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Engineering Selective Desalination Membranes via Molecular Control of Polymer Functional Groups

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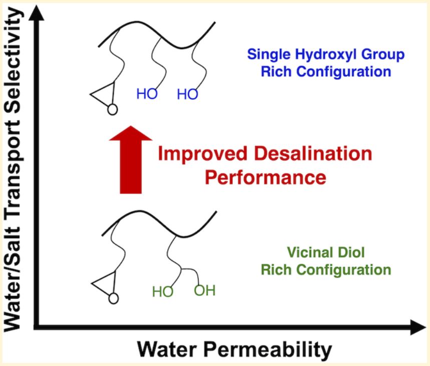
Supporting Information

ABSTRACT: Membrane-based desalination processes are used widely to address increasing global demand for purified water. To continue to meet increasing demand, advanced and highly selective desalination membranes are needed to effectively and efficiently purify water that is increasingly contaminated and saline. A general lack of fundamental structure−property relationships frustrates the development of these membranes. Advanced polymer synthesis capabilities that enable increasingly precise molecular control over the position of functional groups on a polymer backbone could be instrumental in engineering advanced desalination membranes, but little is known about how the position of functional groups influences water and salt transport properties. In this study, we prepared and characterized a series of equivalent water content copolymers to determine how the functional group configuration along the polymer backbone influences desalination-relevant transport properties. Shifting the copolymer composition from one rich in vicinal diol groups to one rich in side chains with a single hydroxyl group drove an increase in the water/salt permeability selectivity, which is directly related to desalination-critical salt rejection. The results suggest that controlled placement of functional groups within a polymer could be a viable strategy for preparing advanced and highly selective desalination membrane materials.



INTRODUCTION

Meeting global demand for clean water is a pressing engineering challenge.[1] Membrane-based technologies are used widely to desalinate water, and more efficient membranes are needed to meet growing demand for purified water from increasingly contaminated and/or saline water.[2−6] Water purification membranes are generally polymeric, and highly selective membranes are needed to meet the growing separation challenges in desalination technologies including reverse osmosis and nanofiltration.[6−10] The selective properties of these desalination membranes result from the preferential transport of water relative to hydrated ions.[11] Engineering highly selective materials has been frustrated by a lack of fundamental structure−property relationships to guide the design of advanced polymer membranes to address global water needs.

The ability to precisely place functional groups along a polymer backbone, with a high degree of molecular control over functional group position, is becoming increasingly viable.[12,13] This structural control, facilitated by advances in synthesis capabilities, could be important for engineering advanced desalination membranes. Little is known, however, about how functional group placement within a polymer influences water/salt selectivity.

We report the desalination (i.e., water/salt) selectivity properties of a series of model materials where the distribution of hydroxyl functional groups along the polymer backbone was varied from a clustered to a more uniform configuration. Importantly, this series of materials was prepared such that the membrane water content did not change as the distribution of the hydroxyl groups changed. Membrane water content has a significant influence on water/salt selectivity properties,[9,14] so the ability to vary the distribution of functional groups within the material without perturbing the water content enabled us to ascribe the observed results to changes in the functional group configuration.

Shifting the functional group configuration to space the hydroxyl groups out more evenly (compared to the more clustered configuration) resulted in increased water/salt permeability selectivity, which is directly related to desalination-critical salt rejection.[11] This increase in selectivity was largely driven by sorption, or thermodynamic, effects. The results suggest that an even distribution of hydrophilic chemical functionality in polymers may lead to more selective membranes to address global demand for desalinated water.

MATERIALS AND METHODS

HEMA:GMA:GMAOH Copolymers. Five copolymers containing 2-hydroxyethyl methacrylate (HEMA), glycidyl

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Table 1. Comonomer Mass Fraction in Prepolymerization Solution Used To Prepare HEMA:GMA:GMAOH copolymers Defines Sample Nomenclature[a]

	Comonomer mass fraction in prepolymerization solution					
Copolymer sample	HEMA	GMA	GMAOH	Water uptake[b]	Dry polymer density (g/cm^3)	K_w
0:60:40	0.0	0.60	0.40	0.24 ± 0.02	1.29 ± 0.02	0.23 ± 0.01
15:55:30	0.15	0.55	0.30	0.24 ± 0.01	1.30 ± 0.03	0.24 ± 0.01
30:50:20	0.30	0.50	0.20	0.24 ± 0.01	1.27 ± 0.01	0.23 ± 0.01
45:45:10	0.45	0.45	0.10	0.23 ± 0.01	1.27 ± 0.01	0.23 ± 0.01
60:40:0	0.60	0.40	0.0	0.23 ± 0.01	1.26 ± 0.02	0.23 ± 0.01

[a] The water uptake and dry density data were measured at ambient temperature, and the water sorption coefficient, K_w, was calculated using the water uptake and dry polymer density. Uncertainty in the measured data is one standard deviation from the mean of at least three measurements, and the uncertainty in the water sorption coefficient was calculated using standard propagation of error.[16] [b] Units: g(water)/g(dry polymer).

methacrylate (GMA), and glycerol methacrylate (GMAOH) comonomers and cross-linked using poly(ethylene glycol) dimethacylate (PEGDMA) were prepared via UV-initiated free radical polymerization. These model materials are chemically different from the aromatic polyamide-based membranes commonly used in reverse osmosis and nanofiltration membranes.[15] The structure of these materials (i.e., the choice of comonomers) was chosen to enable preparation of a series of materials where the distribution of hydrophilic functional groups (in this case, hydroxyl groups) could be varied by changing the composition of the copolymer without changing the water content of the polymer.

The hydroxyl group distribution in the copolymer was varied by changing the comonomer composition of the prepolymerization solution used to prepare the materials (Table 1). The sample nomenclature, HEMA:GMA:GMAOH x:y:z, reflects the composition (by mass) of the prepolymerization solution used to prepare that material (e.g., 15:55:30 was prepared from a prepolymerization solution containing 15%, 55%, and 30%, by mass, of HEMA, GMA, and GMAOH, respectively). The PEGDMA cross-linker and initiator (1-hydroxycyclohexyl phenyl ketone) were added to the comonomer solution at compositions of 0.1 and 0.01 g/g(total comonomer), respectively, to form the prepolymerization solution, which was stirred for 30 min at room temperature to ensure the solution was well mixed. The prepolymerization solution was degassed (via sonication for 10 min), confined between quartz plates (separated by spacers to control film thickness), and irradiated for 5 min with 120 μJ/cm^2 of 312 nm light to form transparent and homogeneous polymer films that were approximately 100 μm thick. The chemical structure and additional information about the copolymers are reported in Section S1 of the Supporting Information.

Water and Salt Transport Property Characterization. To characterize the potential desalination performance of the HEMA:GMA:GMAOH copolymers, we measured water uptake, the salt sorption coefficient, and water and salt permeability properties at ambient temperature. Water uptake was combined with dry polymer density to calculate the water sorption coefficient, K_w (Table 1).[17] Water ($i \to w$) and salt ($i \to s$) sorption coefficients, K_i, were combined with permeability properties, P_i, to calculate, via the solution-diffusion model,[18] apparent diffusion coefficients, D_i, as[19]

$$D_i = P_i/K_i \tag{1}$$

At least three measurements, per sample, were made for each property, and the uncertainty in the measurement was one standard deviation from the mean. The standard propagation of error was used to quantify the uncertainty in calculated quantities.[16] Details about the specific methods used to measure water uptake, salt sorption, pure water permeability, salt permeability, and hydrated polymer dielectric properties are reported in Section S2 of the Supporting Information.

RESULTS AND DISCUSSION

Each composition of HEMA:GMA:GMAOH had an equivalent water content (Table 1). Water content affects the transport (thus, desalination) selectivity of hydrated polymers, and increases in water content often correlate with decreases in selectivity.[9,14] Therefore, preparing materials with equivalent water content is critical for decoupling the influence of the functional group configuration on water/salt transport selectivity from the influence of changing water content on water/salt transport selectivity.

The equivalent water content of this series of HEMA:GMA:GMAOH copolymers likely results from subtle changes in the extent of cross-linking and hydroxyl group content across the series of copolymers. These changes were estimated to be reasonably small, as discussed in Section S1.1 of the Supporting Information. Ultimately, maintaining equivalent water content in the series of materials was prioritized due to the strong influence of water content on the water and salt transport properties of hydrated polymers.[9,14]

We compared the HEMA:GMA:GMAOH transport properties to those of cross-linked poly(ethylene glycol) diacrylate (PEG) hydrogels, as these materials also preferentially transport water over salt via a solution-diffusion mechanism.[20] The water content of these hydrogels can be manipulated by changing the ethylene glycol chain length or by adding a diluent to the prepolymerization mixture.[20] Thus, the PEG materials illustrate how transport properties change with water content to contrast the situation in equivalent water content HEMA:GMA:GMAOH.

The water/salt transport selectivity is defined as the ratio of water to salt permeability, P_w/P_s, sorption, K_w/K_s, or diffusion, D_w/D_s, coefficients, and the three selectivity values are related via the solution-diffusion model[9]

$$P_w/P_s = (K_w/K_s) \times (D_w/D_s) \tag{2}$$

This water/salt permeability selectivity can be directly related to salt rejection, which is a critical characteristic of effective desalination membranes.[11] The salt rejection, **R**, is defined as the salt concentration reduction from the bulk solution on the feed side of the membrane, $c_{s,feed}$, to the bulk solution on the permeate (or product) side of the membrane normalized by $c_{s,feed}$ and depends on the water/salt permeability selectivity

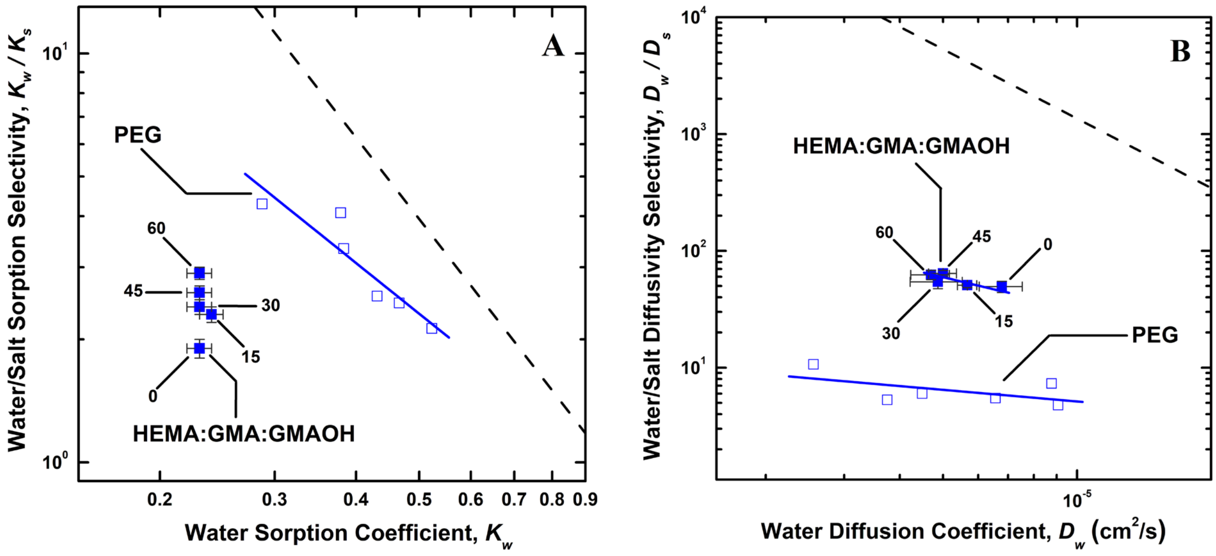

Figure 1. Water/salt sorption selectivity (A) and water/salt diffusivity selectivity (B) as a function of water sorption coefficient and apparent water diffusion coefficient, respectively, for HEMA:GMA:GMAOH (blue solid box) and PEG (blue open box)[20] materials. For HEMA:GMA:GMAOH, the HEMA comonomer composition of the prepolymerization solution used to prepare the copolymer is reported for each data point. The dashed lines represent reported empirical sorption (A) and diffusivity (B) trade-off frontiers for desalination membrane materials,[21,22] and the solid lines are least-squares fits to the data.

$$\mathrm{R} = \frac{c_{\mathrm{s,feed}} - c_{\mathrm{s,permeate}}}{c_{\mathrm{s,feed}}} = \frac{\frac{P_{\mathrm{w}} V_{\mathrm{w}}}{P_{\mathrm{s}} RT}(\Delta p - \Delta \pi)}{1 + \frac{P_{\mathrm{w}} V_{\mathrm{w}}}{P_{\mathrm{s}} RT}(\Delta p - \Delta \pi)} \qquad (3)$$

where V_w is the molar volume of water, Δp is the hydraulic pressure difference across the membrane, $\Delta\pi$ is the osmotic pressure difference across the membrane, R is the gas constant, and T is the absolute temperature.[9]

Water/salt permeability selectivity depends on a combination of both water/salt sorption and diffusivity selectivity properties (eq 2). Functional group configuration significantly influenced the water/salt sorption selectivity of HEMA:GMA:GMAOH (Figure 1A). A distributed hydroxyl group configuration (HEMA-rich copolymer) led to higher sorption selectivity compared to a vicinal diol-rich configuration (GMAOH-rich copolymer), and this result can be attributed to more effective exclusion of salt from the HEMA-rich copolymer compared to the GMAOH-rich copolymer.

Comparing HEMA:GMA:GMAOH water/salt sorption selectivity with that of poly(ethylene glycol) diacrylate (PEG) hydrogels, we observed that the HEMA:GMA:GMAOH data points move vertically upward as HEMA content increases in a manner different from the PEG materials (Figure 1A). The PEG result is expected if water content primarily drives sorption selectivity properties.[20] The HEMA:GMA:GMAOH result suggests that polymer chemistry, not changing water content, is responsible for the change in sorption selectivity of HEMA:GMA:GMAOH. Thus, preparing polymers with a distributed functional group configuration may be a viable strategy to increase the water/salt sorption selectivity.

The HEMA:GMA:GMAOH materials are approximately an order of magnitude more water/salt diffusion selective compared to the PEG materials (Figure 1B). This result may be due to the glassy nature of hydrated HEMA:GMA:GMAOH compared to the rubbery nature of PEG (see Section S1.3 of the Supporting Information).[23] More rigid (glassy) polymer backbones are often more diffusion selective compared to more flexible (rubbery) polymer backbones.[24−26]

The apparent water diffusion coefficient decreases and the water/salt diffusivity selectivity increases as the copolymer composition shifts toward a more HEMA-rich (or distributed hydroxyl group) configuration. This observed trend is similar to that observed for PEG. The water content of the PEG materials was varied systematically, and the explanation for the observed relationship between water/salt diffusivity selectivity and water diffusion coefficient is that reduction in the free volume of the polymer (as water content decreases) causes a general reduction in diffusion that influences the larger hydrated ions to a greater extent than water.[20] In HEMA:GMA:GMAOH, the change in comonomer composition (thus, distribution of hydroxyl groups) results in a situation where water diffusion slows as HEMA content increases. This reduction in water diffusivity is accompanied by an increase in water/salt diffusion selectivity that is similar in proportion to that of PEG. Therefore, changes in water diffusivity, due to compositional changes in the HEMA:GMA:GMAOH materials, may influence water/salt diffusivity selectivity in a manner similar to that in the free volume-based explanation where water diffusion depends strongly on free volume.[9,14]

Water/salt diffusivity selectivity is affected to a lesser extent, compared to water/salt sorption selectivity, by changing the HEMA content of the prepolymerization solution. The water/salt diffusivity selectivity increases by 26% over the range of HEMA compositions considered. The water/salt sorption selectivity, by comparison, increases by 53% over the range of HEMA compositions considered. Importantly, the 53% increase in sorption selectivity comes without a change in the water sorption coefficient, which as discussed subsequently, means that, as copolymer composition changes, the water permeability will not change because of sorption effects.

The decrease in the apparent water diffusivity as the copolymer composition changes at constant water content could be considered unexpected, as diffusivity in hydrated polymers is often a strong function of water content.[9,14,27−29] Dielectric permittivity properties, however, provide insight into the observed water diffusivity. As further discussed in Section S3 of the Supporting Information, the dielectric loss spectra can be interpreted in terms of time constants, which describe the dipole relaxation dynamics of different modes of water motion, and the dielectric strengths of those relaxations, which describe the relative amount of water in the material that is participating in each relaxation mode.[30]

Dielectric spectroscopy suggests three populations of dipolar water motion: highly restricted motion that relaxes on an order 0.1 ns time scale, less restricted motion that relaxes with a time constant of approximately 45 ps, and nonrestricted (i.e., bulk water) motion that relaxes with a time constant of 8.8 ps (see Supporting Information for additional discussion). In general, the dielectric strength associated with each mode of motion decreases as HEMA content increases (Table S1), though the reduction is more pronounced for the nonrestricted relaxation mode compared to the other two modes. This decrease in the dielectric strength associated with all three relaxation modes, coupled with the statistically equivalent water content of the materials, suggests that increasing HEMA content promotes water−polymer interactions that relax at frequencies lower than that probed in our experiments.

An example of such interactions would be water that is very tightly associated with the hydroxyl groups. Such (effectively immobile) water will not be detected by dielectric spectroscopy in the frequency range considered here.[31] As such, the dielectric strength data suggests that distributing the hydroxyl groups in the polymer causes more water to tightly associate with hydroxyl groups compared to the situation in the vicinal diol-rich materials.

This molecular picture is consistent with a steric explanation suggesting that water molecules may be able to hydrate the hydroxyl group on a HEMA side chain to a greater extent compared to the more sterically hindered GMAOH side chain. This explanation is also consistent with estimates of the enthalpy of hydration for the hydroxyl groups on the side chains (see Section S4 of the Supporting Information). Ultimately, this reduction in water motion within the polymer appears to have a similar effect on both water and salt diffusivity to that of reducing the water content of the polymer (as supported by the similar slopes of the data in Figure 1B).

Primarily due to the strong increase in water/salt sorption selectivity at constant water content, the HEMA:GMA:GMAOH water/salt permeability selectivity increases as the HEMA content of the prepolymerization solution used to prepare the materials increases (Figure 2). A distributed hydroxyl group configuration (HEMA-rich) is more selective for water over salt transport compared to the vicinal diol-rich configuration (GMAOH-rich). The overall selectivity of the HEMA:GMA:GMAOH series of materials is greater than that of the PEG materials due to the previously discussed differences in the diffusivity selectivity properties.

The PEG materials exhibit a typical trade-off relationship whereby water/salt selectivity tends to decrease as materials become more permeable to water. This trade-off is often observed in cases where the water content of a series of materials is varied systematically.[22] In these cases, the higher water content polymers tend to have higher water permeability and lower water/salt selectivity compared to the lower water content polymers.

The HEMA:GMA:GMAOH materials suffer less of a reduction in the diffusive water permeability as water/salt selectivity increases compared to the PEG materials (i.e., slope of the HEMA:GMA:GMAOH line is steeper than that of the PEG line in Figure 2). This result stems from the equivalent water content nature of the HEMA:GMA:GMAOH series of materials and the fact that both water/salt sorption and diffusivity selectivity increase with increasing content of HEMA in the prepolymerization solution.

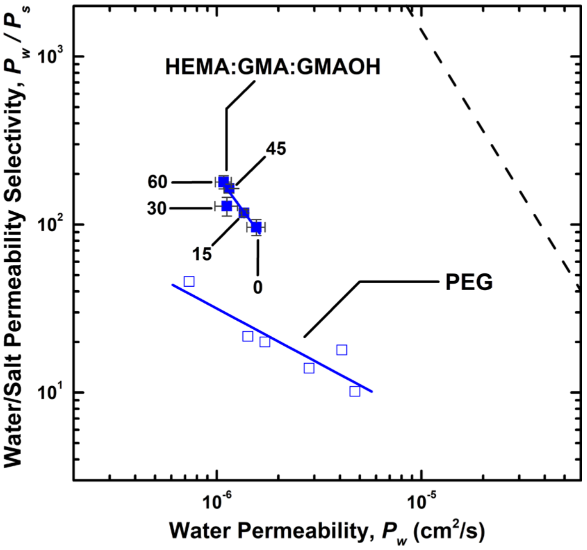

Figure 2. Water/salt permeability selectivity as a function of diffusive water permeability for HEMA:GMA:GMAOH (blue solid box) and PEG (blue open box)[20] materials. For HEMA:GMA:GMAOH, the HEMA comonomer composition of the prepolymerization solution used to prepare the copolymer is reported for each data point. The dashed line represents a reported empirical permeability trade-off frontier for desalination membrane materials,[21,22] and the solid lines are least-squares fits to the data.

Chemical modification of a series of water content-equivalent copolymers, from a vicinal diol-rich to a distributed hydroxyl group-rich configuration, increased water/salt permeability selectivity with a smaller water permeability penalty compared to that often observed in hydrated polymers. These results, obtained using a model series of copolymers, suggest that controlling the spatial arrangement of functional groups in hydrated membrane materials may be important for engineering highly selective polymers for desalination applications. The results on these model materials represent a step toward establishing general water and salt transport structure−property relationships for membrane materials including polymers that are more chemically similar to commercial desalination membranes than those materials considered here. The results suggest that distributed hydrophilic functional groups may lead to increased selectivity and may represent a strategy for improving water/salt selectivity of advanced membrane materials to address global water shortages.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.9b00351.

Additional information regarding experimental methods, material properties, and characterization (molar composition, hydroxyl group content, FT-IR, and glass transition temperature analysis), microwave dielectric spectroscopy data analysis, and hydroxyl group hydration analysis. (PDF)

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Notes

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REFERENCES

(1) Mekonnen, M. M.; Hoekstra, A. Y. Four billion people facing severe water scarcity. *Sci. Adv.* **2016**, *2*, No. e1500323.

(2) Tang, C. Y.; Yang, Z.; Guo, H.; Wen, J. J.; Nghiem, L. D.; Cornelissen, E. Potable water reuse through advanced membrane technology. *Environ. Sci. Technol.* **2018**, *52*, 10215−10223.

(3) Miller, S.; Shemer, H.; Semiat, R. Energy and environmental issues in desalination. *Desalination* **2015**, *366*, 2−8.

(4) Subramani, A.; Jacangelo, J. G. Emerging desalination technologies for water treatment: A critical review. *Water Res.* **2015**, *75*, 164−187.

(5) Amy, G.; Ghaffour, N.; Li, Z.; Francis, L.; Linares, R. V.; Missimer, T.; Lattemann, S. Membrane-based seawater desalination: Present and future prospects. *Desalination* **2017**, *401*, 16−21.

(6) Cohen, Y.; Semiat, R.; Rahardianto, A. A perspective on reverse osmosis water desalination: Quest for sustainability. *AIChE J.* **2017**, *63*, 1771−1784.

(7) Werber, J. R.; Deshmukh, A.; Elimelech, M. The critical need for increased selectivity, not increased water permeability, for desalination membranes. *Environ. Sci. Technol. Lett.* **2016**, *3*, 112−120.

(8) Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D. Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science* **2017**, *356*, 1−10.

(9) Geise, G. M.; Paul, D. R.; Freeman, B. D. Fundamental water and salt transport properties of polymeric materials. *Prog. Polym. Sci.* **2014**, *39*, 1−42.

(10) Geise, G. M.; Lee, H.-S.; Miller, D. J.; Freeman, B. D.; McGrath, J. E.; Paul, D. R. Water purification by membranes: The role of polymer science. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *48*, 1685−1718.

(11) Baker, R. W. *Membrane Technology and Applications*, 3rd ed.; Wiley: New York, 2012.

(12) Solleder, S. C.; Zengel, D.; Wetzel, K. S.; Meier, M. A. R. A scalable and high-yield strategy for the synthesis of sequence-defined macromolecules. *Angew. Chem., Int. Ed.* **2016**, *55*, 1204−1207.

(13) Lutz, J.-F. Defining the field of sequence-controlled polymers. *Macromol. Rapid Commun.* **2017**, *38*, 1700582.

(14) Yasuda, H.; Lamaze, C. E.; Ikenberry, L. D. Permeability of solutes through hydrated polymer membranes Part I. Diffusion of sodium chloride. *Makromol. Chem.* **1968**, *118*, 19−35.

(15) Petersen, R. J. Composite reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **1993**, *83*, 81−150.

(16) Bevington, P. R.; Robinson, D. K. Propagation of Errors. In *Data Reduction and Error analysis for the Physical Sciences*; McGraw Hill: New York, 2003; Chapter 4, pp 56−65.

(17) Chang, K.; Luo, H.; Geise, G. M. Water content, relative permittivity, and ion sorption properties of polymers for membrane desalination. *J. Membr. Sci.* **2019**, *574*, 24−32.

(18) Wijmans, J. G.; Baker, R. W. The Solution-Diffusion Model: A Unified Approach to Membrane Permeation. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Y. P., Pinnau, I., Freeman, B. D., Eds.; John Wiley & Sons, Ltd.: West Sussex, 2006; pp 159−189.

(19) Geise, G. M.; Freeman, B. D.; Paul, D. R. Sodium chloride diffusion in sulfonated polymers for membrane applications. *J. Membr. Sci.* **2013**, *427*, 186−196.

(20) Ju, H.; Sagle, A. C.; Freeman, B. D.; Mardel, J. I.; Hill, A. J. Characterization of sodium chloride and water transport in crosslinked poly(ethylene oxide) hydrogels. *J. Membr. Sci.* **2010**, *358*, 131−141.

(21) Zhang, H.; Geise, G. M. Modeling the water permeability and water/salt selectivity tradeoff in polymer membranes. *J. Membr. Sci.* **2016**, *520*, 790−800.

(22) Geise, G. M.; Park, H. B.; Sagle, A. C.; Freeman, B. D.; McGrath, J. E. Water permeability and water/salt selectivity tradeoff in polymers for desalination. *J. Membr. Sci.* **2011**, *369*, 130−138.

(23) Ju, H.; McCloskey, B. D.; Sagle, A. C.; Kusuma, V. A.; Freeman, B. D. Preparation and characterization of crosslinked poly(ethylene glycol) diacrylate hydrogels as fouling-resistant membrane coating materials. *J. Membr. Sci.* **2009**, *330*, 180−188.

(24) Chang, K.; Korovich, A.; Xue, T.; Morris, W. A.; Madsen, L. A.; Geise, G. M. Influence of rubbery versus glassy backbone dynamics on multiscale transport in polymer membranes. *Macromolecules* **2018**, *51*, 9222−9233.

(25) Chang, K.; Xue, T.; Geise, G. M. Increasing salt size selectivity in low water content polymers via polymer backbone dynamics. *J. Membr. Sci.* **2018**, *552*, 43−50.

(26) Paul, D. R.; Yampol'skii, Y. P. *Polymeric Gas Separation Membranes*; CRC Press: Boca Raton, FL, 1994.

(27) Yasuda, H.; Ikenberry, L. D.; Lamaze, C. E. Permeability of solutes through hydrated polymer membranes Part II. Permeability of water soluble organic solutes. *Makromol. Chem.* **1969**, *125*, 108−118.

(28) Mackie, J. S.; Meares, P. The diffusion of electrolytes in a cation-exchange resin membrane. I. Theoretical. *Proc. R. Soc. London, Ser. A* **1955**, *232*, 498−509.

(29) Meares, P. The mechanism of water transport in membranes. *Philos. Trans. R. Soc., B* **1977**, *278*, 113−150.

(30) Lu, Z.; Polizos, G.; Macdonald, D. D.; Manias, E. State of water in perfluorosulfonic ionomer (Nafion® 117) proton exchange membranes. *J. Electrochem. Soc.* **2008**, *155*, B163−B171.

(31) Smith, G.; Duffy, A. P.; Shen, J.; Olliff, C. J. Dielectric relaxation spectroscopy and some applications in the pharmaceutical sciences. *J. Pharm. Sci.* **1995**, *84*, 1029−1044.