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Influence of the Salt Concentration on the Properties of Salt-Free Polyelectrolyte Complex Membranes

The effect of salt used during the processing of polyelectrolyte complexes displays a counterintuitive behavior regarding their glass transition temperature. PEC membranes fabricated with NaCl concentration ranging from 0 to 1.5 m are made salt-free by an overnight rinse step. The T_g of the PEC is found to increase with the NaCl used in processing possibly due to a lower number of extrinsic sites at higher NaCl content.

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Influence of the Salt Concentration on the Properties of Salt-Free Polyelectrolyte Complex Membranes

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Polyelectrolyte complexes (PECs) prepared by solution mixing of cationic poly(diallyldimethylammonium chloride) and anionic poly(sodium 4-styrene sulfonate) with various NaCl content are processed into films. Salt-free (SF-PEC) membranes are produced by rinsing the PEC in DI water overnight. The main finding of this paper is that SF-PEC films have different properties depending on the NaCl used during the processing step. Dynamic mechanical analysis measurement confirms that hydrated SF-PEC film processed from higher salt content has a higher modulus than when processed without salt and the glass transition temperature appears to shift to higher values. Processing the PECs films in the presence of salt also has an interesting effect on their shape memory characteristics. SF-PEC films prepared under high-salt are shown to maintain a programmed temporary shape better than materials prepared with low salt, while recovery is possible within a short period of time when immersed in hot water.

1. Introduction

Polyelectrolyte complexes (PECs) are formed by mixing solutions of positively and negatively charged polyelectrolytes and their formation is thermodynamically driven by the entropy gain associated with the release of the counterions.^[1,2] Depending on the temperature and the ionic strength of the solution, PECs are obtained in the form of tough complexes, elastic liquid coacervates, or liquid-like solutions, and known to be hardly processable in the solid state and brittle when dry.^[3] It has been realized that water^[4] and salt^[5] are two important factors that allow the softening of the PECs by modifying the chain interactions, enhancing chain mobility, and creating free volume in the ionic network.^[6] PECs are softer when hydrated, but not water soluble, and this makes them useful in applications such

as ultrafiltration,^[7] batteries,^[8] tissue engineering,^[9] and pharmaceuticals.^[10–12] The effect of salt addition on the mechanical behavior of PECs has been the subject of several studies. Schlenoff and co-workers reported that PECs swell and become more rubbery when exposed to salt solutions and can thus be extruded at room temperature.^[13,14] In a systematic study, the authors demonstrated that with increasing ionic strength of the solution, the glass transition temperature (T_g) of the PEC was shifted to lower temperature, on account of electrostatic screening, which in turn reduced the electrostatic interactions between the polymer pairs.^[15,16]

While several studies have investigated the influence of salt annealing after PEC formation,^[17] the study presented here was focused on examining the effect of

salt addition as a processing aid during mixing and formation of the polymer complex. We show that smooth and transparent PEC films can be produced by mixing aqueous NaCl-containing solutions of cationic poly(diallyldimethylammonium chloride) (PDADMAC) and anionic poly(sodium 4-styrene sulfonate) (PSS), shaping the materials formed via compression molding into thin films, and extracting the NaCl by a rinse step. Varying the salt concentration ($[NaCl]$) during processing and hydrating the materials after salt extraction, we show that the T_g of the hydrated salt-free PEC films increases with the $[NaCl]$ used during the mixing step. This trend appears to reflect improved mixing during the polymer complex formation and an increased entanglement density in the final materials. Processing the PEC films in the presence of salt also had an interesting effect on their shape memory characteristics. PEC films prepared under high-salt conditions were shown to maintain a programmed temporary shape better than materials prepared with low salt concentration, while recovery was possible within a short period of time when immersed in hot water.

2. Experimental Section

2.1. Chemicals and Materials

Poly(diallyldimethylammonium chloride) (PDADMAC, medium molecular weight, 20 wt% in water, weight-average molecular weight, $M_w = 200\,000\text{--}350\,000\text{ g mol}^{-1}$), poly(sodium 4-styrene sulfonate) (PSS, $M_w = 70\,000\text{ g mol}^{-1}$), and sodium

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chloride (NaCl) were purchased from Sigma-Aldrich. Double distilled (DI) water was used throughout.

2.2. Fabrication of Polyelectrolyte Complex Films

Polyelectrolyte Complex (PEC) films were prepared as follows. PDADMAC and PSS were individually dissolved in water at a concentration of 0.1 M (16.12 g L⁻¹ for PDADMAC and 20.62 g L⁻¹ for PSS) by stirring with a magnetic stir bar and adding NaCl to the solutions after the polymers were completely dissolved. The NaCl concentration in the two solutions ([NaCl]) was adjusted in a range of 0–1.5 M. Aliquots of the solutions (30 mL of each solution) were combined, stirred for 30 min, and the solid complexes that had formed were compacted into dense precipitates by centrifugation at 8000 rpm for 20 min. The solids were separated from the supernatant solution and, without further drying, compressed in a Carver press at 40 °C under a pressure of 2000 psi for 30 min using spacers to control the thickness to 100 µm. The samples were dried at ambient temperature overnight. To prepare the salt-free films, the films were immersed in 100 mL of water for 24 h and the water was changed every 8 h.

2.3. Characterization of PEC Films

All the results quoted are averages of three independent experiments. The thermal stability and salt content of the PEC films were measured by thermogravimetric analysis (TGA) on ≈3 mg of dry salt-containing as well as salt-free samples with a Mettler-Toledo STAR[®] system under inert N₂ atmosphere in the temperature range of 25–600 °C and applying a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements with heating and cooling cycles from 0 to 250 °C were performed using a heating/cooling rate of 10 °C min⁻¹. The mechanical behavior of the PEC films was characterized by dynamic mechanical analysis (DMA) using a TA Instruments Model Q800. A tension clamp and a heating rate of 5 °C min⁻¹ were employed for measurements of dry, salt-containing films. A submersion clamp and a heating rate of 0.5 °C min⁻¹ with samples immersed in water were used for measurements of hydrated, salt-free films (see Figure S1, Supporting Information) and in this case, the temperature range was limited to 5–55 °C. The DMA tests were conducted in multi-frequency strain mode using a temperature ramp, a frequency of 1 Hz, and a strain amplitude of 15 µm. The experiments were conducted with PDADMAC/PSS film samples of dimension 6 × 15 mm and samples were studied as a function of [NaCl] during mixing: 0, 0.5, 1, and 1.5 M. Stress–strain measurements were conducted on the hydrated, salt-free films on the same instrument at room temperature with a strain rate of 20% min⁻¹. The tensile moduli were calculated from the initial slopes of the linear regions, that is, in the strain range of 0–5%. To measure the water uptake, the dry salt-free films with dimension of 20 × 20 mm (dried for 48 h at 60 °C) were soaked in water for 24 h, and the water uptake was calculated from the weights of the dry (W_d) and the hydrated (W_h) samples by:

$$\text{Degree of swelling (\%)} = \frac{W_h - W_d}{W_d} \times 100 \quad (1)$$

2.4. Shape Memory Behavior of PEC Films

In order to monitor the water-induced shape memory effect (SME) of the PEC films, 6 mm wide strips of an initial length of 2 cm (L₀) were immersed in water maintained at 50 °C, stretched to a length of L₁ = 4 cm (i.e., to a strain S = (L₁ - L₀)/L₀ = 100%) in a manual stretching device (model) as shown in Figure S2, Supporting Information. With the strain applied, the samples were placed in cold water and held at this stage for 5 min, before they were allowed to dry under ambient conditions. After removing the force, the temporary shape (L₂) was determined. Finally, the shape recovery was triggered by placing the samples into water heated at 50 °C and the recovered length L₃ was measured. The shape fixity (R_f) and shape recovery (R_r) were calculated using Equations (2) and (3):

$$\% \text{ Shape fixity } (R_f) = \frac{L_2 - L_0}{L_1 - L_0} \times 100 \quad (2)$$

$$\% \text{ Shape recovery } (R_r) = \frac{L_2 - L_3}{L_1 - L_0} \times 100 \quad (3)$$

3. Results and Discussion

3.1. Fabrication of Salt-Free PEC Films

A variety of salts, including NaCl, have been used to screen electrostatic interactions between cationic and anionic polymers and soften PECs, thereby making them processable by extrusion or compression molding. Unlike several previous studies, in which the influence of salt water on the thermal transition (T_g) of the PEC was investigated, the materials reported here did not contain any salt during testing, but NaCl was merely used during processing and subsequently removed. This approach was explored based on the hypothesis that it would i) allow adequate processing, ii) support the formation of chains entanglements, and iii) possibly allow tailoring of the thermo-mechanical properties of the salt-free PEC films.

The PEC films were prepared as schematically shown in Figure 1 and detailed in Section 2. PDADMAC and PSS were individually dissolved in water containing NaCl in a concentration of 0–1.5 M. The solutions were combined and stirred, and the solid complexes that had formed were compacted into dense precipitates by centrifugation. The materials were then compressed at 40 °C into films of a thickness of 100 µm and dried under ambient conditions. At this point, the NaCl used during mixing of the polyelectrolytes was still trapped in the film, which were transparent, smooth, and of homogeneous appearance. The NaCl was subsequently removed by soaking the PEC films in deionized (DI) water. After thorough drying, smooth salt-free PEC films were obtained, which are referred

Figure 1. Schematic representation of the fabrication process used to create PDADMAC/PSS-based PEC films.

to as PEC(X), where “X” denotes the [NaCl] in the original solution from which the material was processed. The removal of NaCl was confirmed by TGA of the PEC film prepared with 1.5 M NaCl, PEC(1.5), before and after the salt extraction. It can be seen from the thermograms (Figure S3, Supporting Information) that the remaining weight of the sample without rinse is 30%, while the water-soaked film degrades without leaving any residue, confirming the complete removal of NaCl upon extraction with DI water.

3.2. Effect of [NaCl] during Processing on the T_g of Hydrated PEC Films

In an initial step, the thermal and mechanical properties of the dry PEC films were investigated using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). As reported by other groups, no glass transition could be observed in either the DSC scans or the DMA measurements, due to the lack of chain mobility of the dry PECs prepared from all salt conditions (DSC and DMA graphs are provided in Figure S4, Supporting Information). The DMA measurements were particularly difficult to perform, as the dry PEC films were very brittle and could hardly be held in position with the clamp. It is in fact somewhat expected that the dehydrated PECs would become very rigid and brittle, which makes them impractical for high temperature applications.

The thermomechanical behavior of fully hydrated PDADMAC/PSS films, which had been equilibrated by immersion in DI water, was studied using DMA of samples submerged in water. **Figure 2a,b** shows the shear storage modulus E' and $\tan(\delta)$ as a function of temperature and the [NaCl] used during processing. The traces are characteristic of glassy polymers with a glass transition (as established by the maximum of the $\tan(\delta)$ curves) of around 25–40 °C, a glassy regime with an E' of a few hundred MPa at lower temperature, and a rubbery regime characterized by an E' of around 1 MPa above T_g (Table 1). It is interesting to note that both, the T_g and also E' in the glassy state, increase seemingly linearly with the [NaCl] used during processing. Since all samples were salt-free during the testing, the shift in T_g cannot be attributed to the presence

Figure 2. DMA traces at 1 Hz of hydrated PDADMAC/PSS PEC films measured in water. a) Storage modulus E' . b) Normalized $\tan(\delta)$.

of NaCl (and related plasticizing effects). Thus, the data suggest that the polymer complex is characterized by either a more tightly bound network or a higher degree of chain entanglements. This concept is similar to the commonly idea of the ladder model and scramble egg discussed elsewhere.^[18,19] Indeed, at low [NaCl], the PEC is expected to rapidly form and stabilize by the formation of ion pairs without the possibility of much chain motion and therefore few entanglements. On the other hand, at high [NaCl] the electrostatic charge screening imparted by the salt addition reduces the ionic interaction strength, enables more extensive chain movements, and leads to an intricate mixing of the polymer chain and an inducement of the PEC aggregation,^[20] which tends to increase the modulus and T_g of the polymer complex.

It has been reported in a number of papers that water hydrating the polyionic structure in PECs can act as a plasticizer

Table 1. The storage modulus at 1 Hz of PEC films in the dry, salt-containing (rate 5 °C min⁻¹, tension clamp) and hydrated, salt-free (rate 0.5 °C min⁻¹, submersion clamp) state.

[NaCl] [M]	Storage modulus [MPa]					T_g [°C] (hydrated)
	Dry, salt-containing films		Hydrated, salt-free films			
	At 25 °C	At 37 °C	At 5 °C	At 25 °C	At 37 °C	
0	1823 ± 118	1912 ± 36	127 ± 23	2.9 ± 1	0.8 ± 0	24.3
0.5	1842 ± 133	2002 ± 76	199 ± 11	6.6 ± 1	0.9 ± 0	26.3
1	2034 ± 60	2226 ± 32	220 ± 26	35 ± 5	2.0 ± 1	35.6
1.5	2384 ± 73	2541 ± 111	272 ± 20	63 ± 9	4.2 ± 2	39.6

and that, consequently, the T_g usually decreases as the degree of hydration increases.^[6,21] Therefore, the water uptake of the salt-free films prepared here was measured in order to elucidate to what extent the [NaCl] used during processing influences the water content of the samples and how it latter impacts the T_g . The PEC films were thus immersed for 24 h in water, in order to achieve equilibrium swelling. As seen in Figure 3, the water uptake decreases from ≈400% to 150% as [NaCl] used during processing is increased. This result is a somewhat unexpected, since the films are salt-free, and as they have the same composition, one might think that the water uptake should be nearly constant. However the fact that T_g (Figure 2) increases with decreasing water content, and therefore decreasing extent of plasticization (Figure 3) is consistent, and suggests that the water uptake is not only governed by the mere chemical composition of the PECs, but also conformation changes that occur during mixing the components under different salt concentrations.

The mechanical behavior of hydrated salt-free PEC films was further investigated by way of tensile testing at room temperature. The stress–strain curves shown in Figure 4a show strikingly that the mechanical properties are significantly impacted by the processing conditions. In accordance with the DMA data, the Young's modulus increased considerably with the

Figure 3. Equilibrium water uptake of PDADMAC/PSS films at 25 °C as a function of [NaCl] used during processing.

Figure 4. a) Stress–strain curves (strain rate of 20% min⁻¹) and b) Young's modulus and toughness of hydrated PDADMAC/PSS films as a function of [NaCl] used during processing.

[NaCl] employed during processing from 3.0 ± 0.4 MPa for the salt-free solutions to 40 ± 3 MPa for samples processed with [NaCl] = 1.5 M. At the same time, the maximum stress rose from 3.0 ± 1.0 MPa to 10 ± 0.9 MPa, while the elongation at break was reduced from 138 ± 13 to 65 ± 15%. Despite the significant reduction of the strain at break, the films maintained a considerable toughness from 1.3 ± 0.03 to 3.9 ± 0.6 MJ m⁻³ (Figure 4b).

3.3. Shape Memory Effect of PEC

The use of PECs as water-activated shape memory materials has been proposed and demonstrated by Schlenoff et al. who

Figure 5. a) Strain as a function of step during shape memory programming and release of compressed PDADMAC/PSS films and b) a series of photographs illustrating the shape recovery of twisted PEC(1.5) film in 50 °C water.

programmed and released a temporary shape in extruded PDADMAC/PSS fibers by placing them in hot water.^[22] Figure 2 shows that the materials studied here display the features necessary for shape memory, that is, elastic behavior above T_g , which is necessary to recover the original (permanent) shape,^[23–25] and a glass transition around a convenient temperature that can serve to fix a temporary shape. The shape memory behavior of films made from PEC(1.5) and PEC(0) is illustrated in Figure 5a. Films having an original shape that was characterized by an original length $L_0 = 2$ cm were placed in 50 °C water, and thus heated to a temperature $T > T_g$. The heated hydrated samples were stretched to a length $L_1 = 4$ cm and cooled while the strain $S = (L_1 - L_0)/L_0$ remained fixed at 100% by placing them in cold water, that is, at $T < T_g$. When the stress was subsequently removed and the films were allowed to dry under ambient conditions, samples contracted slightly to the temporary shape (L_2). It was found that the PEC(1.5) film had an appreciable shape retention of $R_f = 80\%$ while PEC(0) had an R_f of 58%. One can speculate that this difference is mainly related to the different T_g s of the PECs and the fact that fixing was done at ambient temperature, where PEC(1.5) is already glassy, whereas PEC(0) still displays a significant chain mobility. When re-immersed in 50 °C water ($T > T_g$), both films contracted within 5 s. In both cases, the recovered length (L_3) was slightly longer than the original length, with PEC(1.5) showing a higher recovery rate ($R_r = 72 \pm 6\%$) than PEC(0) ($52 \pm 2\%$). We speculate that the incomplete recovery is due to some reorganization of the ionic cross-links during deformation. The data acquired in the 1st heating, 1st cooling, and 2nd heating cycle of a submersion DMA experiment (Figure S5, Supporting Information) can be nicely correlated to the shape memory behavior of the PEC films. When heating through T_g at about 30–40 °C, the PEC(1.5) film can be stretched, as the

film softens at this temperature. Upon cooling, the sample passes the glass transition at the same temperature, which leads to fixing by hardening of the film. The 2nd heating cycle confirms the ability to recover when E' is again decreased as the sample passes through T_g .

In Figure 5b, the deformation of a PEC(1.5) film into a spiral shape is shown as another example of the shape memory potential of the PEC membranes. After stretching in hot water, the film was rolled around a metal rod and dried at ambient to program a temporary spiral shape. This film returns autonomously to its original shape when immersed in 50 °C water within 5 s (a video of the Shape memory experiment is provided in Supporting Information) and displays a ten times faster recovery speed than when hydrated at room temperature (within a minute). In the first case (recovery in 50 °C water) the dry PEC film is rapidly heated above T_g of the water-swelled material (and the effect is largely diffusion limited), while in the latter case (recovery in room temperature water) the recovery occurs at a temperature where even after water take-up the glass transition has not fully been passed. The PEC films studied here are most useful when fully hydrated and the improved mechanical properties and higher cross-link density should render them useful for potential applications in medical devices where shape recovery is triggered by external humidity or body fluids,^[26] electrical devices such as flexible electrodes used in contact with aqueous electrolyte solutions, and also separating membranes for wastewater treatment.

4. Conclusions

The effect of added salt during the complex formation of PECs has been studied. The T_g of hydrated PEC was observed near room temperature and found to shift toward higher temperature when the [NaCl] during the mixing step was increased. At the same time, the materials became stronger and stiffer, while the elongation at break was reduced. Taken together, the data suggest that the polymer complex has either a more tightly bound network or a higher degree of chain entanglements. This is consistent with the expectation that at low [NaCl], the PEC is expected to rapidly form and stabilize by the formation of ion pairs without the possibility of much chain motion and therefore few entanglements. On the other hand at high [NaCl], the electrostatic charge screening imparted by the salt addition reduces the ionic interaction strength, enables extensive chain movements, and leads to an intricate mixing of the polymer chain and faster PEC aggregation. The PEC films also display interesting shape memory behavior, which certainly need to be further explored although a main limitation is the fact that the PEC needs to be in a moist environment. Further work with composite PEC could be interesting to further extend the T_g range as well as the shape memory behavior.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] A. S. Michaels, *Ind. Eng. Chem.* **1965**, 57, 32.
- [2] A. F. Thünemann, M. Müller, H. Dautzenberg, J. F. Joanny, H. Löwen, *Adv. Polym. Sci.* **2004**, 166, 113.
- [3] Q. Wang, J. B. Schlenoff, *Macromolecules* **2014**, 47, 3108.

- [4] E. Yildirim, Y. Zhang, J. L. Lutkenhaus, M. Sammakorpi, *ACS Macro Lett.* **2015**, 4, 1017.
- [5] Y. Zhang, P. Batys, J. T. O'Neal, M. Sammakorpi, J. L. Lutkenhaus, *ACS Cent. Sci.* **2018**, 4, 638.
- [6] H. H. Hariri, A. M. Lehaf, J. B. Schlenoff, *Macromolecules* **2012**, 45, 9364.
- [7] G. Petzold, S. Schwarz, *Adv. Polym. Sci.* **2014**, 256, 25.
- [8] Q. Zhao, Q. F. An, Y. Ji, J. Qian, C. Gao, *J. Membr. Sci.* **2011**, 379, 19.
- [9] H. H. Hariri, J. B. Schlenoff, *Macromolecules* **2010**, 43, 8656.
- [10] C. H. Porcel, J. B. Schlenoff, *Biomacromolecules* **2009**, 10, 2968.
- [11] S. L. Dakhara, C. C. Anajwala, *Syst. Rev. Pharm.* **2010**, 1, 121.
- [12] S. Lankalapalli, V. R. M. Kolapalli, *Indian J. Pharm. Sci.* **2009**, 71, 481.
- [13] R. F. Shamoun, H. H. Hariri, R. A. Ghostine, J. B. Schlenoff, *Macromolecules* **2012**, 45, 9759.
- [14] R. F. Shamoun, A. Reisch, J. B. Schlenoff, *Adv. Funct. Mater.* **2012**, 22, 1923.
- [15] A. B. Marciel, S. Srivastava, M. V. Tirrell, *Soft Matter* **2018**, 14, 2454.
- [16] Y. Hayashi, M. Ullner, P. Linse, *J. Phys. Chem. B* **2003**, 107, 8198.
- [17] J. Fu, R. L. Abbett, H. M. Fares, J. B. Schlenoff, *ACS Macro Lett.* **2017**, 6, 1114.
- [18] J. A. Jaber, J. B. Schlenoff, *J. Am. Chem. Soc.* **2006**, 128, 2940.
- [19] B. P. Das, M. Tsianou, *Adv. Colloid Interface Sci.* **2017**, 244, 71.
- [20] Y. Zhang, E. Yildirim, H. S. Antila, L. D. Valenzuela, M. Sammakorpi, J. L. Lutkenhaus, *Soft Matter* **2015**, 11, 7392.
- [21] K. Sadman, Q. Wang, Y. Chen, B. Keshavarz, Z. Jiang, K. R. Shull, *Macromolecules* **2017**, 50, 9417.
- [22] Q. Wang, J. B. Schlenoff, *RSC Adv.* **2014**, 4, 46675.
- [23] W. Wang, Y. Liu, J. Leng, *Coord. Chem. Rev.* **2016**, 320–321, 38.
- [24] A. Ledlein, S. Kelch, *Angew. Chem., Int. Ed.* **2002**, 41, 2034.
- [25] S. Erkeçoğlu, A. D. Sezer, S. Bucak, *InTechOpen*, <https://doi.org/10.5772/62199>.
- [26] R. Lange, D. A. Tirrel, *Nature* **2004**, 428, 487.

Q8