressing global needs for water and energy. Polymer membrane-based processes dominate the desalination market because they are more energy efficient than thermal desalination processes, and polymer membranes are crucial components in several rapidly developing power generation and storage applications that rely on membranes to control rates of water and/or ion transport. Much remains unknown about the influence of polymer structure on even basic intrinsic water and ion transport properties, and these relationships must be developed to design next generation polymer membrane materials. For desalination applications, polymers with simultaneously high water permeability and low salt permeability are desirable in order to prepare selective membranes that can efficiently desalinate water, and a tradeoff relationship between water/salt selectivity and water permeability provides a benchmarking tool for evaluating the intrinsic water and salt transport properties of membrane polymers.

The tradeoff relationship between water/salt permeability selectivity and water permeability suggests that both sorption and diffusion selectivity properties contribute significantly to water/salt permeability selectivity. The diffusivity tradeoff relationship can be related to free volume and/or polymer water content using established theories. Desalination membrane polymers often contain substantially less water compared to their hydrogel or ion exchange membrane counterparts. For example, cross-linked polyamide desalination membranes, prepared via interfacial polymerization, often absorb less than 10% water (by mass), though this value is sensitive to the specific chemistry and preparation procedure used to prepare the membrane. Transport in highly hydrated ion exchange membranes is often considered to depend more on the mobility of the bulk water sorbed in the polymer than the mobility of the polymer chains. As water content decreases, however, the role of polymer backbone rigidity may become increasingly important as water-polymer interactions become increasingly important relative to bulk sorbed water interactions.

To determine the influence of polymer backbone rigidity on water and ion transport in low water content polymers, a series of model polymers were developed where backbone rigidity could be controlled in addition to controlling water content and ion sorption properties. These chemically similar hydrophilic polymers, based on acrylic and methacrylic backbones, have different segmental dynamics, as characterized by the glass transition temperature of the hydrated polymers. Ion and water transport property measurements reveal that, at equivalent water content, polymers with slower segmental dynamics are more diffusion selective than those polymers with more rapid segmental dynamics. Additionally, the more rigid backbone polymers appear to be more size selective than the more flexible backbone polymers at comparable water content. These results suggest that polymer backbone rigidity affects water and salt transport properties of low-water content polymers where water-polymer interactions are likely significant, and they provide fundamental structure-property insight into water and salt transport in hydrated polymers of interest for membrane-based desalination applications.