Extruded Saloplastic Polyelectrolyte Complexes

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Tough, dense polyelectrolyte complexes (PECs) with well-defined cross-sections are prepared using a laboratory extruder and plasticizing the complexes with salt water. Stoichiometric starting materials yield stoichiometric complexes of poly(diallyldimethylammonium) (PDADMA) and poly(styrene sulfonate) (PSS). As an example of this enabling technology, macroscopic tubes of PEC are produced. Microscopy images of cross-sections of rods, tape, and tubes show a pore volume of less than 10% in the bulk of the extruded complex and fully dense material towards the surface, where the shear is greatest. Thermal gravimetric analysis reveals the expected salt content for PECs doped with NaCl, and a lack of salt for PECs rinsed in water. The fact that doped PECs are transparent suggests they are supersaturated with salt. Residual stress following extrusion is relieved by exposure to solutions of NaCl. Stress relaxation experiments show decreasing equilibrium moduli as a function of increasing salt doping, consistent with prior results on multilayers of the same polymers.

1. Introduction

Solution-precipitated polyelectrolyte complexes (PECs) are just one example of materials formed by exposing polycations to polyanions.[1] The same polyelectrolytes may be deposited on a substrate in an alternating manner to yield polyelectrolyte multilayers (PEMUs).[2] Alternatively, under certain conditions, such as strong excess of one polymer and dilute solution, colloidally stable complexes are produced– quasisoluble PECs.[3] Under other conditions, especially with well-hydrated polyelectrolytes, liquid-like coacervates may be prepared.[4] In all these morphologies polyelectrolyte/polyelectrolyte interactions are largely driven by ion pairing and the entropic release of counterions and water.[1a,5] Differences between morphologies can be traced to differences in stoichiometry, water, and ion content.

Ion pairing of counterion-compensated polyelectrolyte segments, $\mathrm{Pol^+A^-}$ and $\mathrm{Pol^-C^+}$, is represented in Equation (1). The strength of the $\mathrm{Pol^+Pol^-}$ ion pairs is directly connected to the amount of water released, with stronger associations driven by greater dehydration[5b]

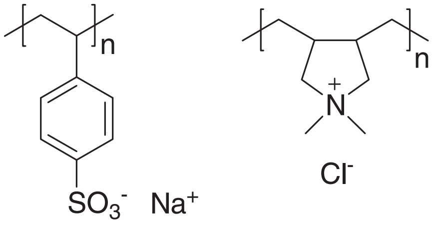
$$\mathrm{Pol^+A^-_{aq} + Pol^-\,C^+_{aq} \rightleftharpoons Pol^+\,Pol^-_s + A^-_{aq} + C^+_{aq}} \tag{1}$$

Where A^- and C^+ are counteranion and countercation respectively and the subscript s represents the PEC phase. A typical pair of polyelectrolytes is poly(styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) (**Scheme 1**).

Much is known about PSS/PDADMAC complexes and multilayers. Though precipitates are easily obtained, the interaction energy of the SS:DADMA ion pair is not strong ($\Delta G^{\circ}_{\mathrm{formation}}$ is about -3 kJ mol^{-1} in NaCl)[5b] and it is only the multiplicity of ion pairing that makes the films and precipitates rugged.

PECs are known to be straightforward to prepare but difficult to process.[1a,6] When dry, they are infusible and brittle, behaving like polymeric salts. They are insoluble in water and other solvents. The polymer ion pairs formed as in Equation (1) may be broken by the addition of sufficient salt to reverse Equation (1) (a process we term "doping").[7] In the 1960s Michaels and co-workers carried out extensive explorations of PEC properties and found that ternary solvents containing a mixture of water, organic solvent, and salt could dissolve PECs,[1a,6a] generally considered "unprocessible." The solutions were presumably substantially unpaired polyelectrolytes, which could be cast into films via standard casting techniques. Thus, PEC membranes were proposed for a number of applications,[6a] many similar to those put forward for PEMUs,[8] such as membranes for dialysis, ultrafiltration, battery separators, fuel cell membranes, electrically conductive coatings, and medical devices including contact lenses and chemical sensors.

Following a fortuitous discovery that diffuse blobs of PSS/PDADMA PECs were transformed into solid plugs while spinning them at high rpm for solid-state NMR experiments, we recently demonstrated that it was possible to compact PECs in an ultracentrifuge at room temperature.[9] For such compaction,



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Scheme 1. Structures of PSS and PDADMAC.

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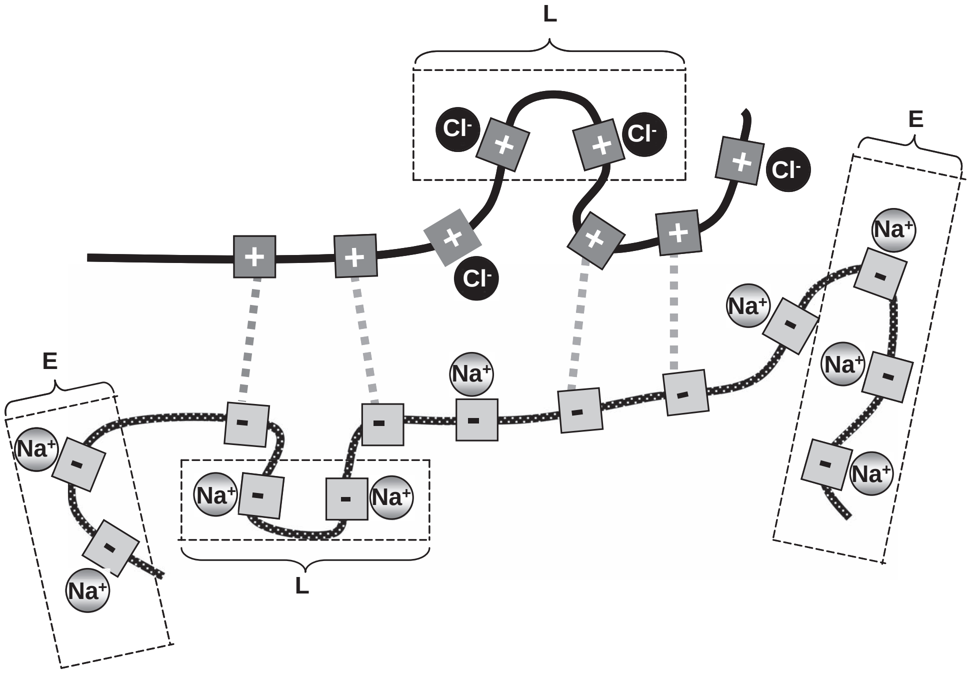

Scheme 2. Possible types of extrinsic charge within a PEC. The upper PE is PDADMA and lower PE is PSS. Ion pairing crosslinks (+ ····· -) are from intrinsic compensation. Extrinsic sites, associated with a counterion, can be caused by doping, then decoupled (see region "L") or there can be an excess of one type of polyelectrolyte (region "E"). The extrinsic charge caused by doping is under reversible equilibrium control, as in Equation (1).

plasticization of the PEC by extensive added salt was required, and the materials were thus termed saloplastics.

PSS/PDADMA PECs compacted by ultracentrifugation showed unexpected but intriguing morphology:[9] although stoichiometric amounts of PSS and PDADMAC were mixed, the PEC had excess PSS. In addition, the PEC had a pore volume of >50% and the pores were closed and contained excess PSS, which generated osmotic pressure.[9b] The porous composite showed resilient viscoelastic properties similar to those of the intervertebral disc.[9a]

Extrusion is one of the major techniques used to process thermoplastic polymer materials. Large quantities of materials with well-defined cross-sections may be rapidly and consistently prepared via extrusion. The strong shear forces occurring during extrusion are used to obtain blends of different polymers and excellent dispersion of various "filler" materials. In the current work, we provide the first demonstration of stoichiometric complexes in a variety of shapes prepared with an extruder.

2. Results and Discussion

In order to understand the role of a salt in controlling the mechanical properties of a PEC it is useful to consider each ion pair as a physically reversible cross link.[10] **Scheme 2** illustrates this concept, as well as the ways charges on polyelectrolytes can be balanced by salt counterions.[7]

Scheme 2 shows ion pairs between polyelectrolytes (intrinsic compensation) as well as a couple of different types of compensation by salt ions (extrinsic compensation). In one type of extrinsic compensation, doping has produced an equal number of counterion-balanced polyelectrolyte repeat units; in another type, excess polyanion (labeled "E") means that there will always be an excess of cations in the PEC, regardless of doping level. Some of the extrinsic compensation (labeled "L") has been separated to emphasize that counterions are decoupled from each other and can remain trapped if the polymer cannot reconfigure itself, i.e., if the loops in Scheme 2 cannot come together, as might occur in dry, doped PEC.

If mechanical properties are controlled by crosslink density, material that is not fully crosslinked, as in Scheme 2, is not at its maximum or intrinsic modulus. In addition, the extra water brought in by the extra ions swells the PEC, making it softer. Pores further soften the material and complicate the analysis. Therefore, the extruded PEC was designed to be homogeneous, stoichiometric, and nonporous. Material with such a composition is expected to have the highest modulus in the spectrum of its possible mechanical properties. The fact that ion pairing drives formation also ensures the molecules are blended at a molecular level.[11] In effect, the blend composition at equilibrium is controlled by the number density of charged repeat units on the backbone.

2.1. Stoichiometric Polyelectrolyte Complexes

Producing large (ca. 1 kg) quantities of stoichiometric PECs was not trivial. Salt was required to promote rapid precipitation, but concentrated solutions of polyelectrolytes yielded nonstoichiometric complexes. Nonstoichiometric complexes, especially those that depend on the order of mixing, are a signature of

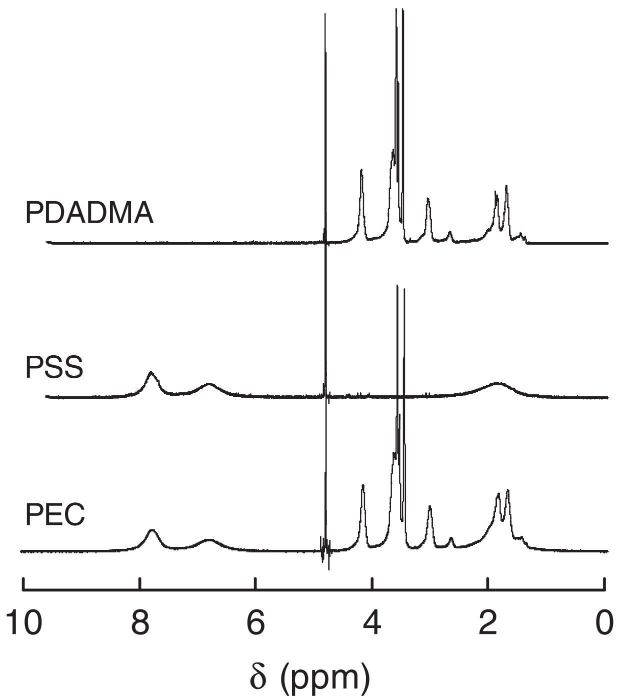

Figure 1. Solution ^{1}H NMR spectra of PEC, PSS, and PDADMA in 2.5 M KBr/D_2O.

kinetic control in polyelectrolyte association.[12] Because each polymer/polymer ion pair potentially forms a crosslink, any deviation from bulk 1:1 stoichiometry decreases the modulus of the PEC by reducing the crosslink density. Porosity also (substantially) decreases modulus and additional polyelectrolyte can reside in these pores, creating a nonuniform distribution of polymer throughout the sample.

To obtain the "true" (maximum) modulus of bulk (i.e., uniform) PEC, it should be stoichiometric and free of pores. Polyelectrolyte multilayers grown in the "linear" mode approach these conditions because the addition of material, layer-by-layer, gives incoming polymer the opportunity to complex fully with existing polymer. Voids are minimized and (near) 1:1 stoichiometry is possible.[2b] Pores still exist in multilayers, but a small amount of osmolyte (e.g., added salt) can be enough to collapse these pores.[13] Thus, we were able to perform micromechanical measurements on thick multilayers.[10]

To evaluate PEC stoichiometry we developed a method based on ^{1}H solution NMR to determine the ratio of PSS to PDADMA. The influence of precipitation conditions on this ratio was then investigated. Complexes were rinsed with a solution of 0.25 M NaCl in D_2O in order to exchange H_2O with D_2O. Then the precipitates were redissolved in 2.5 M KBr in D_2O. In the solution ^{1}H NMR spectra of these dissolved complexes, shown in **Figure 1**, all the protons from the constituent polyelectrolytes were present. Integration of the signal of the four aromatic hydrogens of PSS (between 5.5 and 9 ppm) provided a convenient internal standard for comparison with the 16 aliphatic ^{1}H (between 0 and 4.6 ppm) on PDADMA plus the three aliphatic ^{1}H on PSS. The ratio PSS:PDADMA was obtained using Equation (4). This method was calibrated by NMR experiments on mixtures of known amounts of PSS and PDADMAC under the same conditions. Figure 1 also shows reference spectra for the pure components and indicates that the spectrum of dissolved PEC is a linear combination of both. No broad signals from undissociated polymer were observed.

$$\frac{\mathrm{PSS}}{\mathrm{PDADMA}} = \frac{4\,A_{\mathrm{aromatic}}}{A_{\mathrm{aliphatic}} - \frac{3}{4}\,A_{\mathrm{aromatic}}} \tag{2}$$

where A_{aromatic} and $A_{\mathrm{aliphatic}}$ are the respective NMR areas for aromatic and aliphatic protons. The influence of the NaCl concentration of the precipitation solutions on the PSS to PDADMA ratio was then tested. Equimolar solutions of polyelectrolyte (0.125 M each, with respect to the repeat unit) were made up, and mixed, in 0.25 M, 1.0 M, or 2.5 M NaCl. The PSS/PDADMA ratio calculated with Equation (2) was found to increase with increasing salt concentration. **Table 1** shows that the lowest salt concentration provided nearly stoichiometric complex.

Nonstoichiometry was also observed when PSS/PDADMA complexes in 2.5 M NaCl were compacted by an ultracentrifugal field, and PSS/PDADMA multilayers deposited from 1 M NaCl had a few percent excess PSS units. Thus, it appears nonstoichiometric complexes are obtained when the polyelectrolytes are combined at high ionic strength.

To determine whether the composition of our stoichiometric PEC matches that of a (stoichiometric) PEMU, Fourier transform infrared transmission spectra of both were compared. **Figure 2** depicts nearly identical IR spectra for both forms of PSS/PDADMA, including the water at about 3500 cm^{-1}. The slight differences were attributed to the fact that the PEC could not be sliced thinner than 10 μm, which brings the more absorbing bands into the nonlinear absorbance versus thickness regime.

2.2. Extrusion Conditions

Extrusion of polymers to give homogeneous materials requires the material to flow on the timescale of the experiment in order to allow permanent reconformation of polymer chains during processing.[14] Chemical crosslinks strongly increase the viscosity of polymers and resist permanent macroscopic deformations of articles made from them. In addition, if broken, chemical crosslinks are not usually reformed in the same way, if at all. For these reasons, permanently (chemically) crosslinked materials are more difficult to extrude and they are

Table 1. NMR Integration.

	Ratio of PSS/PDADMA in the nascent complex	Ratio of PSS/PDADMA in the extruded complex
PEC 1: PSS/PDADMA precipitated in 0.25 M NaCl	0.98 ± 0.03	0.99 ± 0.03
PEC 2: PSS/PDADMA precipitated in 1.00 M NaCl	1.03 ± 0.03	1.09 ± 0.03
PEC 3: PSS/PDADMA precipitated in 2.50 M NaCl	1.25 ± 0.03	1.24 ± 0.03

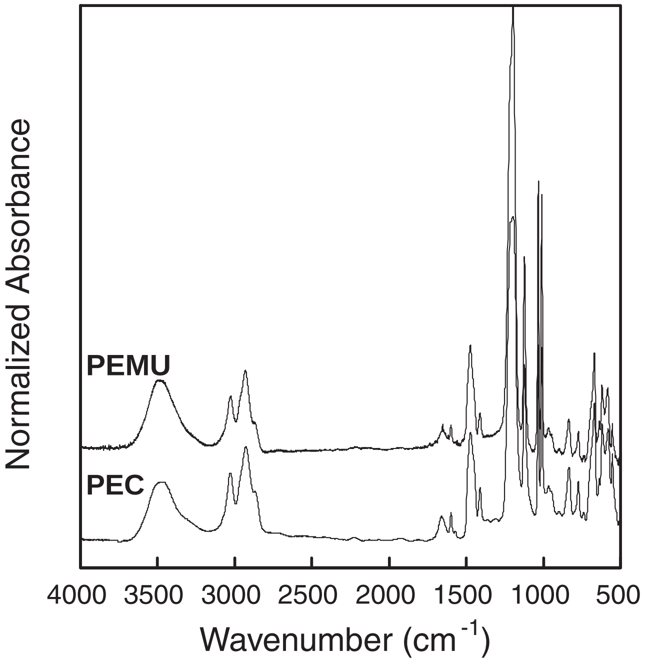

Figure 2. FTIR spectra of 50 layers of PSS/PDADMA built on a silicon wafer (top) and 10 micrometer slice of PEC (bottom). Both spectra were normalized to the C–H stretching bands between 2900 and 3100 cm^{-1}.

either embedded in uncrosslinked components or crosslinking is performed as (reactive extrusion),[15] or after, the material has exited the die.[16]

In contrast, crosslinks in physically crosslinked systems may be broken and reformed. It is hence sufficient to temporarily break the crosslinks or allow them to "slip" so that the chains are allowed to permanently reconform during processing. The conditions needed to reach this mobility depend on the type of physical crosslinks in the system. Heating above the glass transition increases the mobility of the chains and allows them to "reptate" out of entanglements during the processing.[17] For semicrystalline polymers, mobility is promoted by melting crystalline portions. Since temperature is a key parameter in extrusion, different zones within the extruder are usually maintained at different temperatures. In the case of PECs the ionic crosslinks that appear in addition to chain entanglements can be sequentially broken if the doping level is sufficiently increased through the addition of salt, but water is also an essential component to plasticizing the PEC. PECs are not crystalline (unless crystallizing units are built into polyelectrolytes)[18] and we have found no evidence for a glass transition temperature (T_g). However, we have recently reported strongly temperature activated ion transport through PECs,[19] which suggests a significant increase of molecular motion with temperature. A practical trend we have found is one of temperature/doping equivalence of processibility; as noted below, more highly doped material may be fed through the extruder at lower temperatures. Thus, while not essential for extrusion, modification of the temperature of the PEC during extrusion provided accessible conditions, good throughput and good quality extruded material.

The starting material for extrusion was fully hydrated pellets or chunks of stoichiometric PEC. Dried PEC was hydrated by soaking in salt solution for 24 h prior to extrusion. The pellets were removed from the soaking solution, the salt water was allowed to drain, and the material was fed, still wet, into the 12 mm opening of the extrusion chamber through a hopper. A rotating rod of diameter 19 mm pushed the PEC along a screw shape engraved in the extruder barrel at a rate of about 2 g min^{-1}. The shape and size of the orifice depended on the dimensions required for the final extrudate.

Extrusion conditions for PEC soaked in 0.25 M, 1.0 M, or 2.5 M NaCl were explored. The PEC doped with 0.25 M NaCl was too tough to be extruded even after raising the extruder temperature above 120 °C. In contrast, the PEC soaked in 2.5 M NaCl was too fluid to be extruded and did not have a defined shape even after lowering the extruder temperature below 70 °C. Good extrusion conditions were obtained when PEC was soaked in 1.0 M NaCl and the extruder rotor temperature and header temperature were set, respectively, at 90 °C and 115 °C. These conditions were used for all extrusions done in this work. For multiple extrusions, the extruded PEC was pelletized and soaked for 24 h in 1.0 M NaCl before the next extrusion.

Clearly, fine tuning of conditions is possible, and even required for different combinations of polymers. There is a tradeoff between salt concentration and temperature. For example, 1 M NaCl provides a doping level of about 32% (vida infra). The temperature could be lowered with a higher salt concentration. Other salts dope more strongly or weakly.[5b] Thus, if the extrudability is a function of the doping level, the same level can be achieved with other salts but at different concentrations. In addition, given that NaCl solutions at higher temperature challenge the corrosion resistance of stainless steel (and test the resolve of the owner of the extruder), less corrosive counterions, or ions known to actually reduce corrosion, are probably better suited for large-scale use.

2.3. Morphology

During extrusion the PEC experiences considerable shear and compaction forces, which are effective at driving out the pores and pore liquid. For example, **Figure 3**A depicts an epifluorescence micrograph of a 10 μm thick slice of the starting PEC. Though ultracentrifuged at 190 000 g for 4 h, the precipitated

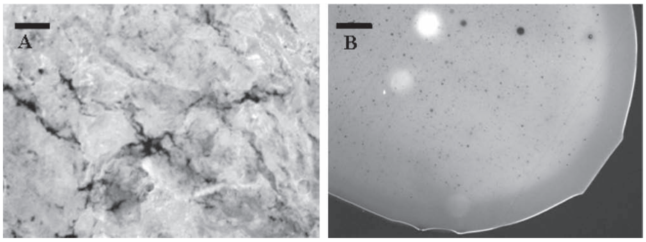

Figure 3. Optical autofluorescence microscopy images of 10 μm thick slices of PEC precipitated in 0.25 M NaCl, ultracentrifuged (A) and extruded (B), and soaked in deionized (DI) water. 450–490 nm excitation and 500–550 nm emission filter cube. Scale bars: 100 μm.

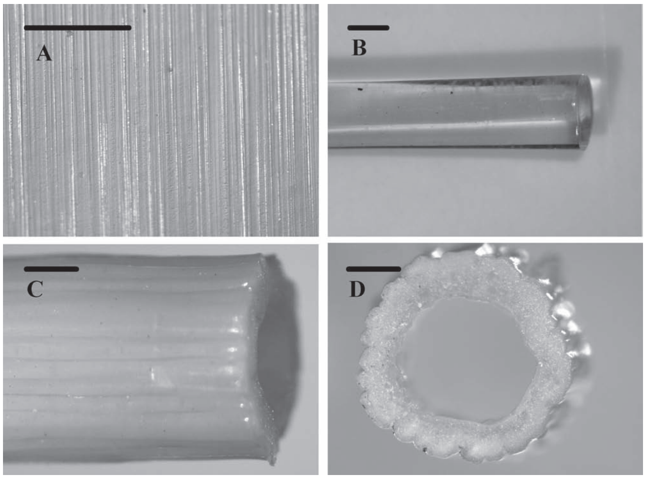

Figure 4. Images of an extruded PEC tape (A), an extruded PEC rod (B), extruded PEC tube (C), and its cross-section (D). Scale bars: 0.5 mm.

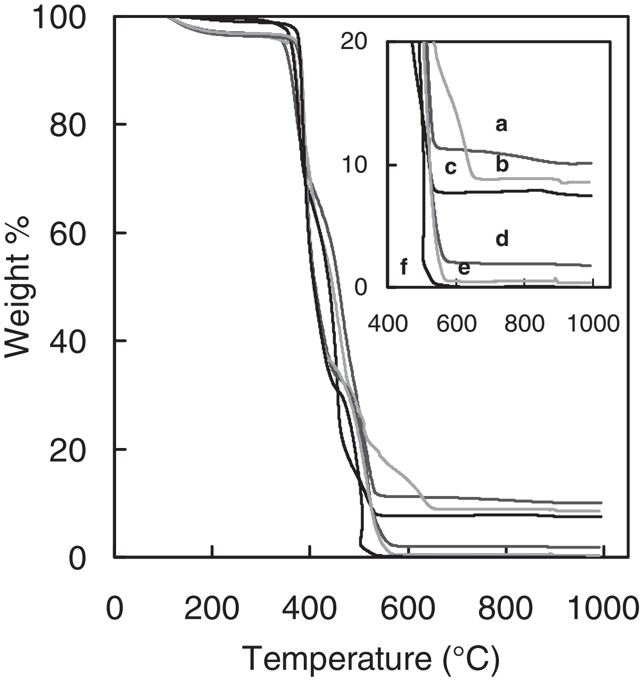

Figure 5. TGA for PEC precipitated in 0.25 M NaCl (a), extruded PEC (b), and double extruded PEC (c). After washing the samples 3 times with DI water, the TGA for PEC (d), extruded PEC (e), and double extruded PEC (f). The samples were dried at 90 °C for 24 h and in the TGA were kept at 110 °C for 20 min to dry before increasing the temperature. The inset shows a magnification of the residual weight, due to NaCl, at high temperature. The heating was done under oxygen flow and at a heating rate of 10 K min^{-1}.

PEC is clearly porous and inhomogeneous. In contrast, the extruded PEC, shown in Figure 3B is almost fully compacted. Most of the pores are less than 10 μm in diameter. Closer inspection of the microscopy image in Figure 3B reveals a band of PEC, close to the surface where the shear is greatest, which appears to be completely free of pores.

By changing the extruder head, various cross-sections could be prepared, such as tapes, rods, and tubes, as shown in **Figure 4**. The tapes were 15 mm wide and 0.2 mm thick. The rods had diameters ranging from 1 mm to 3 mm. The tubes had an outer diameter of 2.25 mm and inner diameter of 1.25 mm. The fine features in the hundreds of micrometer range visible on the tape in Figure 4A and on the external surface of the tube in Figure 4C,D are from surface roughness in the extruder exit. The possibilities for preparing regularly patterned cross-sections on the micrometer scale are clear. The tube cross section shows, as in Figure 3B, that material adjacent to the extruder surface, which experiences the highest shear, appears to be free of pores. An important observation was that the smaller rods and the tape, which experience greater shear at constant volume flow rate, were transparent, indicating the absence of pores larger than roughly 100 nm.

2.4. Thermal Stability and Salt Content

The thermal stability of PSS/PDADMA PECs, in the form of PEMUs, has been evaluated previously.[20] In the present case, the complex also contains salt as it is processed. To verify the thermal stability of the PECs over the temperature range for extrusion, and to determine the amount of salt, doped and undoped PEC samples were subjected to thermal gravimetric analysis (TGA). Samples for TGA were as-precipitated PEC, and single- and double-extruded PEC, all equilibrated in 1 M NaCl for 24 h, then dried. Additional TGAs were run after rinsing similar samples in water three times (to remove the NaCl).

The TGA in **Figure 5** shows that the drying procedure (in an oven at 90 °C for 24 h and in the TGA for 20 min at 110 °C) removed almost all the water (only a small weight loss above 100 °C). Significant weight loss occurred above about 350 °C. Residual weight at >600 °C is from the NaCl, which was 10.1, 8.6, and 7.5 wt% for the three forms of NaCl-doped PEC. In other words, the salt content of the PEC doped in 1.0 M NaCl approaches about 8 wt%. PEC rinsed in water before drying yielded very little residue (see Figure 5).

These TGA results support a number of important conclusions. First, the doped PEC is thermally stable even at temperatures 200 °C higher than those used in the extrusion. Second, the doping level approaches 8 wt%, or 32 mol% (i.e., one in three polyelectrolyte repeat units is extrinsically compensated). Third, substantially all of the salt can be rinsed out of the PEC, implying intrinsically compensated segments are able to pair up again when the salt is removed to yield fully crosslinked material (the “loops” of material in Scheme 2 can come together). Extrusion appears to promote such a pairing, since there is less residual salt on rinsing after extrusion (salt remaining after washing was 1.4, 0.4, and 0.0 wt% for as-precipitated, single- and double-extrusions, respectively). Coupled with the microscopy images in Figure 3, TGA shows the goals of fully dense, fully stoichiometric PEC may be achieved by extrusion.

Despite the high salt content, most of the extruded shapes were transparent (most easily seen in the rod in Figure 4) and remained so, which indicates the absence of pores and salt crystals. Extruded, dehydrated PEC is probably supersaturated with salt, i.e., cations and anions, are prevented from coming together for kinetic reasons. For example, ions in the "loops" in Scheme 2 are "frozen" in place when extruded, unlike samples washed in water for some of the TGA experiments. We noticed that some extruded PECS, especially ones that contained pores, started to develop visible salt crystals when stored in humid atmosphere for several weeks.

2.5. Doping, Hydration, and Residual Stress

On exiting the extruder, the PEC was partially dehydrated but still flexible enough to be wrapped on the take-up roll. After sitting in ambient, extruded PEC further dried. Complexes became brittle and hard when dry. Plasticization coincides with hydration. PSS/PDADMA takes up about 3.7 water molecules for each ion pair doped with NaCl[5b]

$$\mathrm{Pol^+\,Pol^-_{(s)} + Cl^-_{(aq)} + Na^+_{(aq)} + 3.7H_2O_{(aq)}} \\ \rightleftharpoons \mathrm{Pol^+\,Cl^-_{(s)} + Pol^-Na^+_{(s)} + 3.7H_2O_{(s)}} \quad (3)$$

PECs were conveniently stored dry, but for proper extrusion under the conditions employed, they must be fully hydrated at the equilibrium water content corresponding to Equation (3). To determine (re)hydration levels, dry samples of extruded, double extruded, and triple extruded PECs were rehydrated for 2 days in various salt solutions. They were weighed, dried again at 90 °C in vac for 24 h and reweighed. PEC water content as a function of NaCl concentration is presented in **Figure 6**. The same (within error) equilibrium water concentration is reached independent of the number of extrusions, and the hydration level increases with salt concentration, as observed for PSS/PDADMA multilayers.[5b] The water content of PECs and PEMUs made with PSS and PDADMA is comparable. For example, a PSS/PDADMA multilayer immersed in water has 33% water content.[5b] Interestingly, even the slight contraction at low concentration of NaCl ([NaCl] <0.25 M) seen with the PEMU[13] is also observed here. This contraction is attributed to dehydration of residual pores by the external osmotic pressure of the NaCl. The "antipolyelectrolyte" expansion of PEC with additional salt is entirely consistent with doping of stoichiometic complex. Macroporous PEC which contains excess PSS in the pores contracts with added salt.[9a]

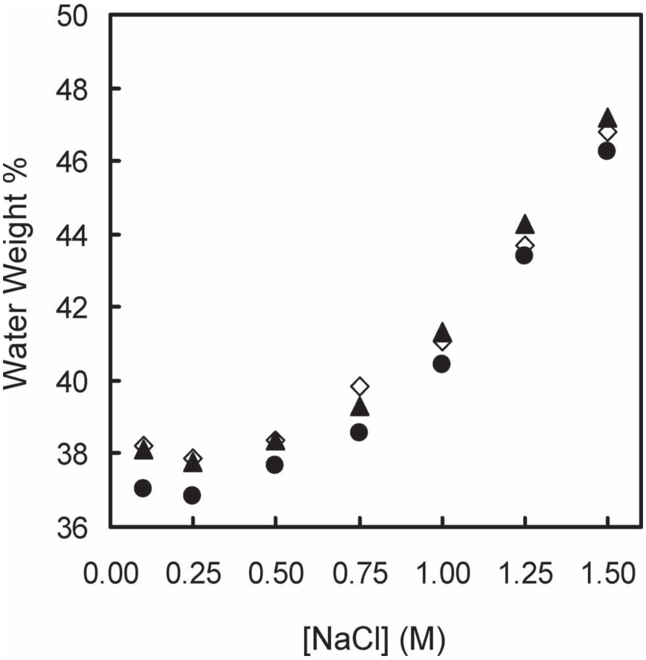

Figure 6. Water content vs. salt concentration for PSS/PDADMA PECs after rehydration for 2 days in salt solution. The data are shown for PEC extruded (●), double extruded (◇), and triple extruded (▲).

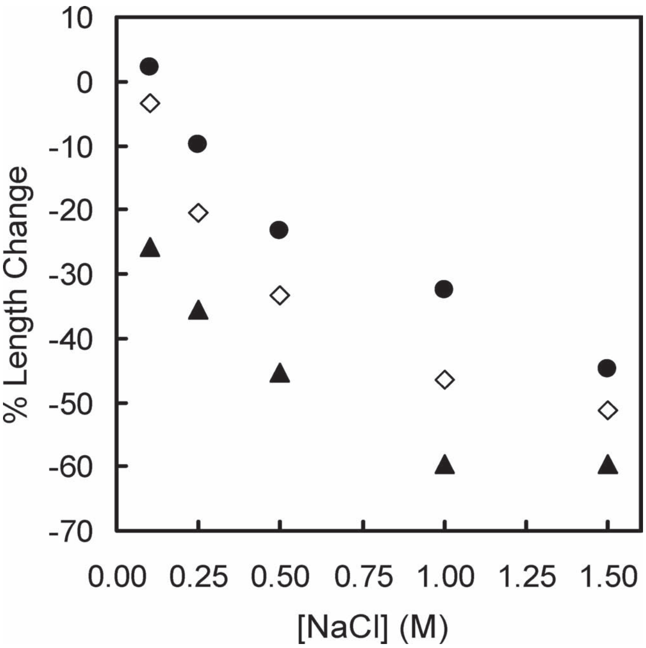

Figure 7. Length change (contraction) of freshly extruded PECs after annealing for 24 h in solutions of different [NaCl]. PEC extruded (●), double extruded (◇), and triple extruded (▲).

The shearing forces in the extruder and the tension of the take-up reel induced residual stresses in extruded PEC, probably leading to slight elongation of the chains. This partial orientation is locked in as the PEC cools and dehydrates as it exits the extruder. These stresses could be released by soaking extruded shapes in salt water, leading to salt doping and rehydration and thus promoting chain motion and relaxation.[1b,21] For example, **Figure 7** shows the contraction of 1 mm diameter extruded rods after soaking in NaCl solutions for 24 h. Supporting Information Figures S2–S4 provide more detail on the kinetics of the contraction. After 24 h in NaCl solutions >1.0 M the samples have relaxed fully.

2.6. Modulus versus Doping Level

Fully dense samples of PEC are typically only prepared via the multilayering method.[2a] Techniques to measure modulus have been limited to those appropriate for the (ultra)thin morphology of PEMUs. For example, nanoindentation has been reported

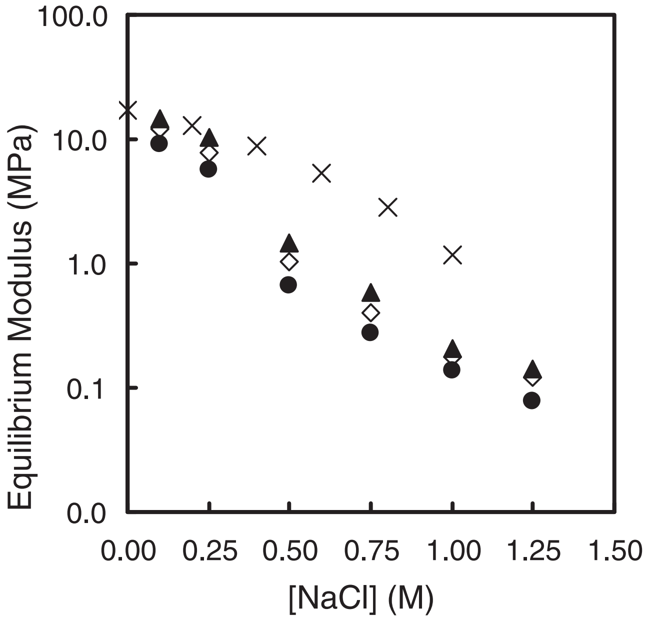

Figure 8. Equilibrium modulus at different salt solutions for PSS/PDADMA samples extruded (●), double extruded (◇), and triple extruded (▲) strained to 2% at 10 mm min^{-1} then allowed to relax for 150 s. The points (×) are the modulus for a PEMU of PDADMA/PSS measured by Jaber et al.[10]

for dry, wet, and crosslinked multilayers.[22] Buckling of multilayers on softer substrates[23] or the deformation of multilayer capsules[24] are alternative methods. We reported direct tensile measurements of micrometer-thickness multilayers of PSS/PDADMA,[10] but the films required extensive preparation and micromechanical testing equipment unlikely to be in a typical polymer laboratory. Extruded PECs were appropriate for measurement in a tensile tester using a sensitive (5 N) load cell. Prior to testing, all samples were soaked in 1 M NaCl for 24 h to remove the residual stresses seen in Figure 7.

Stress relaxation measurements were employed for 1 mm diameter PSS/PDADMA rods soaked in solutions of various salt concentration. Materials strained to 2% were allowed to relax to constant stress (reached after about 150 s, see Supporting Information). Samples exposed to <1.25 M NaCl recovered their original dimensions after the strain was removed.

Stress relaxation curves for the same sample were repeatable. The constant stress values were used to calculate an equilibrium (i.e., low frequency) modulus. As seen in **Figure 8**, modulus decreases with increasing salt concentration for single, double, and triple extruded PEC, as observed with PEMUs made from the same material. Figure 8 also shows modulus versus [NaCl] from our prior work on PEMUs.[10] While the PEC and PEMU values coincide for the lowest salt concentrations they diverge at higher [NaCl]. We believe the difference between the two sets of measurements is the longer time (150 s) allowed for the PECs to relax (in contrast, "equilibrium" PEMU stresses were recorded at 70 mS[10]). Nevertheless, coincidence of the PEMU and PEC mechanical measurements over at least some of the [NaCl] is further evidence that the materials are the same in composition at the macro- and microscopic scales.

Multiple relaxation mechanisms and characteristic times were deduced previously for macroporous saloplastic PECs.[9b] Interestingly, the relaxation behavior of the (nearly) nonporous materials in the present work exhibited similar characteristics. It is possible that because the crosslinks in PECs are physical and reversible, some are broken and reformed under stress and the long-term relaxation for intermediate-doped (0–1 M NaCl) PEC at room temperature is simply a manifestation of what occurs on a faster scale during extrusion at higher temperature. Breaking and reforming a physical crosslink is possible if each crosslink is under dynamic equilibrium. The concept of an elastic slip-link has been applied to account for polymer elasticity[25] and spatiotemporal fluctuations of slip-links,[26] in particular, may be an appropriate description for the present case.

The fact that the triple-extruded PEC is slightly stiffer is probably due to reduction of residual pore volume compared with prior extrusions. An important conclusion of Figure 8 is that multiple extrusions do not degrade the polymers to a significant extent. Were significant chain scission to occur, the modulus would be expected to drop with each extrusion. Multiple extrusions illustrate the recyclable or "green" nature of PECs: all one needs to reprocess the material into a different shape is salt water.

2.7. Strain to Break

A final series of mechanical tests shed light on the toughness of extruded PECs. Samples of PEC ribbon doped with various [NaCl] were strained to break at constant rate. The true stress versus true strain is plotted in **Figure 9**. For the less-doped

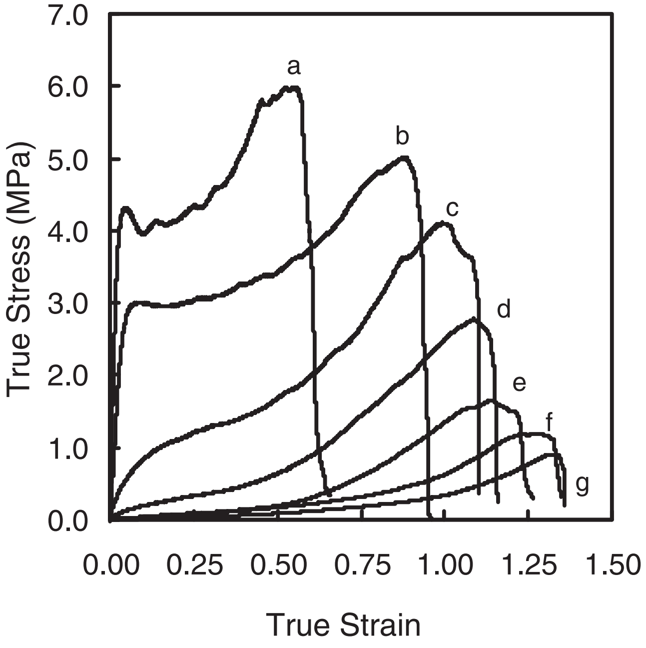

Figure 9. Strain to break test for PEC ribbon immersed in NaCl for 24 h with the following concentrations 0.1 M (a), 0.25 M (b), 0.5 M (c), 0.75 M (d), 1.0 M (e), 1.25 M (f), and 1.5 M (g). Stretching speed: 10 mm min^{-1} (50% strain min^{-1}).

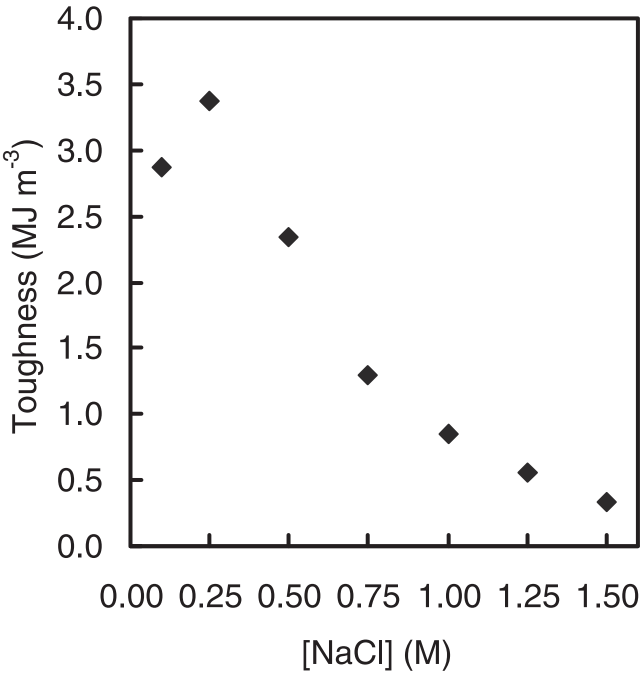

Figure 10. The toughness of the extruded ribbon integrated from the strain to break curve (Figure 9) as a function of salt concentration.

samples, strain-induced softening is clearly observed, but samples maintained their integrity over a wide strain range. More highly doped PECs could be strained more before breaking, consistent with a lower crosslink density. The corresponding toughness (area under the stress/strain curves) is presented in **Figure 10**. PECs clearly possess good toughness (a maximum of about 3 MJ m^{-3}). For comparison, the toughness of poly(methyl methacrylate)[27] is about 2 MJ m^{-3} as is that of tendon.[28]

3. Conclusions

Previously, the composition and properties of polyelectrolyte complexes have been frustratingly inconsistent regardless of the form in which they have been produced. The breadth of properties and morphologies is largely due to kinetic limitations during their formation, which introduces history-dependent variables in the way they are produced and processed. In fact, much of the attraction of making complexes in the PEMU format comes from the reproducibility offered. We have shown here a "starting point" for consistently producing large quantities of dense, stoichiometric, molecularly mixed PECs. An enormous variety of extruded PECs is possible, given the vast array of processing variables for extrusion. For example, in addition to different combinations of polyelectrolytes and salt, and blends of polyelectrolytes, (nano)composites with various additives are possible, including fibers, (nano)particles, clays and carbon (fibers and nanotubes). Because of the low temperatures and aqueous environment, the activity of added biological molecules such as enzymes should be preserved. Additives of high aspect ratio should be aligned, at least partially, under the high shear environment. Thus, there remains much applied and fundamental work in exploring these new materials.

4. Experimental Section

PSS was from AkzoNobel (VERSA TL 130, MW of 200 000 g mol^{-1}) and PDADMAC was from Ondeo-Nalco (SD 46104, with MW of 400 000 g mol^{-1}). Sodium chloride (Aldrich) was used to adjust solution ionic strength. Deionized water (Barnstead, E-pure, Milli-Q) was used to prepare all solutions.

Solutions of PSS and PDADMA were prepared at a concentration of 0.125 M with respect to their monomer units, neutralized to pH 7 with NaOH and their ionic strength adjusted (usually to 0.25 M NaCl). Typically, 1 L of each was poured simultaneously into a 3 L beaker. 1 L of 0.25 M NaCl, used to rinse the flasks, was added to the precipitate. The mixture was stirred with a magnetic stirrer for about 30 min and the precipitated PEC was decanted and washed with 1 L of 0.25 M NaCl. The PEC was chopped into pieces between 5 mm and 10 mm large then soaked in 1.0 M NaCl for 24 h. The salt solution was strained off and excess liquid removed from the PEC pieces by rapid dabbing with a paper towel. The PEC was introduced, still fully hydrated, into the hopper of a Model LE-075 laboratory extruder from Custom Scientific Instruments, Inc. The extruder parameters were set as follows: rotor temperature, 90 °C; header temperature 115 °C; gap space 3.8 mm; and rotor speed 60% (110 rpm). The extruded complex was continuously collected on a Model CSI-194T takeup reel with a 3 cm diameter drum at 10 rpm. These parameters allowed the extrusion of fiber at approximately 2 g min^{-1}. The extruded fibers were cut into 5 mm pellets, soaked in 1 M NaCl for 24 h and re-extruded with the same parameters as in the first extrusion. The re-extrusion allowed the fabrication of more uniform compact shapes.

Proton NMR spectroscopy (Bruker Avance 600 MHz spectrometer) was used to measure the ratio of PSS to PDADMAC in the PECs as follows: excess solution was removed from a piece of complex (50–100 mg) using paper wipes. To exchange most of the hydration H_2O with D_2O the complex was rinsed with 0.25 M NaCl in D_2O (in three 1 mL aliquots over 24 h). The piece of complex was then dissolved in 1 mL 2.5 M KBr in D_2O. For calibration, spectra of mixtures of known amounts of PSS and PDADMAC in 2.5 M KBr were recorded under the same conditions.

For imaging, samples soaked in DI water were cut into 10 µm slices using a cryostat microtome (Leica CM 1850) and imaged with a Nikon Eclipse Ti inverted microscope using a Photometrics Cool Snap HQ2 camera and NIS Elements AR 3.0 software. The magnification was 100× or 200×. The autofluorescence of PSS was exploited using excitation at 485–505 nm and emission at 510–540 nm.[9b]

To determine the salt content of the PECs, TGA was performed with a SDT Q600 TGA from TA Instruments. Prior to thermal analysis, samples were dried for 24 h at 90 °C in vac and gently ground.

To determine the equilibrium hydration level, extruded PECs were rehydrated for 2 days in solutions of various salt concentrations and weighed. These samples were then dried in vacuum at 90 °C for 24 h and their dry weights were determined. The water weight% of PEC (W%) was calculated.

To measure dimensional changes during annealing of as-extruded PECs in $NaCl_{aq}$ rod samples were soaked in solutions of different [NaCl] and imaged continuously for 24 h using a Nikon SMZ1000 equipped with a Nikon DS-Ri1 camera.

FTIR spectroscopy (Thermo Nicolet Avatar 360) was used to compare PEC to PEMU built from consecutive layers of PSS and PDADMA. The PEC was cut into 10 µm thick slices and allowed to dry on a double-side polished Si wafer. The PEMU was built on a similar Si wafer by alternate immersion into two 10 mM polymers solutions in 0.25 M NaCl for 5 min with three 1 min rinses of deionized water between layers using a robotic platform (StratoSequence V, nanoStrata Inc.).

Mechanical properties of extruded PECs was measured via stress relaxation[9b,29] using a TH2730 (Thümler GmbH) tensile testing unit equipped with a 5N or 100N load cell. To remove residual stress induced by extrusion, samples were first immersed in 1 M NaCl for 24 h. Samples were then soaked in solutions of various [NaCl] for 24 h prior to mechanical testing. Samples of diameter 1 mm and length 20 mm were stretched to a strain, ε, of 2% at a speed of 10 mm min^{-1} and the relaxation in stress recorded. Stress, σ, which relaxed to an "equilibrium" value, σ_0, was recorded versus time. The equilibrium modulus, E_0, is given by $E_0 = \sigma_0/\varepsilon$.

Strain to break measurements[30] were carried out on annealed samples at a stretching speed of 10 mm min^{-1}. Samples were cut into dogbone shapes of dimension 20 mm × 15 mm. The toughness was calculated by integrating the area under the stress-strain (to failure) curve (ε_f'):

$$\text{Toughness} = \int_0^{\varepsilon_f'} \sigma' \mathrm{d}\varepsilon' \qquad (4)$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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