Swelling and inflation in polyelectrolyte complexes

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ABSTRACT

The properties of polyelectrolyte complexes, PECs, made from blended polycations, Pol^+, and polyanions, Pol^-, are routinely studied under conditions where they are at least partially swollen with water. Water plasticizes PECs, transforming them from an intractable, glassy, and brittle state when dry, to tough and viscoelastic when wet. In the present work the supreme efficiency of water, compared to other solvents on a polarity scale, in swelling a PEC is illustrated. Using a PEC of poly(diallyldimethylammonium) and poly(styrenesulfonate) with precisely determined density, it is shown that swelling tracks a Dimroth-Reichardt polarity scale until the molecular volume exceeds about 50 Å^3, whereupon the degree of swelling drops sharply. Long term (>1 year) swelling of this PEC in pure water reveals an instability, wherein the material substantially inflates, generating large pores even though $T < T_g$. The mechanism for this instability is attributed to a small population of counterions, resulting from slight nonstoichiometry of polyelectrolytes, as well as the polymers themselves, a contribution estimated using Des Cloizeaux's theory of osmotic pressure for overlapping chains. Low concentrations of salt in the bathing solution are enough to overcome the osmotic pressure within the PEC and it remains dimensionally stable over the long time periods studied. The universal practice of rinsing PECs, whether they are in macroscopic or thin-film morphology, in pure water should be re-evaluated.

Introduction

Swelling is a property of all polymers exposed to "good" solvents. In the absence of crosslinks, swelling is followed by dissolution. The presence of physical or chemical crosslinks prevents dissolution and an equilibrium level of swelling is often observed. Polyelectrolyte complexes (PECs) are blends of oppositely charged polymers incorporating a high density of physical crosslinks which are the result of ion pairing interactions between positive, Pol^+, and negative, Pol^-, repeat units.[1] The polyelectrolyte chains bearing charged repeat units are randomly intermixed to give a "scrambled salt" amorphous structure, rather than having ladder-like pairings of opposite charges.[1] These complexes boast an interesting range of properties that make them candidates for functional materials.[2]

Solvent uptake in polymers is typically controlled by the distance between crosslinks, and the degree of interaction between solvent and polymer (χ-parameter). Being ionic, the individual components of PECs, polyelectrolytes, have strong favorable interactions with water. The high degree of ionic character of these materials also means they have a high modulus, but are also rather brittle when dry. Plasticization by water reduces the modulus[3, 4] but enhances toughness, which means most PECs are processed, used and studied with some degree of hydration.

There has been a recent surge of interest in PECs in their various morphologies from multilayered thin films,[5] to tough extruded fibers, tubes, and tapes, capsules nanoparticles,[6] to liquid-like coacervates.[7, 8] The hydration of the assembled complex has been the subject of many studies that focused on their swelling behavior and properties.[9] For example, PEC prepared from poly(diallyldimethylammonium), PDADMA, and poly(styrenesulfonate), PSS, a widely investigated polyelectrolyte combination, has been found to contain around 10 molecules of water per individual pair of PDADMA/PSS repeat units, corresponding to about 30 to 40 weight%, at room temperature when in contact with (and presumably equilibrated with) aqueous solutions.[10, 11, 12]

Adding an inert osmotic stressing agent, such as polyethylene glycol, PEG, increases the osmotic pressure in solution and causes the material to shrink as its water content decreases and stiffness increases.[13] On the other hand, adding salt increases the doping, or breaking of the Pol^+/Pol^- interactions, which causes the material to swell as its hydration increases significantly.[11, 14] Studies have shown how this difference in hydration affects the glass transition temperature, T_g, of the PEC,[15, 16] some focusing on the role of water during the thermal transition.[17, 18, 19] These investigations compliment early work that described water as a strong plasticizer in PECs.[1]

This study explores two fundamental questions related to swelling and solvation in PECs. First, which solvents in addition to water might swell PECs? Water is intricately attached to PEC in all its processing but there is a lack of key information on whether other solvents could also be used to swell PECs. Second, is swelling by water under equilibrium or at least steady-state conditions? This question is relevant to both the fundamental understanding of PECs and also to their long-term stability in many of the proposed applications. To answer these questions macroscopic, stoichiometric, dense fibers of PEC, prepared by extrusion,[11, 20] were used as starting material in their dried form.

Experimental

Poly(diallyldimethylammonium) PDADMA, as the chloride form, PDADMAC, was obtained from Ondeo-Nalco (SD 46104, molecular weight, MW, ca. 400 000 g mol^{-1}), and poly(4-styrenesulfonic acid, sodium salt), was from AkzoNobel (VERSA TL130, MW ca. 200 000 g mol^{-1}). The slightly acidic PSS solution was neutralized with NaOH. Sodium chloride was obtained from Fisher. Deionized water (18 MΩ, Barnstead, E-pure) was used to prepare all salt solutions, and for water swelling experiments. Solvents were used as received: methanol (99.8%), isopropanol (99.5%), acetone (99.5%) (all from BDH), ethanol (99.5%, Koptec), dichloromethane (99.5%), dimethyl sulfoxide (99.9%) (both from Macron), chloroform (99.5%), trifluoroethanol (99%) (both from Alfa Aesar), tetrahydrofuran (99.5%, EMD Millipore), p-dioxane (99%, J.T. Baker), acetic acid (glacial, 99.7%, Fisher), hexane (98.5%, VWR chemicals), N,N-dimethylformamide (anhydrous, 99.8%), pyridine (99%), toluene (99.9%), cyclohexane (99.9%), tetrachloromethane (99.5%), and 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES, 95%) (all from Sigma-Aldrich).

Solutions of PDADMAC and PSSNa, were prepared in 0.25 M NaCl at a concentration of 0.125 M with respect to the monomer units. Stoichiometric amounts of polymers, where stoichiometry is based on the total number of positive to negative polyelectrolyte repeat units, were mixed simultaneously while stirring to yield a white PEC precipitate. Water was used to wash the salt out from the complex. Hydrated salt-free PEC was then shaped into cylindrical fibers using a Model LE-075 extruder (Custom Scientific Instruments) with a 1.95 mm-diameter round exit nozzle. The extrusion was performed according to a previously reported procedure:[20] the rotor and header temperatures were 98 °C and 102 °C respectively, the gap space 3.8 mm, and the rotor speed 110 rpm. The resulting fibers, collected with a Model CSI-194T takeup reel rotating at 10 rpm, were around 1 mm in diameter. Alternatively, salt-free PEC precipitate was dried in an oven at 110 °C then ground into a powder using a coffee grinder.

The density of the PEC was measured using two methods: 1) density matching in a mixture of solvents, and 2) using a specific gravity bottle – a pycnometer. In the first method, dry powdered PEC was inserted in a vial with around 7 mL CCl$_4$ (d = 1.5867 g cm^{-3}). Cyclohexane (d = 0.7781 g cm^{-3}) was slowly added to adjust the density of the solvent mixture until the powder became homogeneously suspended in it. Both CCl$_4$ and cyclohexane do not swell the PEC (see below). The solvent mixture density was then accurately determined using a pycnometer calibrated with water (d = 0.9975 g cm^{-3} at 23 °C).

In the second method, a dry PEC fiber was weighed. The weight of a volume of water and a volume of DMF were then separately measured using the pycnometer. Finally, the weight of PEC + DMF + pycnometer were obtained. The density of PEC obtained using the first method (with dried powdered PEC) was 1.268 ± 0.002 g cm^{-3}, and the density obtained using the second method (dried fiber) was 1.257 ± 0.002 g cm^{-3}.

To perform the aqueous swelling experiments, PEC fibers of around 1 cm in length were first annealed in water at 60 °C to relax and hydrate them according to prior studies.[7] Then they were dried at 120 °C for 24 h. The swelling experiment consisted of immersing fibers in water and salt solutions ranging between 0.0001 M and 1.0 M NaCl. The fibers were taken out at every time point, carefully and quickly dabbed dry with a Kimwipe^{TM}, then weighed.

The mass gain on soaking was attributed to water uptake plus salt doping, where Pol$^+$Pol$^-$ pairs are broken by the addition of salt, M$^+$A$^-$, as follows

$$Pol^+Pol^- + M^+ + A^- \rightarrow Pol^+A^- + Pol^-M^+$$
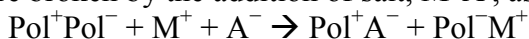
The mass of doped salt within the PEC was subtracted using the doping level, $y = 0.3[NaCl]$, where y is the fraction of PDADMA/PSS ion pairs converted to PDADMA$^+$Cl$^-$ and PSS$^-$Na$^+$ as above.[21] Any ions that enter the PEC carry with them additional water molecules.[22] The molar ratio of water to PDADMA/PSS was obtained by dividing the mass ratio by the molecular weight ratio (PDADMA/PSS ion pair = 309.42 g mol^{-1}). All time points were an average of three samples.

An FEI Nova nanoSEM 400 was used to obtain electron micrographs. Samples were briefly immersed in liquid nitrogen then cut with a razor blade into ca. 2 mm-long pieces which were coated with a 4-nm layer of iridium using a Cressington HR 208 sputter coater. Imaging was done at 2 kV using the through-the-lens detector.

To monitor swelling in organic solvents a batch of dry PEC fibers was used. The fibers were soaked in the solvents for 4 days, enough time to reach constant weight, after which they were removed, gently dabbed dry then weighed.

Static contact angles were determined on a stoichiometric 10-layer PDADMA/PSS polyelectrolyte multilayer, PEMU (thickness ~ 50 nm), built with a robot (Stratosequence V, NanoStrata Inc.) from 10 mM (prepared with respect to the monomer unit) polymer solutions in 1 M NaCl. The substrate, a silicon 100 wafer (Okmetic Inc.), was fixed face down on a shaft rotating at 180 – 200 rpm and dipped sequentially between the polymer solutions for 5 min with three 1-min water rinses after each "layer". A droplet of around 10 μL of water or diiodomethane (99%, Sigma-Aldrich) was deposited on the film and captured with a KSV Cam 200 static contact angle instrument. Each value was an average of 4 contact angle measurements.

The total ion content as well as the ratio of positive to negative repeat units within the undoped ("salt-free") PEC was determined using radiolabeled ions. 2 mL each of 0.10 M NaCl and 0.10 M Na$_2$SO$_4$ were prepared. The NaCl solution was spiked with ^{22}NaCl (^{22}Na$^+$ as NaCl, half life 950 d, E$_{max}$ = 0.546 MeV (positron, γ-emitter) supplied by Perkin Elmer with a specific activity of 1700 Ci mol^{-1}) to a specific activity of 0.1 Ci mol^{-1} by adding 20 μCi ^{22}NaCl, while the Na$_2$SO$_4$ solution was labeled to a specific activity of 0.2 Ci mol^{-1} with 40 μCi Na$_2$^{35}SO$_4$ (half life 87.4 d, E$_{max}$ = 0.167 MeV (β-emitter) supplied with a specific activity of about 1300 Ci mmol). The same samples used for the long-term immersion in 0.15 M and 0.25 M NaCl were separately doped in triplicate with the ^{22}Na$^+$ and ^{35}SO$_4$$^{2-}$ solutions for 18 h at room temperature. The samples were then each rinsed sequentially in 2 batches of 10 mL 10^{-5} M of the 0.1 Ci mol^{-1} or 0.2 Ci mol^{-1}, sodium or sulfate, respectively, isotopes for 18 h each (total of 36 hours) to extract all ions not involved in doping. The activities of the ^{22}Na$^+$ labeled samples were determined by placing the fibers on top of a piece of scintillator plastic monitored with a RCA 8850 photomultiplier tube (PMT) connected to a counter as described previously.[23] The activities of the ^{35}S labeled samples were determined by extracting the labeled sulfate ion from the PEC into water by soaking PEC samples in 2 mL 0.1M unlabeled Na$_2$SO$_4$. 500 μl of the extracted solution was mixed with 6 mL liquid scintillation cocktail (LSC, EcoLite(+) MP Biomedicals), shaken, and counted on top of the PMT. Calibration curves to convert counts to moles were constructed by adding aliquots of the 0.10 M labeled solutions to the top of the scintillator (^{22}Na$^+$) or to the LSC. (^{35}SO$_4$$^{2-}$).

Results and Discussion

Importance of the State of Solvation/Hydration

Acting as plasticizers, small solvent molecules which are able to swell PECs have a significant impact on their mechanical and transport properties. Water, almost universally employed for PEC swelling, controls, for example, ion conductivity,[24, 25] modulus,[4, 26, 27 13, 28] gas permeability,[29] and the glass transition temperature, T_g.[17] In the current work the exceptional affinity for water relative to other solvents was illustrated.

Density of the Polyelectrolyte Complex

Accurate accounting for the volume, weight, or molar composition of components in plasticized polymers is essential for understanding their properties. Despite extensive studies of hydrated PDADMA/PSS PEC in the form of ultrathin films, made *via* the layer-by-layer assembly method, or macroscopic pieces, made by bulk extrusion, the density of pure PDADMA/PSS PEC is not known with precision. Using two methods – density matching with a solvent mixture and solvent displacement with a specific gravity bottle or pycnometer – this value was determined in dry powdered PEC and a dry PEC fiber. The results of the two methods were very close: 1.2678 g cm^{-3} for the powdered sample and 1.2568 g cm^{-3} for the fiber. The density is relatively high compared with other polymers,[30] and explains the low gas permeability in thin membranes of PEC.[31, 32, 33] The slight difference in density values can be attributed to porosity of the dry extruded PEC fiber, calculated to be 0.86 vol%. Electron microscopy (see below) shows these pores in extruded PEC.

Swelling in Water *versus* Organic Solvents

Swelling with a series of organic solvents and water was first performed to obtain an overview of the response of the PEC to these different environments. As-made PECs contained very few salt counterions when exposed to pure water, a property known for decades[3] and verified more recently with sensitive radioisotopic measurements, e.g. using ^{22}Na$^+$.[21] Common solvents were selected to represent a broad range of molecular sizes and polarities. Table 1 presents the swelling in terms of the ratio of molecules of solvent to PDADMA/PSS ion pair. Solvents that are able to swell, or more precisely increase the mass of, the complex are separated by a dashed line from those that do not. The volume of each solvent molecule was estimated using Chem3D software (ver. 16, PerkinElmer) by calculating the Connolly solvent-excluded volume. This is the volume obtained by rolling a theoretical spherical probe over a model of the molecule. While there are many methods for estimating molecular volume[34] this approach yields values that are similar to sizes estimated from molar volumes with the voids between them subtracted.[35]

Various approaches were taken to identify trends in swelling. For example, except for trifluoroethanol (TFE), a molecular size less than 50 Å^3 seemed to be required for swelling. Swelling trends related to polarity were also considered. While solvents that are known to be highly, or relatively, polar such as water, alcohols, and acetic acid clearly showed an increase in solvent intake, other polar solvents such as dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) did not swell the PEC to any significant extent. Table 1 compares swelling based on a traditional scale of solvent polarity related to the ability of solvents to exhibit strong intermolecular forces with test solutes in chromatographic separations.[36] This scale, and

one ranking dielectric constants (not shown), showed poor correlation to swelling.

Table 1 Solvent to PDADMA/PSS PEC ratio after immersion of the dried fibers in the solvents for 4 days. Also shown are the polarity indices,[36] the E_T^N of the solvents[37] – the normalized solvatochromic polarity parameter – and the calculated solvent molecule size.

Solvent	Solvent:PEC ratio		Polarity index	E_T^N	Solvent molecule size (A^3/molecule)
Water	8.99	± 0.17	9.0	1.000	10.3
Trifluoroethanol	6.22	± 0.10	-	0.898	57.3
Methanol	3.57	± 0.14	6.6	0.762	20.6
Acetic acid	3.73	± 0.01	6.2	0.648	35.9
Ethanol	2.14	± 0.03	5.2	0.654	48.2
Isopropanol	-0.01	± 0.13	4.3	0.546	65.4
DMSO	0.13	± 0.02	6.5	0.444	67.0
Dimethylformamide (DMF)	-0.02	± 0.03	6.4	0.386	69.2
Acetone	0.47	± 0.03	5.4	0.355	57.2
Dichloromethane (CH_2Cl_2)	0.56	± 0.01	3.4	0.309	52.9
Pyridine	0.45	± 0.02	5.3	0.302	67.1
Chloroform ($CHCl_3$)	0.33	± 0.01	4.4	0.259	67.0
Tetrahydrofuran (THF)	0.12	± 0.01	4.2	0.207	72.1
1,4-Dioxane	0.75	± 0.13	4.8	0.164	81.3
Toluene	0.21	± 0.01	2.3	0.099	84.7
Tetrachloromethane (CCl_4)	0.08	± 0.01	1.7	0.052	80.8
Hexane	0.16	± 0.06	0.0	0.009	109.5
Cyclohexane	-0.02	± 0.05	0.0	0.006	99.4
Ionic liquid (EMIES)	0.00	± 0.01	-		-

Another widely used polarity parameter that did show a correlation is the normalized solvatochromic parameter, E_T^N (or the Dimroth-Reichardt scale).[38] Positive or negative solvatochromism is a measure of the ability of the solvent to shift the absorbance of a chromophore towards longer or shorter wavelengths respectively.[39] The molar electronic transition energies (E_T) are first determined in kcal mol^{-1} from the wavelengths. The E_T values are then normalized to tetramethylsilane (0) and water (1), extreme nonpolar and polar solvents, to provide the normalized parameter (E_T^N).[37] Swelling showed better correlation with E_T^N down to about $E_T^N = 0.6$, below which there was a sharp cutoff in the extent of swelling. Some solvents below this E_T^N exhibited minor swelling, while others gave no evidence of swelling.

Materials used in E_T^N are usually dyes such as the zwitterionic dye pyridinium N-phenolate betaine[37] in the case of the values in Table 1. The shift in absorbance is mainly a measure of the effect of the solvent on the stability of the ground or excited states of the dye. Interestingly, the disposition of charges in zwitterionic dyes mimics the proximity of sulfonate

and quaternary ammonium ion pairs within the PEC (PECs have been termed "zwittersolids"[40]). Thus, the affinity between dye and solvent might be expected to parallel the affinity between PEC and solvent.

Surprisingly, the ionic liquid EMIES did not swell the PEC at all, despite being of similar ionic character. Ionic liquids have been used to dope PECs. For example, Parveen and Schönhoff used 1-hexyl-3-methylimidazolium chloride (HMIM) and 1-ethyl-3-methylimidazolium chloride (EMIM) to swell PEC films of PDADMA/PSS and poly(allylamine), PAH/PSS.[41]   However, these ionic liquids were all dissolved in water and behaved like a hydrophobic doping salt, even causing the decomposition of the film in higher concentrations.[41] Likewise, Zhang et al. reported uptake of ionic liquids into PDADMA/PSS PECs, also from aqueous solutions,[42] but to the authors' knowledge there are no reports of dry PEC swelling by pure ionic liquid.

The swelling trend in Table 1 is probably related to a combination of two factors: a molecule should be small enough to fit through the physical barrier ("mesh size") created by packing the polyelectrolytes within the PEC. At the same time, a solvent should have enough polarity to interact with the charged groups on the polyelectrolytes (i.e. a χ-parameter conducive to solvation). There is evidence of size selectivity in PECs. For example, films made from PAH/PSS were 150 times less permeable to sucrose than to glucose, which itself permeated the membrane more slowly than glycerol and methanol.[43] In Table 1 there is a sharp cutoff in swelling between ethanol and propanol although the polarities and E_T^N values are rather similar. A molecular volume cutoff of about 50 Å^3 corresponds to a diameter of about 5 Å, comparable to the 10 Å determined for the pore size in PAH/PSS PECs by NMR cryoporometry.[44]   Ionic liquids may be too large to enter the PEC, even if the ions are separated (EMI and ES are estimated to have respective volumes of 108 and 82 Å^3). A pore size, or mesh size, of 5 Å may be compared to recent results of neutron scattering in PDADMA/PSS PECs, where 20% of the PSS chains were deuterated.[45] In that study the mesh size between deuterated chains of PEC hydrated in water was about 17 Å. Correcting for the fact that the volume doubles when hydrated (divide by $\sqrt[3]{2}$), only 20% of the PSS was deuterated (divide by $\sqrt[3]{5}$) and PSS represents about half of the polymer volume (divide by $\sqrt[3]{2}$) the corresponding pore size for dry PDADMA/PSS would be about 6.3 Å, close to the value determined above.

The question of permeability becomes more complex when solvent mixtures, such as water and other solvents, are employed. Smaller molecules co-absorbed into PECs could enhance the free volume for larger molecules. Oppositely-charged polymerized ionic liquids have been complexed[46] but these can be viewed simply as PECs made with more hydrophobic polyelectrolytes. It is possible that hydrophobic polyelectrolytes with greater free volume could accept larger, less polar solvent molecules.

Polar water-miscible solvents that do not significantly swell the PEC can be used to extract water from it. This property was recently exploited for actuating thin PEC films of poly(ethylenimine) and poly(acrylic acid) using organic solvents, where negative swelling (dehydration) was caused by ethanol, DMSO, and THF.[47] The slight swelling observed here (Table 1) in ethanol is consistent with a somewhat larger mesh size for PDADMA/PSS complexes. Ethanol was also used to dehydrate soft coacervate-like samples to toughen them for measurements.[48] The hydrogen bonding ability of the solvents was proposed as the driving force behind this dehydration effect,[49] although simple osmotic pressure arguments might also explain the effect. No statistically significant water loss was observed in Table 1 because the PEC samples were thoroughly dried before use.

At about 9 molecules per PDADMA/PSS pair (Table 1), water is clearly the most

effective solvent for swelling the material. TFE, a somewhat exotic solvent, is also quite good at swelling the PEC. TFE is also one of the very few solvents (in addition to water) that dissolve zwitterionic monomers and polymers.[50]

Long-Term Swelling in Water *versus* Salt

Pairing between Pol^+ and Pol^- is not a phenomenon restricted to aqueous systems, but the ability to prepare and process PECs in water is considered a great advantage and has undoubtedly contributed to the widespread interest and research activities into these materials. Some fundamental questions, especially regarding the long-term use of hydrated PECs, have not been answered. For example, if crosslinks are physical, will the material be stable over time under stress or will they "slip" leading to creep deformation? Some odd behavior in water has been reported in the literature. For example, we noticed a strong upturn in water content of PDADMA/PSS PEMUs as $[NaCl] \rightarrow 0$.[22] O'Neal et al. also recently noted swelling in PEMUs at low salt concentration.[51] This rapid and substantial swelling in multilayers is believed to result from a high concentration of $PDADMA^+Cl^-$.[23] Hamad et al. reported similar swelling of coacervates for $[NaCl] < 0.1$ M.[52] Over many years of preparing larger articles of PEC we have been puzzled by swelling of samples if they are left in pure water for extended periods, even if they are nominally stoichiometric and thus free of salt counterions. Treatment in pure water, to wash out salt and to avoid carryover of polyelectrolyte from one beaker to another, is a common step in making thin films of PEC using layer-by-layer adsorption. Figures 1A and B show the amount of water in weight percent and in moles per PDADMA/PSS ion pair, respectively, in dry PEC immersed in solutions of increasing salt concentration. Their water content at short times of around 10 molecules of H_2O per polymer PDADMA/PSS is consistent with previous studies on this system.[11, 18] The samples in pure water swelled slowly, increasing in water content to around 65 wt% over a year – more than doubling the water/polymer pair ratio. The corresponding volume expansion (V_{1year}/V_0) is around 3.5. In contrast, even in the lowest concentration of NaCl (0.15 M, Figure 1) the sample did not take up water. In fact, slight downward trends in the salt solutions were observed, indicative of minor shrinking.
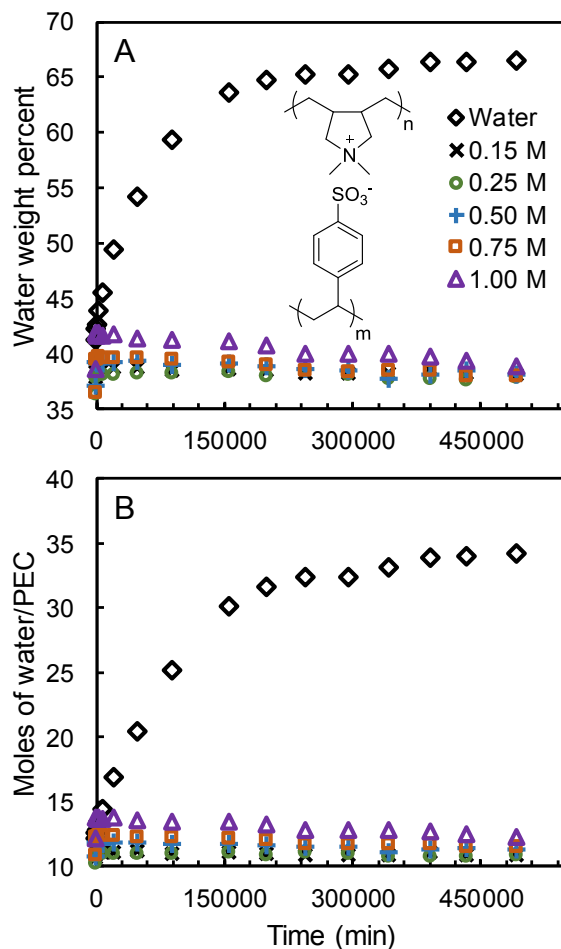
Figure 1. A) Water weight percent in PDADMA/PSS PEC samples that were first dried then soaked in pure water and different concentrations of NaCl over a period of around 1 year. B) Molar ratio of water to PDADMA/PSS ion pair in the same originally dried samples. Precision was on average ± 1%.

The difference between the water and salt solution samples is evident from photographs of the fibers taken towards the end of the experiment, seen in Figure 2. Although all starting samples were the same length, the photo shows larger samples in pure water after ca. 400 days which are also white – an appearance that can be attributed to the high porosity of the PEC.[45] Lower scattering of the samples in salt solution cannot be a result of better index matching as the refractive index, *n*, of water (*n* = 1.335) and, for example, 0.15 M NaCl (*n* = 1.350) are close.
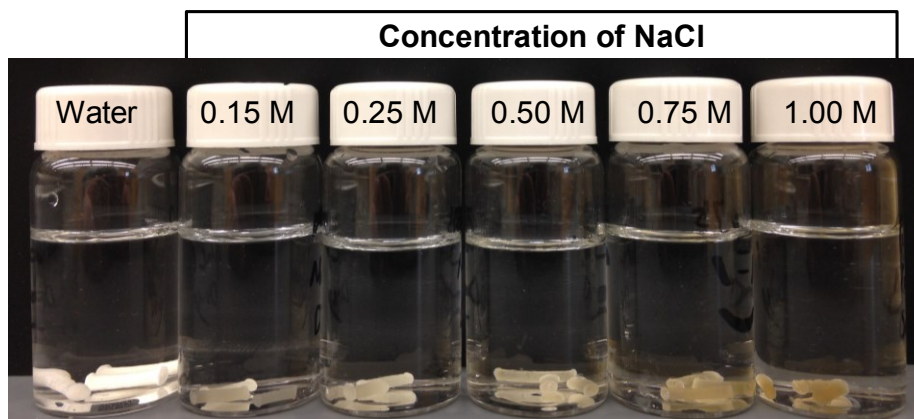
Figure 2. Photographs showing PEC samples after around 400 days of immersion in water and different salt solutions. Samples in water became more porous, a feature that is evident from the opaque white appearance arising from light scattering. The other samples are increasingly translucent.

Scanning electron microscopy, SEM, was used to probe PEC morphology. PEC hydrated for a relatively short time is mildly scattering and SEM (Figure 3) reveals a few pores, consistent with previous studies on hydrated extruded PDADMA/PSS.[48] Almost no porosity is seen at the edges of the sample, where the shear forces on exiting the extruder are the greatest.
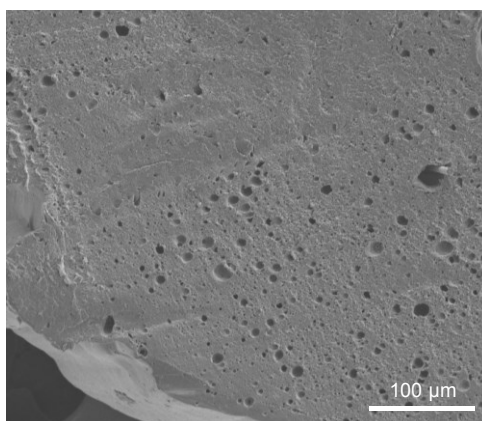
Figure 3. Reference scanning electron micrograph showing a cross-section of an extruded PDADMA/PSS PEC fiber that was hydrated for 24 h only.

After around 1 year, Figure 4 shows that samples immersed in pure water have accumulated a significant number of large pores in addition to smaller ones. In comparison, samples allowed to sit in 0.5 or 1.0 M NaCl exhibit much lower porosity. The center of the 1.0 M NaCl PEC sample showed some smearing (caused by the razor used to cut the samples) which is a result of softening the PEC by salt doping.
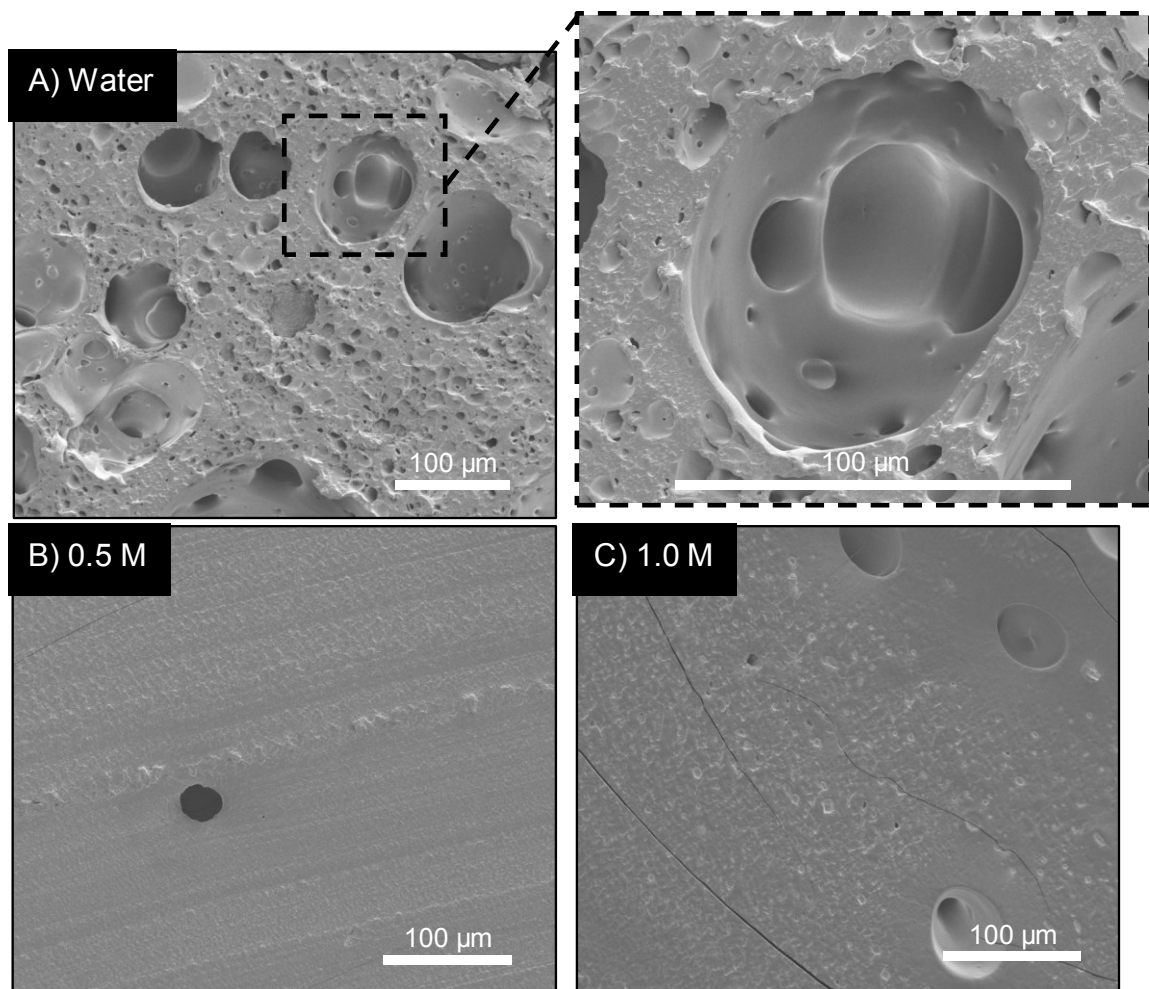
Figure 4. SEM images of cross-sections of PDADMA/PSS PEC soaked for 405 days in A) pure water, B) 0.5 M NaCl, and C) 1.0 M NaCl. A zoom-in in the upper right panel is shown to emphasize the details of the pores.

It is clear from the magnification of Figure 4A that large pores, some of which have fused with each other, are responsible for the substantial expansion of PECs sitting in pure water. The water content for all the other samples of PEC exposed to salt water remained almost constant, supporting the idea that the dimensions and composition of the PECs was close to equilibrium (at least with respect to water). These findings raise a red flag for extended uses of PEC in pure water, but they are reassuring for applications in salty water. For example, PECs exposed to "fresh" water may be unstable whereas those used in physiological ([NaCl] ~ 0.15 M) or salty environments will maintain their dimensions.

Figure S1 shows the entire cross-sections of the PEC fibers after soaking in 0, 0.5, and 1.0 M NaCl. When compared with the sample in Figure 3 showing the morphology at a short time of soaking in water it appears that the samples in salt may have lost some porosity. A magnification of water content *versus* time, shown in Figure 5, reveals a slight but steady loss of volume, especially for those PECs in the higher [NaCl]. Figure 5 shows that the rate of water loss is proportional to the salt concentration, suggesting higher polymer mobility, at the segmental and chain length scales, caused by salt doping[53, 54] allows the material to consolidate or "anneal" more rapidly, reducing the porosity. These samples also become less scattering

(Figure 2).
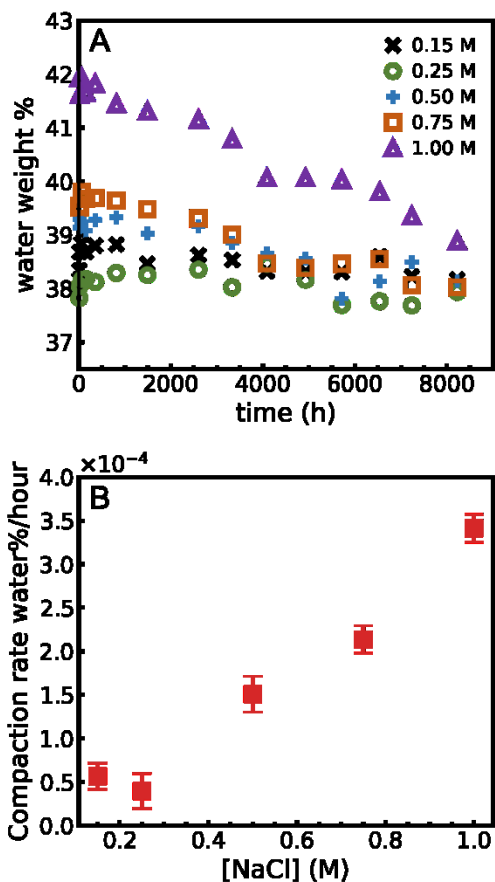
Figure 5. A) Long-term water content of dry PDADMA/PSS PEC that was soaked in different concentrations of NaCl over a period of around 1 year. B) Compaction rate of water per hour taken from the slope of the data shown in A).

To narrow down the lower limit of salt concentration required to prevent long-term inflation of PEC, a new batch of dry extruded PEC samples was immersed in a range of [NaCl] between 0 and 0.15 M over a period of around 6 months. Figures 6A and B show that the cut-off salt concentration at which the PEC mass increased was between 0.001 M and 0.01 M. In other words, 0.01 M NaCl was enough to prevent water intake.
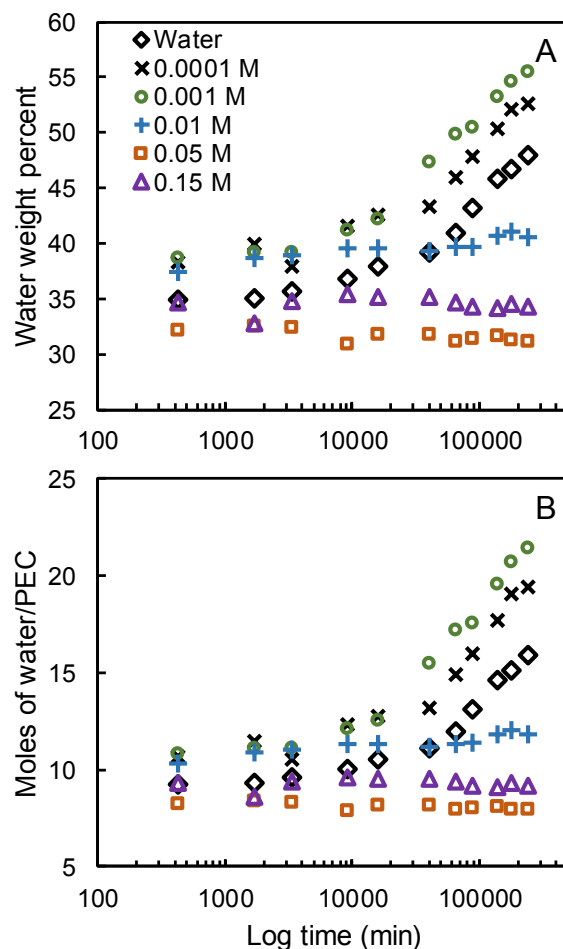
Figure 6. A) Water weight percent in extruded PDADMA/PSS PEC of dried fibers soaked in pure water and a range of low salt concentrations between 0 and 0.15 M NaCl, over a period of ca. 6 months. B) Molar ratio of water to PDADMA/PSS ion pair in the same samples during the same time. The x-axis is a log scale to emphasize the cut-off point. Precision is on average 1%.

SEM images of these samples taken after 1112 days (Supporting Information, Figure S2) show abundant porosity in PEC exposed to [NaCl] < 0.01 M, but less so in the 0.01 M NaCl sample. The remaining porosity in the 0.01 M NaCl sample is consistent with the idea that the material has not annealed over the time allowed.

Swelling Mechanism - The Role of Osmotic Pressure

There are at least three driving forces which bring water into a PEC. The first is solvation of the Pol^+Pol^- ion pair. Since they are ionic, water is expected to surround these charged repeat units with at least one shell of hydration – a process which must involve considerable enthalpy change. Second, the doping of PECs by salt M^+A^-, in which the Pol^+Pol^- ion pairs are transformed into Pol^+A^- and Pol^-M^+ pairs, may also introduce water along with the counterions – which is mainly an entropic effect.[22] Nonstoichiometric PECs, having an excess of Pol^+ or Pol^-, require counterions to balance the polyelectrolyte in excess. Swelling of these nonstoichiometric PECs at low [salt] is driven by these counterions.[52] The third mechanism is also entropic: while

polymer chains generate much less osmotic pressure than small molecules, any phase composed of polymers and water will generate osmotic pressure relative to pure water.

The starting PECs used in this study have been shown to be stoichiometric ([Pol⁺]/[Pol⁻] = 1.00) by NMR measurements[11] but the level of accuracy of this method is about ± 2%. The stoichiometry and counterion content of PECs was determined with about 100-fold greater precision using radiolabeled counterions. This technique involved doping PECs with ^{22}Na⁺ labeled NaCl or ^{35}S-labeled Na$_2$SO$_4$. Samples were then placed back in a highly dilute (10^{-5} M) solutions of these labeled salts and allowed to spontaneously undope for 36 h. These dilute solutions were employed for undopin g instead of water to ensure counterions were not displaced by dilute adventitious ions (H⁺, OH⁻). The final contents of Na⁺ and SO$_4{}^{2-}$ were 0.0005 mol% and 0.3 mol% compared to PEC (~100 mol%), which gives a PSS:PDADMA stoichiometry of 1.0000:1.0061. Using a PEC water content of 40% (Figure 1A), 0.6% excess PDADMA⁺Cl⁻ is equivalent to a concentration of 0.013 M Cl⁻ which exerts the same osmotic pressure as 0.0065 M NaCl, slightly lower than the 0.01 M cutoff seen in Figure 6.

The contribution of polymer chains to PEC osmotic pressure was estimated following the work of Des Cloizeaux, who developed an insightful understanding of the osmotic pressure, π, in concentrated polymer solutions and its dependence on the concentration C, within the network, and the overlap concentration, C^*:[55]

$$\pi \sim \left(\frac{C}{C^*}\right)^{1.25} \tag{1}$$

Noda et al. explored this relationship experimentally with concentrated solutions of poly(α-methylstyrene) in toluene to obtain:[56]

$$\pi = F\frac{CRT}{M_w}\left(\frac{C}{C^*}\right)^{1.32} \tag{2}$$

with π in atm, C the polymer concentration in g L⁻¹, R equal to 0.0821 L atm mol⁻¹ K⁻¹, T the temperature, and M_w the polymer molecular weight in g mol⁻¹. In Equation 2 the (empirical) proportionality constant F depends on the polymer system. For example, in the study by Noda, F was 1.5.[56] In another study focused on a more hydrophilic polymer, poly(ethylene glycol), Cohen et al. determined an F that was three-fold higher.[57] With the same scaling, this value could be used for the polyelectrolyte system here, PDADMA/PSS, as it is also hydrophilic. For the overlap concentration, Equation 3 yields a value of 0.95 M, or 148 g L⁻¹, when N is 1935 (M_w is assumed to be an average of 300 000 g mol⁻¹ with an average monomer mass of 155 g mol⁻¹) and a radius of gyration of 15 nm[58] is used:

$$C^* = \frac{N/N_A}{R_g{}^3} \tag{3}$$

Using a PEC density of 1.26 g cm⁻³ with 10 water molecules per polymer ion pair, the total concentration of polymer (C in Eq 2) was estimated to be 727 g L⁻¹, or around 4.7 M of average repeat units, which yields an osmotic pressure of approximately 2.2 atm for T = 298 K. Using the van't Hoff equation, $\pi = iMRT$ where i = 2 for NaCl, and assuming the osmotic coefficient for [NaCl] is about 1 (for NaCl the osmotic coefficient ranges between 0.93 and 0.98 over the range 0.001M[59]) the corresponding concentration of NaCl that would provide this pressure (2.2 atm) is around 0.045 M. This means that the PEC should swell if the concentration of sodium chloride is below 0.045 M. This value is somewhat higher than the highest [NaCl]

used to prevent swelling (0.01 M). The discrepancy could be caused by the wide molecular weight distribution of the polymer employed in addition to the other assumptions used.

The Des Cloizeaux theory emphasizes the large difference in entropy between a polymer, even one in a highly concentrated, overlapped state, and a small (salt) ion: a polymer concentration of about 5 M repeat units generates as much osmotic pressure as 1/100th the concentration of NaCl. ,

Even if osmotic pressure is generated, the role of crosslinks is to prevent swelling beyond a certain level, yet swelling continues to induce expanding pores. Because the pores themselves can equilibrate with the outside solution (i.e. $[NaCl]_{pores} = [NaCl]_{solution}$) they should not induce an osmotic pressure. An additional mechanism is needed to explain the slow inflation of pores: a Laplace pressure, ΔP, is generated by interfacial tension γ_{sl} between PEC and pore solution and by the curvature of the pores of radius R:

$$\Delta P = \frac{2\gamma_{sl}}{R} \tag{4}$$

Using contact angle measurements with water (26.6°) and diiodomethane (20.3°) on a stoichiometric PDADMA/PSS polyelectrolyte multilayer similar to the PEC used throughout this study, the surface energy was calculated according to[60]

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_{lv}}\right) + 2\sqrt{\gamma_s^h}\left(\frac{\sqrt{\gamma_l^h}}{\gamma_{lv}}\right) \tag{5}$$

where θ is the measured contact angle and γ_{lv} the free energy of the liquid against its saturated vapor (72.8 and 50.8 mN m^{-1} for water and diiodomethane, respectively).[60] The surface free energy of the liquid can be split into two components: γ_l^d, the nonpolar dispersion force component (21.8 and 49.5 mN m^{-1} for water and diiodomethane, respectively), and γ_l^h, the polar hydrogen bonding and dipole-dipole component (51.0 and 1.3 mN m^{-1} for water and diiodomethane, respectively).[60] Similarly, the surface energy of the solid, γ_s, has two components that stem from the different forces. For example, if the surface is nonpolar, one contact angle measurement would be enough to estimate the main surface energy component, γ_s^d, since only dispersion forces contribute. Here, with PEC, measuring the contact angle with two liquids possessing different polarities, one can obtain the two components of the surface free energy, γ_s^d and γ_s^h, which can then be summed to obtain the total solid surface free energy arising from the various forces. The θ's here yield γ_s^d and γ_s^h equal to 37.0 and 32.2 respectively, with a total γ_s of 69.2 mN m^{-1}. The interfacial tension can then be obtained using:[60]

$$\gamma_{sl} = \left(\sqrt{\gamma_s^d} - \sqrt{\gamma_l^d}\right)^2 + \left(\sqrt{\gamma_s^h} - \sqrt{\gamma_l^h}\right)^2 \tag{6}$$

Solving this equation yields a γ_{sl} of 4.2 mN m^{-1}. This parameter was previously measured in a PEC coacervate system made of poly(2-(methacryloyloxy)-ethyltrimethylammonium chloride) and poly(3-sulfopropyl methacrylate) – another combination of hydrophilic polyelectrolytes. In the absence of salt, it was estimated to be on the same order of the value found here – around 1 mN m^{-1}.[61] Using $\gamma = 4.2$, and a starting $R = 5$ μm (see Figure 3), the resulting Laplace pressure is around 0.017 atm.

If the PEC were completely elastic, the pore size would remain static. It appears that long term viscous creep of PEC allows pores to expand slowly. As pores grow they fuse and the growth rate slows since R increases and ΔP decreases. Pore growth must be a combination of

osmotic pressure and Laplace pressure, since samples immersed in [NaCl] ≥ 0.01 M did not expand although the initial porosity (Figure 3) was present. The overall mechanism for this instability is summarized in Scheme 1.
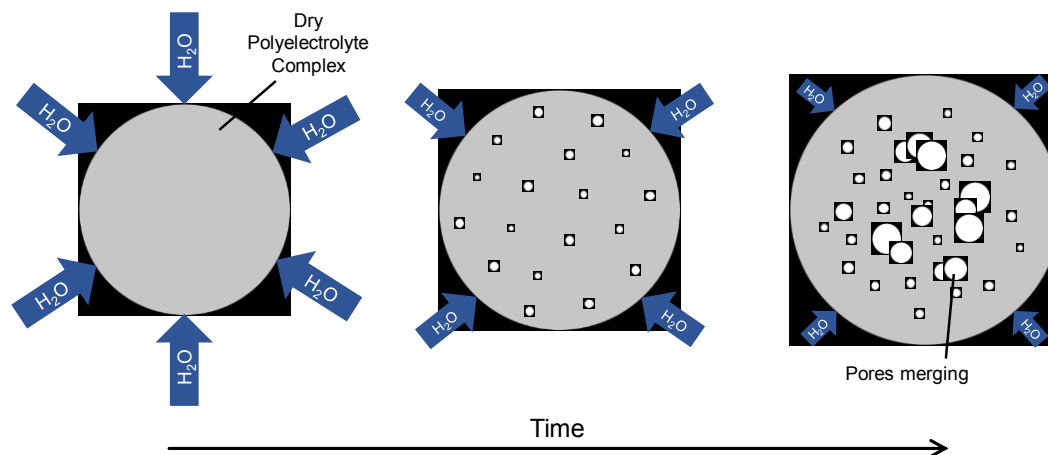
Scheme 1. Illustration of the proposed mechanism of PEC swelling. Short term water uptake is the result of hydration of Pol^+Pol^- ion pairs plus osmotic pressure exerted by the polymer network. Small pores form quickly, probably from defects remaining from extrusion. Under continual osmotic stress and Laplace pressure small pores expand and fuse, a process which requires flow of PEC. The bulk swelling rate slows as the pore radius increases and the Laplace pressure decreases.

The polyelectrolyte concentration in all PEC morphologies – solid complexes to liquid coacervates – is, almost by definition, likely to be at or above the overlap concentration. Pairwise interactions between polyelectrolyte chains occur when they are in contact and substantial numbers of these contacts can only be made at $C \geq C^*$.

Long-term instability in osmotically stressed solid PECs is one example of the ways in which the fundamental behavior of PECs is governed by phase separations which are caused by weak interactions. Coacervate droplets are formed by liquid-liquid phase separation. These droplets slowly coalesce into a macroscopic phase, but phase separation can again be induced by a small change in conditions, such as a change in temperature or salt concentration.[7] In solid PECs, decreasing the salt concentration leads to shrinkage where some of the lost water can be accommodated as pores within the network instead of being expelled to bulk solution.[45]

Conclusions

Water is highly efficient at swelling PECs because of its high polarity and small size. Trifluoroethanol, the next most efficient swelling agent, falls in second place along the E_T^N polarity scale. Since water is the most likely solvent to come into contact with PECs when they are used in almost all of their (proposed) applications, it is somewhat fortunate that this solvent is the most efficient at swelling. Many solvents, though polar, are excluded from PECs and are therefore likely to dessicate them and substantially change their properties, including modulus and permeability.

An unexpected but problematic issue with long-term inflation and microphase separation of PEC in pure water was observed and was believed to result from osmotic pressure generated by a small amount of residual Cl^-, caused by a 0.6% excess in the amount of PDADMA

compared to PSS, and the overlapping polymer chains themselves. These long timescale measurements revealed creep in the materials, although they are nominally still at a temperature lower than their glass transition temperature (but only by about 10 $^\circ$C). A low solution salt concentration removed this instability and placed the material in an equilibrium swelling state. Water is used extensively to process then rinse PECs. For example, rinsing in pure water between layers is an almost universal step in producing thin PEC films using the layer-by-layer assembly method. As a general recommendation, any PEC should be exposed only briefly to pure water to avoid the osmotic instability described above. It may be preferable to define a minimal salt concentration (for example, > 0.01 M NaCl) for rinsing solutions instead of using pure water. Along the same lines, the long term use of PECs in "fresh" water, as membranes and coatings, may be compromised by this instability.

SUPPORTING INFORMATION
Additional scanning electron microscopy images of PEC samples.

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Notes
The authors declare no competing financial interest

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