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Desalination Membranes

Highly Chlorine-Tolerant Polymers for Desalination**

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An urgent need in the 21st century is access to secure, sustainable sources of fresh water.[1] Membrane-based desalination is an energy-efficient, low environmental impact route to produce clean water for a variety of applications. Capital, operation, and maintenance costs for membrane systems continue to decline, making them increasingly attractive for water purification applications.[2] Membrane separation processes, such as nanofiltration (NF) and reverse osmosis (RO), have developed rapidly over the last three decades into the dominant technology for desalination of water.[3] Commercially available RO membranes are derived from two basic classes of polymers: cellulose acetate (CA) and aromatic polyamides (PA). However, CA membranes are susceptible to microbiological attack, undergo compaction at higher temperatures and pressures, and are limited to a relatively narrow pH range.[4] On the other hand, PA membranes exhibit better transport properties at a given applied pressure and are more stable over a wider range of pH values than CA membranes.[5] Thus, PA thin-film composite membranes are currently the most widely used desalination membranes.

However, PA membranes suffer from poor resistance to continual exposure to oxidizing agents such as chlorine.[6] Chlorine is the most widely used oxidizing biocide in water treatment because it is inexpensive and highly effective when present in water at levels of a few parts per million.[7] Disinfection of feed water to membrane desalination units is required to prevent biofilm growth on the membranes, which significantly degrades their performance.[8] However, PA membranes cannot tolerate continuous exposure to water containing more than a few parts per billion chlorine.[6,9] Consequently, membrane manufacturers recommend that feed-water chlorine concentration to such membranes be limited to concentrations lower than 0.1 ppm. To meet these conflicting requirements, water to be purified is often chlorinated, to disinfect it and ultimately inhibit biofouling of the membranes, then dechlorinated before being fed to membrane desalination units. After passing through the membranes, the water is then rechlorinated before being sent to the distribution network.[10] Thus, the sensitivity of PA membranes to chorine leads to significant additional processing steps and, in turn, increased water purification costs.[11]

We describe a new platform of highly chlorine-tolerant polymers for use as desalination membranes. Such materials could expand the processing window for using chlorine in conjunction with desalination membranes, remove costly process steps, such as dechlorination and rechlorinations, and yield significant increases in membrane lifetime. The removal of processing steps, leading to process intensification, and increase in membrane lifetime could lower water desalination costs. These chlorine-tolerant polymers are based on polysulfone, a rugged, widely available, engineering thermoplastic having excellent mechanical properties and good biological, chemical, and thermal stability.[12] Polysulfone has much better chlorine resistance than aromatic polyamides because its main chain consists of aromatic rings and chemically strong bonds between carbon, sulfur, and oxygen, so it does not have the amide linkages that are sensitive to attack by aqueous chlorine.[13] Unfortunately, conventional polysulfone is hydrophobic, so it does not allow water permeation at significant rates. Therefore, the chemical structure of polysulfone must be altered to induce controlled levels of hydrophilicity, to enable high rates of water transport while maintaining good salt rejection, and to retain the excellent physical properties of polysulfone.

Sulfonation and amination have been reported as materials design strategies for increasing the hydrophilicity of polysulfone membranes.[14,15] In particular, sulfonated polysulfones have attracted interest, because they have promising property profiles for desalination as they exhibit selective ion transport and are highly tolerant to aqueous chlorine over a broad range of pH values.[16–18] However, previous sulfonated polysulfone desalination membranes were prepared by post-polymerization sulfonation methods.[16–19] Sulfonation of polysulfone with strong acids (e.g. sulfuric and chlorosulfuric acids) leads to undesirable side reactions (e.g. cross-linking),

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heterogeneous (i.e. nonuniform) reaction, and chain cleavage, which can make it difficult control sulfonation levels and maintain good mechanical properties in the final polymer.[20] Moreover, such sulfonated polymers are limited to low sulfonation levels, owing to the low reactivity of the aromatic rings directly attached to the sulfone groups.[20] In the 1980s, these synthetic challenges prevented the preparation of sulfonated polysulfone membranes with flux/rejection capabilities equivalent to those of PA membranes, so sulfonated polysulfones have not been used extensively, despite their promising desalination properties and excellent chlorine stability.

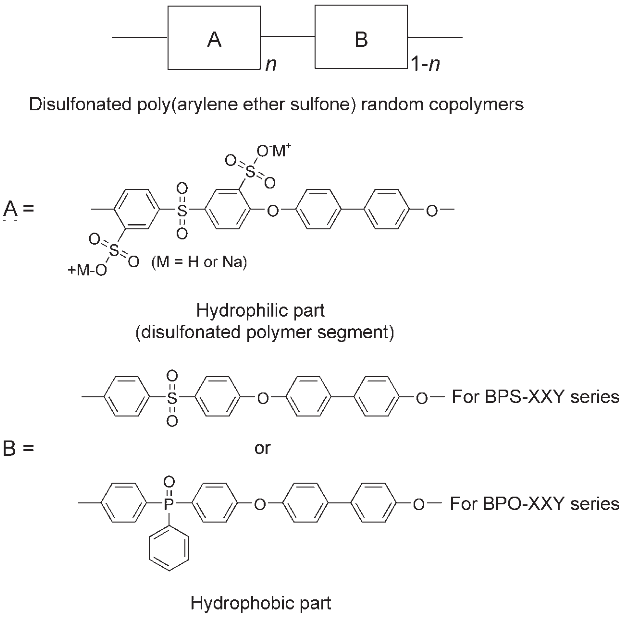

Figure 1. Chemical structure of random, disulfonated poly(arylene ether sulfone)s. A = hydrophilic segment, B = hydrophobic segment; XX = mol% disulfonated monomer (20, 30, 35, and 40); Y = H (free acid form) or N (sodium salt form).[21–23]

In contrast, the random copolymers described herein are synthesized by direct polymerization of a disulfonated monomer (3,3′-disulfonato-4,4′-dichlorodiphenyl sulfone (SDCDPS)) and other monomers (e.g. 4,4′-dichlorodiphenyl sulfone (DCDPS), 4,4′-biphenol (BP), and 4,4′-difluorotriphenylphosphine oxide (DFTPPO)) as indicated in Figure 1.[21–23] Such random, disulfonated poly(arylene ether sulfone) copolymers circumvent the challenges associated with sulfonated polysulfones prepared by more traditional, post-polymerization sulfonation routes. For example, use of sulfonated monomers affords precise control of the ionic group concentration in the final polymer, which leads to highly reproducible materials. Additionally, since no post-polymerization synthesis steps are required, the problems encountered with post-polymerization sulfonation, such as side reactions, molecular weight degradation, and cross-linking, are completely eliminated. In the sulfonated monomer approach, the ionic groups are located at inherently more chemically stable positions than those obtained by post-polymerization sulfonation, which sulfonates the most reactive, least stable positions of the polymer chain.[22] Because the chemistry of polysulfone synthesis is well-developed, using a sulfonated monomer permits the rapid preparation of entire libraries of new membrane materials for desalination applications. Finally, since the ionic group location in sulfonated monomer based materials is different from that in post-polymerization sulfonation based materials, it is reasonable to anticipate that new property sets could be accessible with the sulfonated monomer approach.

As shown in Table 1, water uptake, an indicator of hydrophilicity, increases systematically as sulfonated monomer concentration (or, equivalently, ion exchange capacity (IEC)) increases. The nomenclature is BPS-XXY or BPO-XXY, where XX is the molar percentage of hydrophilic sulfone groups (i.e. SDCDPS) in the polymer, and Y is H (free acid sulfonate form) or N (sodium sulfonate form). For example, BPS-20N is a disulfonated copolymer in the sodium sulfonate form containing 20 mol% SDCDPS and 80 mol% DCDPS. In general, materials with higher water uptake exhibit both higher water and salt permeability as well as lower salt rejection.[24] Thus, there is a tradeoff between water permeability and salt rejection, with materials having higher water permeability exhibiting lower salt rejection, and vice versa. This trend is reminiscent of the permeability/selectivity tradeoff in gas separation polymers[25,26] and suggests that a similar effect is operative in desalination materials.

Table 1: Fundamental physical and transport properties of disulfonated poly(arylene ether sulfone) films at 25 °C.

	Dry density [g cm^{-3}]	Water uptake [%]	IEC[a] [meq g^{-1}]	Water permeability[b] [L µm m^{-2} h^{-1} bar^{-1}]	NaCl rejection[c] [%]	NaCl permeability[d] [10^{-8} cm^2 sec^{-1}]
BPS-20N	1.324	4.5	0.92	0.03	99.2	0.004
BPS-30N	1.349	9.1	1.34	0.18	96.2	0.3
BPS-35N	1.353	12.3	1.52	0.34	94.3	0.9
BPS-40N	1.358	17.3	1.78	0.62	92.5	1.6
BPO-40N	1.193	15.7	1.56	0.43	97.5	0.2
BPS-20H	1.353	18.1	0.92	0.21	98.7	0.01
BPS-30H	1.370	30.7	1.34	1.20	92.1	1.3
BPS-35H	1.386	39.7	1.52	2.34	88.2	4.5
BPS-40H	1.420	59.5	1.78	4.21	85.9	9.4
BPO-40H	1.212	25.6	1.56	0.76	95.3	0.7

[a] Measured by ^{1}H NMR spectroscopy. [b] Measured at 25 °C using cross-flow filtration (feed pressure 27.6 bar). [c] Measured at 25 °C using cross-flow filtration (feed pressure 27.6 bar; feed flow rate 3.0 L min^{-1}; Reynolds number Re = 3747; feed concentration 2000 ppm NaCl). [d] Measured by kinetic desorption experiments at 25 °C.

A highly polar hydrophobic segment was also explored in the polymer design. As shown in Figure 1, the sulfone linkage in BPS-40Y was replaced with a more polar triphenyl phosphine oxide (TPPO). The TPPO group is highly polar, leading to strong interactions with other polar groups (e.g. sufonic acid groups) through hydrogen bonding or acid–base complexation.[27] As a result, BPO-40Y exhibits lower water uptake and water permeability than the analogous BPS-40Y polymer. On the other hand, the BPO-40Y membranes exhibits significantly higher NaCl rejection than BPS-40Y membranes by suppressing membrane swelling under fully hydrated conditions. That is, the strong interaction between polymer chains appears to contribute to lower water permeability and higher salt rejection. Thus, the water and salt transport properties are also sensitive to changes in the chemical structure of the hydrophobic elements of the polymer chains.

Interestingly, materials with a wide range of water and salt permeation properties may be prepared by varying hydrophilic monomer content and form (either acid or salt) as well as hydrophobic group type (BPS vs. BPO). As indicated in Table 1, properties ranging from those of nanofiltration (88.2 % NaCl rejection) to those similar to reverse osmosis (99.2 % NaCl rejection) membranes are obtained. Among the materials considered, water permeability may be varied by more than two orders of magnitude.

As indicated earlier, current commercial PA-based desalination membranes are chemically attacked by exposure to even low levels of chlorine.[6,9,13,28] Low pH values exacerbate the sensitivity of PA membranes to chlorine.[6] As shown in Figure 2, the water permeability and contact angle of BPS materials were unaffected by exposure to even high levels of chlorine over a wide range of pH values (from 4 to 10). These chlorine stability tests were conducted by immersing membrane coupons in buffered aqueous solutions of sodium hypochlorite (NaOCl) at concentrations of 10, 100, and 1000 ppm, as described in the literature, and then measuring water permeability and contact angle.[27] For comparison, in aromatic PA membranes, permanent changes in water permeability and loss in salt rejection occur more rapidly at low pH values (3–5).[13] The contact angle of water on the membrane surface was independent of chlorine concentration and pH value, thus demonstrating that the membrane surfaces were not changed by exposure to chlorine. Table 2 presents the influence of chlorine exposure on salt diffusivity, distribution coefficient, and permeability in BPS-35Y. The salt distribution coefficient and diffusivity were determined by kinetic desorption studies of salt from films that had been exposed to aqueous chlorine solutions, and the salt permeability was estimated as the product of salt distribution coefficient and salt diffusivity.[29] As shown in Table 2, chlorine exposure did not measurably alter these fundamental transport properties in either the acid or salt forms of the polymer.

Commercial RO membranes consist of a thin, selective coating layer that is, at most, a few hundred nanometers thick (100–250 nm) and is supported on a microporous sublayer.[3] Thus, the preparation of membranes with very thin skin layers is important for achieving high flux. Moreover, the coating layer must be defect-free to obtain high salt rejection. In this study, composite membranes were prepared by brush coating dilute polymer solutions (e.g. 0.5 wt % by w/v) in 96 % formic acid onto commercial microporous polysulfone RO support membranes, which were subsequently air-dried to remove solvent. Figure 3 presents a cross-sectional scanning electron microscope (SEM) image of an acid form BPS-40H composite membrane. The water permeance of these composite membranes varies from 1.3 to 4.5 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$, and NaCl rejection values were in the range of 83–89 %, depending on coating conditions. These results were obtained in cross-flow experiments at a feed pressure of 27.6 bar and with a feed containing 2000 ppm NaCl. Based on the water permeability (4.0 $\mathrm{L\,\mu m\,m^{-2}\,h^{-1}\,bar^{-1}}$) of a dense, thick BPS-40H film, the effective thickness of these composite membranes is approx-

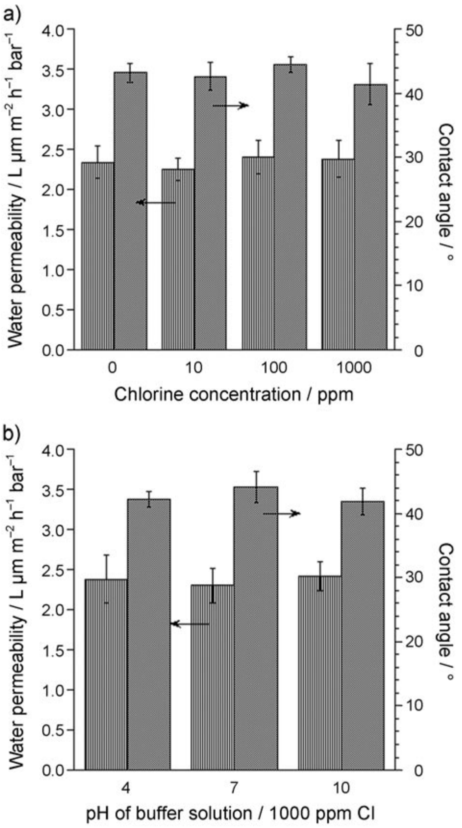

Figure 2. Changes in water permeability and contact angle of BPS-35H (in acid form) as a function of a) chlorine concentration at pH 4 and b) pH in buffer solution including 1000 ppm Cl. Feed pressure 27.6 bar, feed flow rate 3.0 liter $\mathrm{min^{-1}}$ (Re = 3747), feed composition 2000 ppm NaCl, cross-flow cell, 1 day at 10, 100, 1000 ppm Cl exposure.

Table 2: Effect of free chlorine exposure on NaCl diffusivity (D), solubility (K), and permeability (P) coefficients of disulfonated poly(arylene ether sulfone) membranes at 25 °C.[a]

Polymer	D [10^{-6} $\mathrm{cm^2\,sec^{-1}}$]	K	P [10^{-8} $\mathrm{cm^2\,sec^{-1}}$]
BPS-35H (control)	1.4	0.064	9.0
BPS-35H (pH 4)	1.6	0.063	10.1
BPS-35H (pH 10)	1.4	0.063	8.8
BPS-35N (control)	3.5	0.033	1.2
BPS-35N (pH 4)	3.7	0.036	1.3
BPS-35N (pH 10)	3.6	0.034	1.2

[a] All samples were immersed in 1000 ppm Cl at pH 4.2 and pH 10 buffer solutions for 1 day. Permeability was calculated as $P = D \times K$.

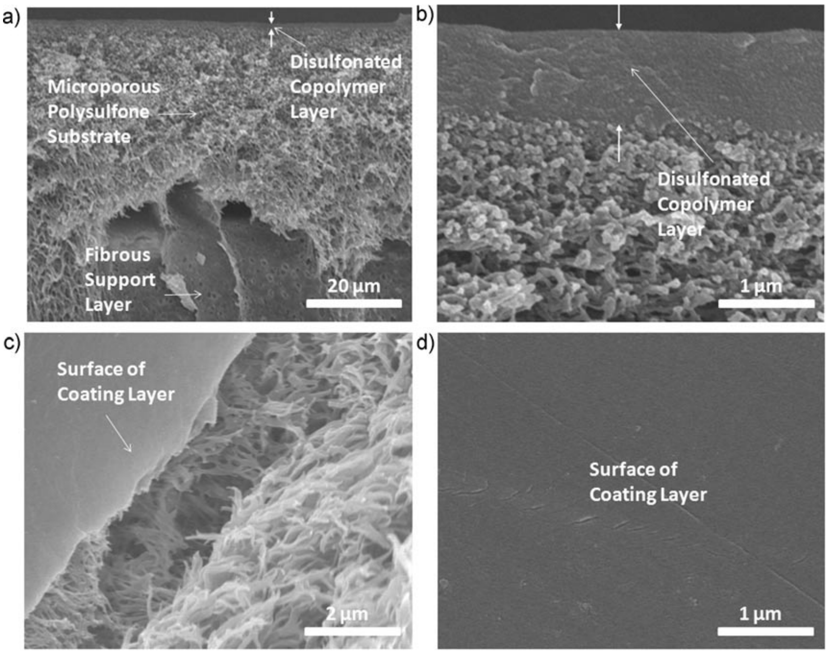

Figure 3. SEM micrographs of the cross-section and surface of disulfonated poly(arylene ether sulfone) random copolymer coated composite membranes: a) the three layers of the membrane; b) the top two layers of the membrane; c) the surface of the coating layer; d) a magnified view of the coating surface.

imately 0.7–1.2 μm, which is similar to the coating thickness observed by SEM, indicating negligible penetration of the polymer coating solution into the pores of the microporous support during coating. The rejection of many of the composite membranes was comparable to that of the dense film (85.9 %), indicating defect-free coatings.

The order of salt rejection in a BPS-40H composite membrane was as follows: Na_2SO_4 (97.3 %) > NaCl (89.5 %) > $MgSO_4$ (86.3 %) > $MgCl_2$ (77.8 %) > $CaCl_2$ (69.4 %). This order of salt rejection is reported in other negatively charged polymers.[24,30] Rejection generally increases with increasing anion valence. $CaCl_2$ rejection is less than that of NaCl, which may be due to the presence of a higher valence cation in $CaCl_2$; the divalent cation (Ca^{2+}) at the membrane surface may shield the repulsive force of the membrane's negative charge on the anions, thereby lowering rejection to divalent cations.

Chlorine-tolerance studies were performed on composite membranes. In these studies, the membrane was operated continuously in cross-flow filtration with a feed solution containing 2000 ppm NaCl and 500 ppm chlorine as NaOCl; the feed was buffered to pH 9.5. Figure 4 presents NaCl rejection and permeate flux as a function of chlorine exposure. The sulfonated polysulfone sample was a composite membrane prepared from BPS-40H (BPS-40H TFC). A commercial RO membrane (SW30HR, Dow FilmTec) was run side-by-side for comparison. The feed-water chlorine concentration was 500 ppm for this accelerated continuous test, and the pH value was maintained at 9.5 using a small amount of sodium hydroxide. The NaCl rejection of the commercial PA membrane decreases by more than 20 % after only 10 000 ppm-hours (20 h) of continuous exposure to chlorine and falls off even more rapidly thereafter. Such significant loss of salt rejection prohibits the use of chlorine for controlling biofouling in water being fed to such membranes without rigorous dechlorination to protect the membranes from chlorine exposure. In sharp contrast, there is no significant change in either NaCl rejection or water flux for the disulfonated copolymer composite membrane. This result is an example of the behavior obtained with other sulfonated polysulfone samples tested in our laboratories. As indicated earlier, salt rejection of these composite membranes can be improved by varying sulfonation level, hydrophobic moiety type, and form (i.e. acid or salt). For example, in an acid-form BPO-40H composite membrane, NaCl rejection values of 95 % are achieved in cross-flow filtration using 2000 ppm NaCl at a feed pressure of 27.6 bar.

In summary, disulfonated copolymer membranes, derived from direct copolymerization of a sulfonated monomer with non-sulfonated monomers, exhibit high tolerance to chlorine over a wide pH range. In

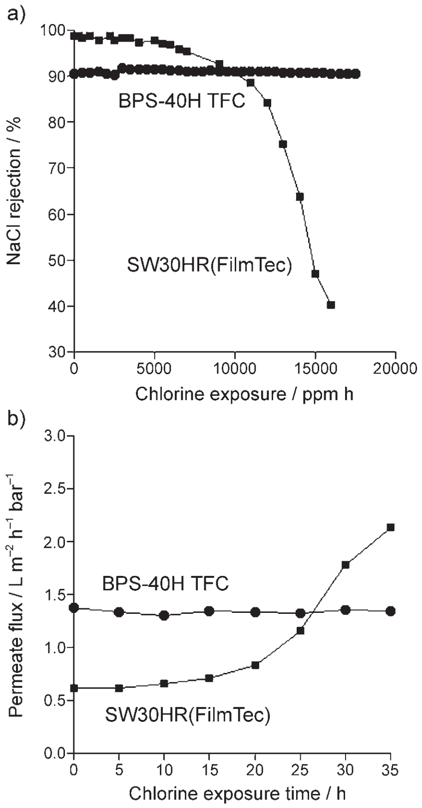

Figure 4. Effect of chlorine exposure on a) NaCl rejection and b) permeate flux of thin-film composite membranes of disulfonated copolymer (BPS-40H) at 25 °C. Feed pressure 27.6 bar, feed flow rate 3.8 $L\,min^{-1}$ (Re = 4683), feed composition 2000 ppm NaCl, cross-flow cell, pH 9.5, chlorine concentration = 500 ppm.

earlier studies, these materials were also shown to have good resistance to fouling by, for example, protein solutions or oil/water emulsions.[31] Depending on polymer structure and sulfonation level, these membranes can be tailored for specific separation purposes (e.g. NF or RO). Given their high chlorine tolerance, these membranes offer the possibility of desalinating and purifying water without the dechlorination steps that are now used before water is fed to membrane desalination units. Further studies are aimed at optimizing polymer design by employing cross-linked structures,[32] block copolymers, and blends of sulfonated and non-sulfonated polymers to simultaneously achieve high water permeability and high salt rejection while maintaining excellent chlorine tolerance.

Experimental Section

Membrane preparation: The synthesis of disulfonated copolymers was performed as previously reported.[21–23] Films of these materials were prepared as follows: polymer powder (in the sodium sulfonate form) was dissolved in *N*-dimethyl acetamide (DMAc, Aldrich, Milwaukee, WI) to form a 5 wt % solution. Then the polymer solution was filtered through a 0.45 μm PTFE syringe filter (Millipore, Billerica, MA). After degassing, the viscous solution was cast onto a clean glass plate, and the solvent was slowly evaporated over 24 h using an infrared lamp to assist the drying process. Residual solvent was thoroughly evaporated under vacuum for 48 h at 120 °C. To prepare films in the acid form, salt-form films were boiled in 0.5 M sulfuric acid for 2 h. Then the acidified films were treated in boiling deionized water to eliminate excess acid. Finally, the films were dried under vacuum at 110 °C before use.

Water permeability and salt rejection measurements: Water permeability P_w was calculated from the volume of water V permeated through a membrane of area A and thickness l divided by the pressure difference Δp at time t [Eq. (1)].

$$P_{\mathrm{w}} = \frac{V \cdot l}{A \cdot t \cdot \Delta p} \qquad (1)$$

Sodium chloride was used as the primary solute for monovalent ion rejection studies. The salt rejection experiment was performed in cross-flow filtration systems using feed solutions containing 2000 mg L^{-1} (2000 ppm) NaCl. The salt rejection R was calculated according to Equation (2).

$$R(\%) = \left(1 - \frac{C_{\mathrm{p}}}{C_{\mathrm{f}}}\right) \times 100 \qquad (2)$$

C_p is the salt concentration in the permeate and C_f is the salt concentration in the feed water. Both C_p and C_f were measured with an NIST-traceable expanded range digital conductivity meter (Oakton CON 110 conductivity and TDS meter, Oakton Instruments, Vernon Hills, IL).

Kinetic desorption measurement: Salt diffusivity was determined from the rate of desorption of salt into deionized water from a film previously equilibrated with a 1 M NaCl solution (50 mL) at 25 °C for at least 48 h while slowly stirring the solution at approximately 100 rpm. The temperature of the deionized water (50 mL) in the extraction bath and in the conductivity cell was maintained at 25 °C. A conductivity cell with a cell constant of 0.1 cm^{-1} (LR 325/01, WTW, Germany) and a conductivity meter (Inolab Cond 730, WTW) were used to record the conductivity in the extraction bath as a function of time. The diffusivity was determined by fitting the linear portion of the salt desorption as a function of the square root of extraction time to Fickian diffusion models.[29,33,34] The salt distribution coefficient was determined by measuring the total amount of NaCl extracted during the kinetic desorption study and calculated as the amount of salt extracted per unit volume of polymer divided by the salt concentration in the solution that the film was initially equilibrated with (i.e. 1 M NaCl).[29,34]

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