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Mechanical Properties of Reversibly Cross-Linked Ultrathin Polyelectrolyte Complexes

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Abstract: Tensile properties of microcoupons of polyelectrolyte complex, formed by the multilayering method, were determined using a micromechanical analysis system. The degree of internal ion-pair ("electrostatic") cross-linking was reversibly controlled by exposure to salt solution of varying concentration, which "doped" counterions into the films, breaking polymer/polymer ion pairs in the process. Linear stress−strain behavior was observed for a poly(styrene sulfonate)/poly(diallyldimethylammonium) multilayer up to 2% deformation. The dependence of modulus on cross-link density could be rationalized well by classical theories of rubber elasticity, including some insight on the topology of polyelectrolyte complexes.

Introduction

Cross-linking endows polymer-based composites with desirable properties such as resistance to solvents and flow, high softening temperatures, and excellent dimensional stability.[1] The classic example of cross-linking technology is the vulcanization of rubber,[2] where polymer chains are linked via sulfur bridges to form a resilient network.[3] Most cross-linking strategies currently applied to materials employ irreversible chemical cross-links. However, methods of forming reversible physical cross-links are also known. Examples include hydrogen-bonded networks,[4] ionomer gels with junctions formed by ionic aggregation,[5] networks cross-linked by functional groups attached via chain ends,[6] and networks with junctions stabilized by segmental crystallization.[7]

Electrostatic, or ion-pairing, interactions between polyelectrolytes of opposite charge also yield cross-linked structures with reversible physical junctions.[8] The driving force in the formation of these polyelectrolyte complexes (PECs) is ion pairing between polyelectrolyte segments, driven by the release of counterions and water.[8a] Under this entropically driven regime, the counterions that were lost during PEC formation may be reintroduced by exposing the complex to a solution containing these ions. For example,[9]

$$\mathrm{Pol^{+}Pol^{-}_{c} + Na^{+}_{aq} + Cl^{-}_{aq} \rightleftharpoons Pol^{+}Cl^{-}_{c} + Pol^{-}Na^{+}_{c}} \qquad (1)$$

where $\mathrm{Pol^{+}}$ and $\mathrm{Pol^{-}}$ are respective positive and negative polyelectrolyte repeat units. The subscript "c" refers to components in the complex phase.

When ions enter the PEC according to eq 1, they break ion-pairing cross-links (it is possible to decompose the PEC fully at sufficiently high salt concentrations[9d]). We have verified the reversible nature of the equilibrium above directly and indirectly.[9a−c] A PEC immersed in a solution of salt therefore represents a very intriguing system: an amorphous composite, blended at the molecular level (due to the attractive segment−segment interactions), with cross-linking density under *reversible thermodynamic control*.

The swelling of PECs by immersion in salt solutions has been known for many decades.[8] It was also observed in the early literature, primarily that of Michaels and co-workers, that as counterion-free, glassy PECs swell, they become progressively more rubbery on exposure to electrolytes.[8a,d−f] While swelling

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may be assessed directly by volume changes,[8c] very little quantitative work has been reported on the mechanical properties of PECs as a function of their counterion content, although the trend of softening in salt has been measured[8f] most recently on capsules of polyelectrolyte complex.[10]

With the advent of polyelectrolyte multilayers (PEMUs), PECs are widely available in a much more tractable thin-film format. Multilayers are formed by alternately exposing a substrate to the charged polymers.[11] The resulting film is dense, uniform, and of highly defined stoichiometry (i.e., 1:1 matching of positive and negative polyelectrolyte segments), with very little residual counterion content.[12] This new PEC morphology has stimulated much recent work on the mechanical properties of PEMUs, employing innovative methods such as nanoindentation[13] of PEMUs on planar substrates, deformation of PEMU-based microcapsules, PEMCs, using atomic force microscopy[14] and osmotic swelling,[15] strain-induced elastic buckling instabilities to measure the modulus of PEMU in both the dry and wet states,[16] and quartz crystal microbalance measurements on thick, planar films.[17] These studies revealed a material with an elastic modulus in the range of 0.001−1 GPa.

In this work, we embrace the concept that PECs represent an opportunity to address some of the basic predictions of rubber elasticity, enumerated many decades ago by Flory and other workers.[3,18] In particular, we exploit the reversible cross-linking concept summarized by eq 1. Success in this approach relies on the use of a PEC that is moderately easy to dope with counterions. We have had much experience with the poly(styrene sulfonate)/poly(diallyldimethylammonium) (PSS/PDADMA) multilayer system, which is doped to varying degrees over the 0.1−1.0 M range of NaCl concentration.[9a−c] A further critical feature of this work was the ability to prepare PEMUs on fluorinated surfaces,[19] which could then be peeled off to yield free-standing films for mechanical testing. Due to the very small sizes of the samples, traditional polymer testing equipment was unsuitable, and we therefore resorted to apparatus designed to test individual muscle fibers having widths in the range of micrometers. Coordinating theory to experiment also shed light on the morphology of PECs in general.

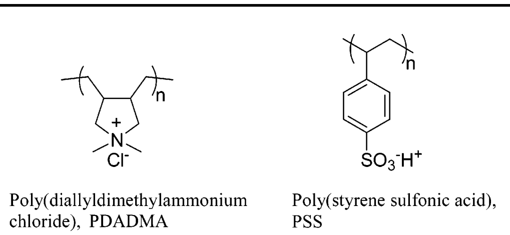

Figure 1. Structure of polyelectrolytes used.

Experimental Section

Reagents and Materials. PSS (molecular weight 6.8 × 10^4, $M_w/M_n = 1.06$) and PDADMA (molecular weight 3.7 × 10^5, $M_w/M_n = 2.09$) (Figure 1) were from Aldrich, and NaCl was from Fisher. Deionized water (Barnstead, E-pure, Milli-Q) was used to prepare all aqueous solutions.

PEMU Coating. A poly(tetrafluoroethylene) (Teflon) substrate (50 × 24 × 1.6 mm^3) was cleaned in ethanol and then exposed alternately to the two polymer solutions for 5 min using a robotic platform (StratoSequence, nanoStrata Inc.), with three rinses of deionized water for 1 min each. Rinse and polymer solution volumes were 50 mL. Polymer solution concentrations were 0.01 M (quoted with respect to the monomer repeat unit), with an ionic strength of 1.0 M NaCl. The multilayer was then annealed at room temperature in 1.0 M NaCl for one week.[9a]

The "dry" thickness of the multilayer was determined accurately using Fourier transform infrared (FTIR) spectroscopy comparison (using the strong sulfonate stretch at 1100 cm^{-1}) of a PDADMA/PSS multilayer of known thickness (measured with a Gaertner Scientific L116S ellipsometer) with the "thick" PEMU used for mechanical analysis

Microscopy and Mechanical Analysis. PEMUs were peeled off the Teflon substrate using flat-ended tweezers and cut into microcoupons (length 2.0 mm, width 150 μm, dry thickness 9.0 μm) with a razor blade. The ends were wrapped in aluminum foil clips and secured by applying a drop of silicone rubber before closing the clips.

The aluminum clips were connected to minuten pin hooks on a capacitance-type force transducer (3.3 kHz resonant frequency; Aurora Scientific, Ontario, Canada; calibrated with small weights) and a moving iron galvanometer motor (step time $\leq$300 μs; Aurora Scientific), designed for monitoring contractile behavior of single muscle fibers,[20] mounted on the base of a Leitz Diavert (Wetzlar, Germany) inverted microscope. Silicone sealant was used to stabilize the clips on the minuten pins. Position was monitored by a capacitance-type transducer in the motor. Calibration was done by applying a control voltage input (square wave) to the motor and measuring (using a microscope) the linear distance traveled in the horizontal plane by a clip attached to the motor hook. This allowed for rapid determination of the delta-position for a given input wave amplitude.

A temperature-controlled stage containing salt solutions of variable ionic strength was used to soak the PEMU for in situ measurements. Solutions were held in 200-μL anodized aluminum wells. The temperature was maintained at 28 ± 1°C with an ATR-4 regulator (Quest Scientific, North Vancouver, BC, Canada). Before every measurement, the microcoupon was conditioned in a specific salt solution for 10 min. Experimental control, data collection, and analysis of raw data were carried out using a PC-based system with a DT2831-G board (Data Translation, Marlboro, MA) and custom software. The software performs a fast Fourier transform method, converts to polar notation,

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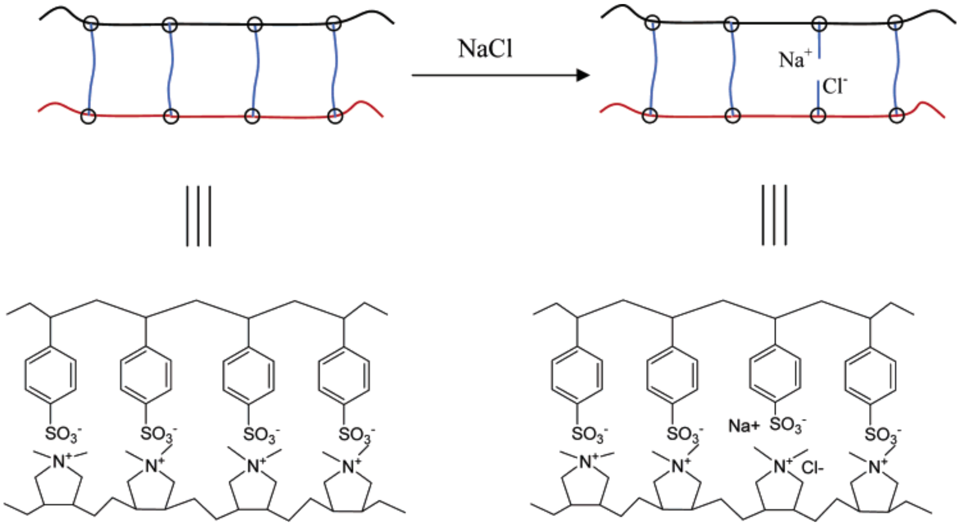
Scheme 1. Complexed Chains of PDADMA and PSS[a]



[a] Open circles represent junctions. Blue, black, and red lines represent the ion-pair chain, the PSS, and the PDADMA backbone chains. A “chain” appears between junctions.

finds the maximum amplitude index, calculates stiffness values and phase shift values, writes them to a file, converts to complex notation, and performs an inverse fast Fourier transform. Force was normalized to the multilayer microcoupon cross-sectional area, which was calculated from the wet thickness at different salt concentrations (assuming a rectangular geometry, see Supporting Information for more details).

Background and Theory

Doping of Networks. The concentration and length of polymer chains extending between cross-links, whether physical or chemical, are two important factors that influence the viscoelastic properties of a polymeric network.[18] According to the molecular theory of rubber elasticity, the equilibrium shear modulus, G, of a Gaussian polymeric network is directly proportional to the concentration of network chains, ν, and is given by[18b]

$$G = \Phi \nu R T \tag{2}$$

where Φ is the “front factor”, a geometrical factor close to unity (described in more detail and determined in Supporting Information). Equation 2, though simple, has been used with great success in rationalizing elasticity. Estimating the modulus is a straightforward geometric analysis of the density of chains, each chain defined by a junction point to which a cross-link is attached. Scheme 1 represents the approach of considering an ion pair as an electrostatic cross-link. Four negatively charged segments are paired with four positive segments, each pair a cross-link. When salt ions enter the structure, cross-links are broken, as depicted. The density of chains may be calculated if the cross-link density is known.

Intrinsic (polymer/polymer ion pairs) and extrinsic (polymer/counterion pair) charge are accompanied by water molecules, which additionally swell the PEC. The precise number of water molecules (which affects the density of cross-links) can be determined with FTIR.[21] In the absence of any counterion content, the PEMU is intrinsically compensated and the ion-pair density, c_0 (mol cm^{-3}), is given by

$$c_0 = \left(\frac{M_{\mathrm{PDADMA}} + M_{\mathrm{PSS}}}{\rho} + \frac{N_{\mathrm{H_2O}} M_{\mathrm{H_2O}}}{\rho_{\mathrm{H_2O}}} \right)^{-1} \tag{3}$$

where M_{PDADMA}, M_{PSS}, $M_{\mathrm{H_2O}}$, $N_{\mathrm{H_2O}}$, ρ, and $\rho_{\mathrm{H_2O}}$ are the molecular weights of PSS, PDADMA repeat units, and water, number of water molecules per ion pair, average density of PDADMA and PSS (1.1 g cm^{-3}), and density of water, respectively.

In ionic media, ions will dope the multilayer as in eq 1, transforming intrinsically compensated PEMU to extrinsically compensated. Swelling by hydrated ions is reversible and rapid.[22] The corresponding equilibrium constant, K, is[9a]

$$K = \frac{y^2}{(1-y)[\mathrm{NaCl}]_{\mathrm{aq}}^2} \approx \left(\frac{y^2}{[\mathrm{NaCl}]_{\mathrm{aq}}^2} \right)_{y \to 0} \tag{4}$$

where y is the fraction of the multilayer in the extrinsic form (the “doping” level) and $1 - y$ is the intrinsic fraction. For PDADMA/PSS multilayers, $y \to 1$ at >2.5 M NaCl, and the multilayer dissolves.[9d]

Although individual polymer charges are well matched[12] with minimal participation of salt counterions, we have shown that there is some residual extrinsic compensation in PDADMA/PSS multilayers at a level of about 3% after annealing.[9b] We combine this finding with doping data of PDADMA/PSS in $\mathrm{NaNO_3}$[9f] to yield the following empirical relationship between solution salt concentration and doping level:

$$y = 0.03 + 0.34[\mathrm{NaCl}]_{\mathrm{aq}} \tag{5}$$

The functional dependence of y on salt concentration, which must be determined experimentally, depends on the polyelec-

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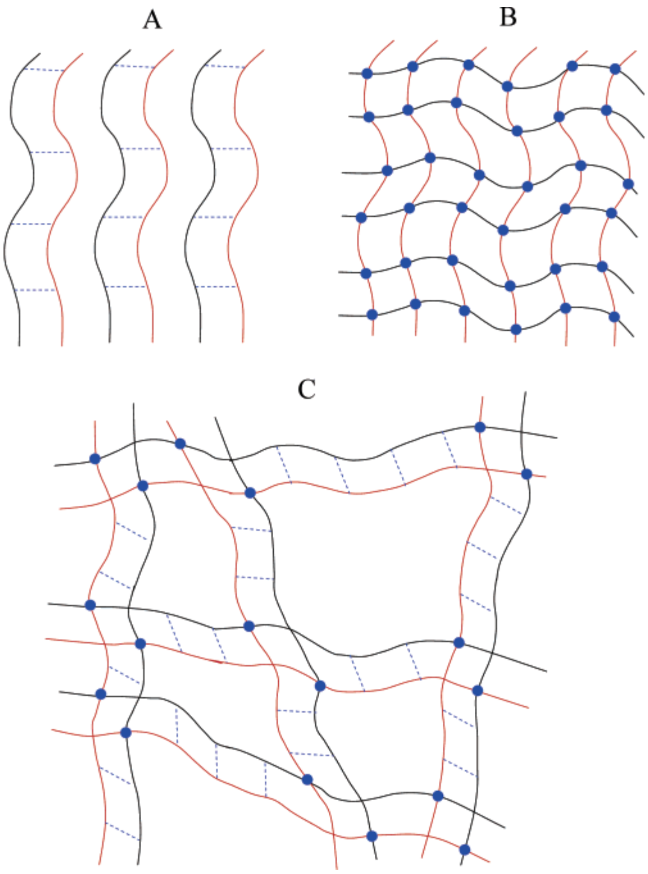

Figure 2. Ladder vs network topologies of polyelectrolytes in a complex. Blue, black, and red lines represent ladder ion pairs, PSS, and PDADMA backbone chains, respectively. Solid blue circles represent a network cross-link. (A) A ladder array of polyelectrolyte complexes. (B) A full network showing no ladder pairing. (C) A network of ladders, or "scrambled salt" (shown for the case when $\Omega = 0.46$).

trolytes forming the PEMU and the salt type. Generally, PEMUs from hydrophobic polyelectrolytes will be more difficult to swell/dope. The polymer/polymer ion-pair (cross-link) density at $[\mathrm{NaCl}]_{\mathrm{aq}} > 0$, $c_{[\mathrm{NaCl}]}$, is directly related to the doping level,

$$c_{[\mathrm{NaCl}]} = c_0(1 - y) \tag{6}$$

Ladder vs Network Pairing. At this point, we address an interesting topological conundrum which was the topic of intense debate during the early years of PECs.[23] Chains of complexed polyelectrolytes can exist with a mixture of topologies: ladder or network. In a ladder complex ($\mathrm{Pol^-Pol^+_L}$), sequential segments on a polyelectrolyte backbone pair up with likewise sequential partners, as shown in Figure 2A. At the opposite extreme, alternating segments pair up with those on different chains ($\mathrm{Pol^-Pol^+_N}$) to form a network (see Figure 2B). The impact on the mechanical properties will be profound, as ladder pairing does not produce a network. In reality, a mixture of ladder and network pairing is expected. The representation in Figure 2C can be considered a "network of ladders". Neighboring chains forming ladder pairs have a similar impact on modulus as termination of a chemical cross-link on the same chain. While it was concluded, some time ago, that the pairing of segments in a PEC is random and network-like (the "scrambled salt" morphology),[8d,23] the dilemma has not been addressed in a quantitative fashion. We attempt to do so here by defining a network fraction, Ω, that is, the fraction of ion pairing that exists in the network mode (the cartoon in Figure 2C demonstrates a fraction of 0.46):

$$\Omega = \frac{[\mathrm{Pol^+Pol^-_N}]}{[\mathrm{Pol^+Pol^-_N}] + [\mathrm{Pol^+Pol^-_L}]} \tag{7}$$

If ion-pairing associations were completely random and isoenergetic, every other segment, on average, would be paired network style (i.e., $\Omega = 0.5$ for 2-dimensions). Bias toward ladder ($\Omega < 0.5$) or network ($\Omega > 0.5$) topology would influence the bulk modulus accordingly. In parallel with copolymerization terminology, the "ideal" PEC would be one in which $\Omega = 0.5$ (i.e., random ion-pair sequences). For the purposes of the theory, the effective cross-link density of the network is defined by

$$c'_{[\mathrm{NaCl}]} = \Omega c_{[\mathrm{NaCl}]} \tag{8}$$

The network is characterized by having three types of chains (Scheme 1): the PSS backbone chain, the PDADMA backbone chain, and the cross-link chain. Following the definitions provided by Smith,[24] on average, for every two cross-links there exist four network junctions and six chains, and ν is given by

$$\nu = 3c'_{[\mathrm{NaCl}]} \tag{9}$$

There may be some sample history dependence of Ω. It is likely that the distribution of ion-pair types directly following the synthesis of a complex (for example, by the multilayer method) reflects the fact that complexes (multilayers) are usually prepared in the kinetic limit.[9e] The thermodynamically controlled topology is expected following some kind of "annealing" step. For example, we have recently shown, using neutron reflectometry studies of deuterated multilayers, that NaCl concentrations above about 0.8 M destroy the fuzzy layering in PDADMA/PSS multilayers.[25] In a recent example, the stiffness of PDADMA/PSS PEMCs decreases somewhat after annealing at elevated temperatures.[26]

Energy differences in ladder vs network pairing may be presented quantitatively by the following equilibria:

$$\mathrm{Pol^+Pol^-_L} + \mathrm{Na^+_{aq}} + \mathrm{Cl^-_{aq}} \overset{K_L}{\rightleftharpoons} \mathrm{Pol^+Cl^-} + \mathrm{Pol^-Na^+} \tag{10}$$

$$\mathrm{Pol^+Pol^-_N} + \mathrm{Na^+_{aq}} + \mathrm{Cl^-_{aq}} \overset{K_N}{\rightleftharpoons} \mathrm{Pol^+Cl^-} + \mathrm{Pol^-Na^+} \tag{11}$$

where

$$K_L = \frac{[\mathrm{Pol^+Cl^-}][\mathrm{Pol^-Na^+}]}{[\mathrm{Pol^+Pol^-_L}][\mathrm{Na^+}][\mathrm{Cl^-}]} \tag{12}$$

$$K_N = \frac{[\mathrm{Pol^+Cl^-}][\mathrm{Pol^-Na^+}]}{[\mathrm{Pol^+Pol^-_N}][\mathrm{Na^+}][\mathrm{Cl^-}]} \tag{13}$$

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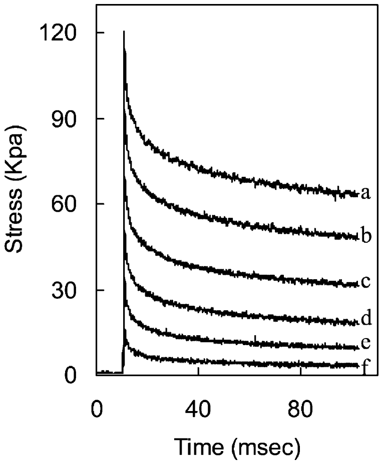

Figure 3. Stress relaxation of a $(PDADMA/PSS)_{250}$@1.0 M NaCl[29] multilayer at different salt concentrations with an applied strain of 0.4%. **a**, **b**, **c**, **d**, **e**, and **f** correspond to salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively. The stress was corrected for the actual cross-sectional area of the microcoupons, with consideration of water volume fraction.

The difference in the free energy of association (the reverse of eqs 10 and 11) between ladder and network pairs is given by

$$\Delta G^0_{\mathrm{L}} - \Delta G^0_{\mathrm{N}} = -RT \ln\frac{K_{\mathrm{N}}}{K_{\mathrm{L}}} \qquad (14)$$

$$\frac{K_{\mathrm{N}}}{K_{\mathrm{L}}} = \frac{[\mathrm{Pol}^+\mathrm{Pol}^-_{\mathrm{L}}]}{[\mathrm{Pol}^+\mathrm{Pol}^-_{\mathrm{N}}]} = \frac{1-\Omega}{\Omega} \qquad (15)$$

Ladder pairing could reasonably be expected to be somewhat more stable, as neighboring segments would pair cooperatively. For linear growing multilayers, where layers are “frozen” in place during synthesis, annealing would be required to reach the thermodynamic distribution. Exponentially growing multilayers,[27] where at least one of the polyelectrolyte components has access to the entire multilayer, may establish the thermodynamic distribution of ladder and network pairs on formation. If network fractions of multilayers drift with time, so will their mechanical properties, which might influence the response of cells growing on them.[28] Our evidence for high ladder fraction in our “annealed” materials comes from a comparison with published moduli for PDADMA/PSS multilayers[15a,26] which are significantly higher than ours. We are currently attempting to follow the evolution of modulus with time for PEMUs.

Results and Discussion

Viscoelasticity of PEM. Figure 3 depicts some typical tensile testing results. In this figure, a 0.4% uniaxial strain, *e*, was applied to the PEMU microcoupon immersed in salt solutions of various ionic strength, and the stress, σ, was recorded over a period of 100 ms.

At any given ionic strength, the initial tensile stress, σ_0, increased instantly in response to the applied constant strain and then decayed. A pseudo-steady-state regime, σ_{eq}, was obtained at $t > 70$ ms.

Stress relaxation is a well-documented phenomenon that characterizes viscoelastic materials.[1a,b,30] When cross-links are introduced into polymers, the viscosity becomes infinite and a viscoelastic network is produced, exhibiting an equilibrium modulus and compliance.[1b] In contrast to the PEMU above, which is characterized by a relatively fast stress relaxation, polymer networks typically exhibit long viscoelastic relaxation times.[31a] For example, it can take several hours for a lightly cross-linked natural rubber to equilibrate in a stress relaxation experiment.[31b] The origin of this difference in relaxation rate is the contrasting relaxation modes a polymer chain can undergo in PEMU and lightly cross-linked rubber. When a constant strain is applied to deform either polymeric network, the free energy of the molecular segments will increase, and the chains respond by readjusting themselves (viscous-like flow) to relieve the ensuing stress. Every time a segment reorients to a new, lower free energy, the stress will decrease.[32] In lightly cross-linked rubber, reorientation is accomplished when branched chains or dangling ends diffuse in the presence of entanglements.[1b,33] If more cross-links are introduced, the chains can diffuse less and the extent of stress relaxation decreases dramatically.[31a]

Classically, polymers are heated to accelerate their flow and relaxation properties, especially when the temperature is raised beyond the glass transition temperature, T_{g}.[34] PECs are multicomponent systems that cannot be heated to melting due to their salt-like properties.[8a] Further temperature constraints are obviously present when PECs are immersed in aqueous solution. Instead, PECs may be softened by the addition of salt (under isothermal conditions) in a process of *counterion-induced plasticization*. The enhanced mobility of polyelectrolytes under the influence of salt has recently been presented by Cohen Stuart and co-workers as a glass-to-rubber phase transition.[35] While the influence of salt on mechanical properties is strong, we believe the effect is best characterized as a continuous change in properties rather than a (discontinuous) first-order phase transition. We were not able to locate a T_{g} in well-hydrated PDADMA/PSS complexes using differential scanning calorimetry over the temperature range −20 to 90 °C.

Salt-Dependent Viscoelastic Behavior in PEMUs. The observations summarized by Figure 3 demonstrate the influence of solution ion strength on PEC mechanical properties. To

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(29) Polyelectrolyte nomenclature: $(A/B)_x@y$, where A and B correspond to the first and second polyelectrolytes in a layer pair, starting with A. *x* is the number of layer pairs. *y* is the ionic strength of the buildup solution.

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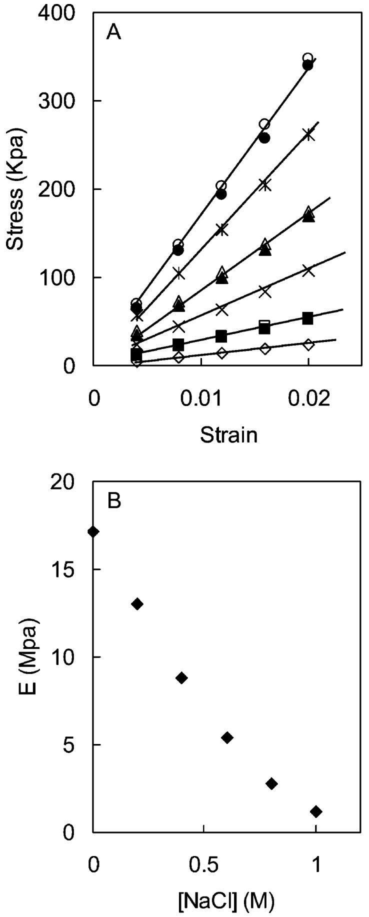

Figure 4. (A) Stress−strain curves of a $(PDADMA/PSS)_{250}$@1.0 M NaCl multilayer at different salt concentrations. Open circles, asterisk, triangles, crosses, squares, and diamonds correspond to the stretching cycle (in increasing order of elongation) with salt concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 M NaCl, respectively. Solid circles, triangles, and squares indicate a decreasing elongation cycle at 0.0, 0.4, and 0.8 M. A similar trend was observed at the other salt concentrations. (B) Elastic modulus obtained from the slope of the curves in panel A. At 0.0 M NaCl, $E = 17$ MPa. Dimensions were corrected to account for swelling. (See Supporting Information for more details.)

generate steady-state (“static”) stress/strain data and investigate the dependence of elastic modulus, E, on doping, the microcoupons were subjected to a series of transient uniaxial strains, elongating the PEMUs by 0.4−2% of their original length (Figure 4A). The experiment was again carried out in situ with microcoupons immersed in salt solutions of various ionic strength. σ_{eq} was recorded at $t = 70$ ms and used to construct the stress−strain curves.

E measures the resistance to deformation of a material when stress is applied, and it is defined by[1a,30a]

$$E = \frac{\sigma}{e} \tag{16}$$

$$e = \frac{L - L_0}{L_0} \tag{17}$$

where e, σ, L_0, and L are strain, stress, and the lengths of polymer network at rest and after applying a certain strain, respectively.

In agreement with eq 16, the relationship between applied strain and resulting stress in PEMUs for $e < 2\%$ was found to be linear. Further, when the elongation cycle was repeated at a certain ionic strength, σ_{eq} was reproducible with minimal hysteresis. This means that the multilayer recovered almost completely when the applied strain was removed (i.e., there was no residual deformation).

E, evaluated from the slopes of the stress−strain data (Figure 4B), was observed to decrease as the ionic strength increased. The material becomes softer as more salt is added, and a lower amount of energy is stored. A reduction in stiffness as a function of ionic strength was previously observed in the case of polyelectrolyte complexes in contact with salt-containing solutions[8f] and other multilayer systems[35] that have been studied in the framework of mechanical properties, such as poly(allylamine hydrochloride) (PAH)/PSS.[10,16] In the case of PEMCs made from PAH and DNA, an interesting stiffening of the multilayer was seen on adding salt. Hydrogen-bonded systems may become more strongly associated as ionic strength increases.[14c,36]

At 0.0 M NaCl, the elastic modulus reached a maximum of 17 MPa, which is an order of magnitude less than the reported elastic modulus of polyelectrolyte multilayer capsules made from PDADMA/PSS[15a,26] but close to a value of 24 ± 15 MPa deduced from quartz crystal microbalance studies on planar PEM films of the same composition.[17b] Much of the published work relating to the mechanical properties of PEMUs was carried out on PEMCs[37] made by sequential deposition of oppositely charged polyelectrolytes on melamine formaldehyde (Mf) or poly(lactic acid) (PLA) colloidal particles. Dissolution of the core template particles was accomplished via treatment with organic solvents and/or acid media,[37j] which was found to affect the physical properties of the produced polyelectrolyte multilayer shells.[37f] For example, PAH/PSS PEMCs prepared on PLA templates are 2 orders of magnitude softer than same PEMC prepared on MF templates.[14a] Even if the same template was used, the resulting PEMCs showed an elastic modulus ranging from 30 to 100 MPa.[37e] More recent data on PAH/PSS multilayers indicates E values consistently in the 400 MPa range.[10c,15b,16] After synthesis, the modulus of a PEMC may or may not be influenced by the presence of an organic solvent.[37k]

In the present case, PEMU microcoupons were peeled from the planar substrate using physical and not chemical means. Thus, we are able to rule out variability in E caused by dissolution/delamination steps.

Linear vs Nonlinear Viscoelastic Behavior in PEMU. When the PEMU microcoupons were stretched by more than 2%, the resulting stress curved upward. This was more

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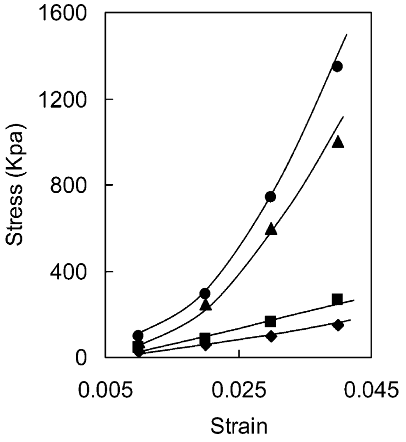

Figure 5. Stress−strain curves of (PDADMA/PSS)$_{250}$@1.0 M NaCl multilayer at different salt concentrations and higher strain amplitudes. Circles, triangles, squares, and diamonds correspond to salt concentrations of 0.2, 0.4, 0.8, and 1.0 M NaCl, respectively. Solid lines are a guide to the eye.

pronounced when the salt concentration decreased below 0.8 M (Figure 5). Here, nonlinear response comes into play at quite low extensions.

Polyelectrolyte multilayer microcapsules immersed in water were shown to behave similarly when deformed using an atomic force microscope. However, the critical deformation limit for the linear stress−strain relationship for PEMCs was 1 order of magnitude higher than observed here for PEMU.[37i] When PEMCs are significantly expanded using high internal osmotic pressure, the modulus decreases to the range of a few MPa, although deformation is not reversible.[37l]

Nonlinear stress−strain is also observed in cross-linked rubber, but at much higher strains, and is interpreted on the basis of strain-induced crystallization.[18d] This is highly unlikely in the case of PEMUs because the extension limit at which the upturn occurs is insufficient to align the polymer chains and cause crystallization. A more plausible explanation for the nonlinear stress−strain behavior at low ionic strength takes into account the finite chain extensibility[38] of the PDADMA/PSS network. Due to a high cross-link density, the network is comprised of a population of short chains. The network is so dense that the chains reach their extensibility limit quickly.[38]

Rodd et al.[39] reported that, for a system undergoing gelation, the critical strain limit of linear viscoelasticity decreased as the number of cross-links increased. In Figure 5, when the ionic strength of the bathing solution is 0.8 M or higher, the cross-link density is reduced and PEMU is plasticized enough to achieve extensibility limits beyond 2%. It is possible that a heterogeneous mixture of chains with varying lengths and flexibilities emerges at this point. The longer chains possess higher degrees of freedom and are more efficient in relieving applied deformations.

Modulus vs Cross-Linking. The modulus vs solution salt concentration data (Figure 4) may be combined with swelling behavior (eqs 1 and 4) specific to PDADMA/PSS (eq 5) to correlate experiment with theory (eq 2). Included in the treatment is the extent to which ion pairs form network cross-links vs ladder cross-links (Figure 2). It is known that PEMUs are highly interpenetrating and no actual stratification of material between adjacent "layers" is observed.[11,40] Such a randomized amorphous composition would support the scrambled salt topology ($\Omega \rightarrow 0.5$). It is possible, however, to create "fuzzy" strata by separating materials by several layers. This has been done, for example, using isotope labeling of select layers for structural studies,[11,41] or on a longer length scale by composition variations to produce dielectric filters.[42] Even diffuse layering indicates a nonequilibrium structure which could contain residual stresses or partial alignment of polymer chains in the plane of the substrate. Anisotropic orientation would bias the mechanical properties, depending on the direction of the applied stress. For uniaxial elongation, as performed here, the stress tensor is in the plane of the film, and residual in-plane orientation would increase the apparent modulus. It is known that exposure to salt "anneals" residual extrinsic charge from films by assisting polyelectrolyte interdiffusion. We have shown that exposing PDADMA/PSS multilayers to NaCl of approximately molar concentration induces interdiffusion at the surface[9a] and in the bulk.[25] In the present experiments, PEMUs were thoroughly annealed for 1 week in 1 M NaCl to yield truly amorphous, isotropic films. Conditions for efficient annealing depend on a number of factors, including the pair (or blend) of polyelectrolytes, the salt concentration, and the salt type. Specifically, hydrophilic polymers, such as those containing carboxylates, are easier to swell and would anneal at lower salt concentrations. Other PEMUs, including the popular PAH/PSS couple, are much more difficult to swell[9a] and only soften at high NaCl concentration.[14b] An alternative to high NaCl concentration would be the use of hydrophobic salts (such as NaBr) or polyvalent salts (e.g., $CaCl_2$).[9e,f]

Substituting eq 9 into eq 2 and combining with eqs 6 and 8 yields the following for the dependence of shear modulus on doping level:

$$G = 3\Phi RTc_0\Omega(1 - y) \qquad (18)$$

For the specific PDADMA/PSS case, the dependence of y on $[\mathrm{NaCl}]_{\mathrm{aq}}$ is estimated (eq 5). Thus,

$$G_{\mathrm{PDADMA/PSS}} = 3\Phi RTc_0\Omega(0.97 - 0.34[\mathrm{NaCl}]) \qquad (19)$$

Assuming that the network is isotropic (a condition promoted by annealing) with a Poisson ratio of 0.5,[1a] G can be obtained from the elastic modulus using $G = E/3$.[1a] The only fit parameter to eq 2 is the network fraction, Ω, which for an ideal, "scrambled salt" PEC $\rightarrow$ 0.5. As can be seen from Figure 6, the data are roughly fit with $\Omega = 0.3$. This suggests that the PDADMA/PSS network comprises 70% ladder character (after annealing). According to eq 14, with a network fraction of 0.3, the respective free energy difference value is -2.1 kJ mol^{-1}; i.e., ladder pairs are more stable than network pairs by 2.1 kJ mol^{-1}.

The theory represented by eq 2 assumes a network having point cross-links and that the distribution of the network chains

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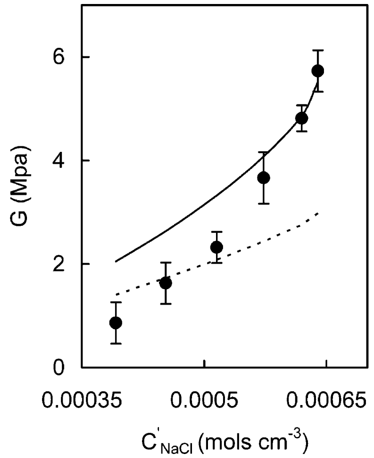

Figure 6. Experimental shear modulus, using $G = E/3$, as a function of effective cross-link density. The dashed and continuous lines are fit to the data using eqs 2 and 20, respectively. The parameters used to construct the theoretical fit are summarized in Table 1.

Table 1. Values of Different Parameters Characterizing the Morphology of PDADMA/PSS

[NaCl], M	y	$c_0 \times 10^6$	n	$\bar{C}_n$	Φ
0.0	0.03	2235	7.2	3.1	0.55
0.2	0.09	2329	7.6	3.16	0.53
0.4	0.14	2329	7.9	3.23	0.51
0.6	0.2	2281	8.2	3.32	0.49
0.8	0.25	2200	8.6	3.4	0.47
1.0	0.31	2108	9.1	3.5	0.45

obeys Gaussian statistics[18b] (heterogeneous distribution of chain length). As the cross-linking is under thermodynamic control, in contrast to chemically cross-linked materials, there should be a distribution of chain lengths, but not necessarily a Gaussian distribution. At high cross-link density (low salt concentration), the junctions are connected by short, stiff segments without many degrees of freedom. Thus, G is no longer directly proportional to ν and a "non Gaussian form of the theory becomes essential".[18b]

Smith[24] developed theory for the non-Gaussian distribution of chain lengths and derived the following expression:

$$\frac{\nu RT}{G} = \frac{1}{\Phi_n} - \frac{6\bar{C}_n}{5q^2\bar{n}} \tag{20}$$

where $\bar{n}$ is the geometric mean number of bonds in the network chains, $\bar{C}_n$ is a characteristic ratio[24] given by $\bar{C}_n = n^{0.57}$, and q is a dimensional factor determined by bond angles and length of the backbone chain (for a network containing only carbon–carbon single bonds, $q = 0.83$[24]). Smith[24] prescribes the methods for estimating Φ, $\bar{n}$, and $\bar{C}_n$ which were applied here and are described in more detail in the Supporting Information (they are somewhat tedious). The calculated front factors of the PDADMA/PSS multilayer, summarized in Table 1, are in agreement with the findings of Smith, who reported a Φ close to 0.5 for highly cross-linked systems.[24]

Equation 20 performed well in describing G of polymeric networks prepared from ethyl acrylate and ethylene, trimethylene, or tetramethylene glycol dimethacrylate, with cross-link densities in the range of 0.3×10^{-3} to 2×10^{-3} mol cm^{-3}.[24] Here, the scaling at the highest cross-link densities is more reasonable, although the Gaussian model (eq 2) is closer in magnitude at lower densities. Note that all dimensional changes (i.e., size changes due to incorporation of ions and water) have been included in the data (Figure 4). Deviations at lower cross-linking level (higher doping/swelling) could be caused by weaker association due to loss of binding cooperativity (a phenomenon documented for PDADMA/PSS multilayers[9b]) or a stronger degree of doping by NaCl than by $NaNO_3$ (i.e., eq 5 underestimates the doping constant). Since this constant is determined from FTIR measurements,[9b] NaCl swelling could not be determined directly. It may also be possible that network ion pairs are broken preferentially because they are weaker than ladder pairs.

Experimental values of E are much lower than reported previously for the same PEC and lower than would be estimated by either the classical (eq 2) or the non-Gaussian (eq 20) theories. For example, assuming a Ω of 1.0 (i.e., every ion pair is a network cross-link), Smith's equation would yield a G of ca. 260 MPa for undoped PEC. Introducing substantial ladder pairing is the only way we are able to reconcile the experiment with theory.

Conclusion

The agreement between theory, postulating ion pairs as reversible cross-links, and experiment is satisfactory, considering that geometrical estimates are made for parameters, and the only freely adjustable "fit" parameter was Ω, which was assigned an intuitive value near 0.5. The agreement is not perfect, but the scaling and magnitude are quite reasonable. Our experimental modulus values are lower than some others reported in the literature, but we believe that our emphasis on chain relaxation by annealing, leading to isotropic materials[25] (and possible migration toward more ladder-like composition), may contribute to this difference. A very recent publication reports that the room-temperature modulus of PDADMA/PSS capsules falls after annealing at 50 °C.[26]

The insight on topology of PECs afforded by Ω addresses the seemingly intractable semantics questions of where a counterion goes when it enters the PEC. In a mean-field electrostatics model, the ions float around, experiencing an average electrostatic potential within the PEC. In the ion-pairing approach taken here, ions are associated with particular polyelectrolyte segments. The success of treating electrostatic cross-links as ion pairs and breaking them when ions enter the PEC reinforces the idea that ions are specifically associated with polymer charges.

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Supporting Information Available: Diagram of mechanical testing apparatus; calculation of various geometric factors, including front factor. This material is available free of charge via the Internet at http://pubs.acs.org.

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