

Novel Solid-State Polymer Electrolyte Consisting of a Porous Layer-by-Layer Polyelectrolyte Thin Film and Oligoethylene Glycol

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A novel solid-state polymer electrolyte was constructed using layer-by-layer (LbL) polyelectrolyte assembly of linear poly(ethylenimine) (LPEI) and poly(acrylic acid) (PAA), combined with a plasticization step using oligoethylene glycol dicarboxylic acid (OEGDA). This composite film exhibits a relatively high ionic conductivity of 9.5×10^{-5} S/cm at 25 °C and 22% relative humidity. Detailed characterization of the composite was undertaken using grazing-angle Fourier transform infrared (GA-FTIR), atomic force microscopy (AFM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and impedance spectroscopy. After immersing the LPEI/PAA films into OEGDA aqueous solutions, the films exhibited a swelling behavior and increased surface roughness indicative of porosity induced by reorganization of ionic interactions between LPEI and PAA in acidic solution. This internal porous structure allows inclusion of OEGDA within the multilayer and increased ionic conductivity under ambient conditions due to the combined effects of plasticization of the LbL matrix by atmospheric water as well as the added mobility of ions in molten OEGDA within the composite.

Introduction

Solid-state ion conducting materials are in high demand for applications in power sources, sensors, and electro-optical devices. Compared to liquid electrolytes, solid-state polymer electrolytes have the primary advantage of improved mechanical properties as well as the possibility of enhanced chemical compatibility and easier processing conditions.¹ The main issue for the further development of these materials is increasing the ionic conductivity while retaining the beneficial mechanical and chemical stability.

Layer-by-layer (LbL) deposition of polyelectrolytes, pioneered by Decher et al.,² involves the alternating adsorption of oppositely charged species from solution. The LbL technique has been extended to many functional materials such as conducting polymers,³ electrochromics,^{4,5} light emitting materials,^{6,7} and nanoporous materials.⁸ The morphology and thickness of LbL films can be modulated by changing the deposition solution ionic strength and pH value.^{9–13} In addition, methods have been developed for patterning LBL films onto any substrate to

create highly complex systems.^{14–16} Recently, we demonstrated relatively high room temperature ionic conduction in layer-by-layer (LbL) polyelectrolyte multilayer films, which included linear poly(ethylenimine) (LPEI) as a polycation.¹⁷ LPEI has a hydrophilic backbone, which is amenable to the transport of ions in aqueous solutions. LbL films of LPEI with poly(acrylic acid) (PAA) (denoted as LPEI/PAA) demonstrated an ionic conductivity of more than 10^{-5} S/cm at nearly 100% relative humidity (RH).¹⁷ To achieve a solid-state polymer electrolyte using the LbL technique at room temperature and atmospheric relative humidity, oligoethylene glycol dicarboxylic acid (OEGDA) was introduced as a plasticizing element via absorption from aqueous solution; the resulting swollen films are denoted as (LPEI/PAA)OEGDA.¹⁸ The ionic conductivity of (LPEI/PAA)OEGDA was 9.5×10^{-5} S/cm at ambient temperature (25 °C) and humidity (22% RH), a level at which potential applications in solar energy conversion and batteries can be realized. It was found that a critical aspect of the enhanced ionic conductivity observed at room humidity is the transformation of the LPEI/PAA multilayer thin film upon exposure to a low pH OEGDA aqueous solution. This transition is similar to the microporous morphological transition reported by Mendelsohn et al.⁸ The resulting polymer multilayer is a nanoporous composite thin film containing pores filled with hydrated OEGDA molecules. Potential extension of these electrolyte systems to water-free electrolytes will be addressed in separate publications. In this paper, detailed characteristics of the hydrated (LPEI/PAA)OEGDA composite are investigated and the reason for its relatively high ionic

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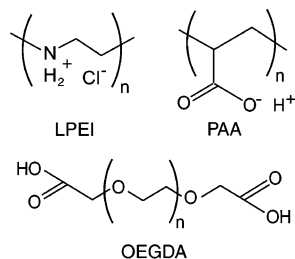


Figure 1. Molecular structures of LPEI, PAA, and OEGDA.

conductivity is discussed. Morphological effects due to the presence of OEGDA oligomer on the phase transition will also be described.

Experimental Section

Materials. The molecular structures of the materials used in this study are shown in Figure 1. LPEI ($M_w = 25\,000$, Polysciences, Inc.) was used as a polycation. PAA ($M_w = 90\,000$, Polysciences, Inc.) was used as a polyanion. The polyelectrolytes were dissolved in Milli-Q water and then pH adjusted with dilute HCl or NaOH solutions; the pHs of both the LPEI solution and the PAA solution were adjusted to 5.0 (hereafter denoted as LPEI_{5.0}/PAA_{5.0}). The concentration of the polyelectrolyte solutions was 0.020 M (polyelectrolyte concentrations are with respect to repeat unit). Indium tin oxide (ITO) substrates, used for conductivity measurements, were purchased from Donnelly Applied Films and patterned by DCI, Inc., to form multiple 3 mm ITO stripes. The ITO film resistance was measured to be 28 Ω/cm^2 after patterning. The ITO substrates were cleaned by ultrasonication in a series of solvents including detergent, deionized Milli-Q water, acetone, ethanol, and 1,1,1-trichloroethane for 30 min each. Immediately before use, the ITO glass substrates were plasma etched for 5 min in a Harrick PCD 32G plasma cleaner with oxygen bleed.

Film Assembly. Films were constructed using a modified Carl Zeiss DS50 programmable slide stainer. Substrates were exposed first to a polycation solution for 15 min, followed by 4 min of rinsing in three Milli-Q water baths. Then, they were exposed to a polyanion solution for 15 min and then rinsed; then, the cycle was repeated for 60 bilayers. After preparing the LBL films, substrates were dried with a N_2 stream and lightly cross-linked by heating at 120 $^\circ\text{C}$ for 30 min. OEGDA (Fluka) was introduced by immersing the film into a 20 wt % OEGDA aqueous solution at a pH of 2.0–3.0 for 20 min. LiI was added to the OEGDA solution as a mobile species in the composite films. After OEGDA treatment, films were blown dry with a N_2 stream and kept at room temperature overnight to dry. Thermally evaporated Au was used as a counter electrode. Free-standing (LPEI/PAA)₉₀ samples for thermal analysis were assembled on polystyrene substrates. After being air-dried for 24 h, the films were peeled away from their substrates and vacuum-dried for 1 h. OEGDA treatment of the free-standing films was done at pH 3.0 for 20 min, and then, they were isolated with a Buchner funnel. The treated samples were vacuum-dried for 1 h and then stored in a desiccator overnight. Prior to differential scanning calorimetry (DSC) testing, the samples were exposed to ambient conditions for 30 min.

Film Characterization. Thickness measurements and surface roughness measurements were performed with a Tencor P10 profilometer using a 2 μm stylus with 6 mg stylus force and a Digital Instruments Dimension 3000 atomic force microscope, respectively. Grazing-angle Fourier transform infrared (GA-FTIR) was used to characterize the polymer electrolyte film composition.¹⁶ GA-FTIR spectra were obtained in single reflection mode using a Digilab Fourier transform infrared spectrometer (Biorad, Cambridge, MA). The p-polarized light was incident at 80 $^\circ$ relative to the surface normal of the substrate, and a mercury–cadmium–telluride (MCT) detector was used to detect the reflected light. A spectrum of a self-assembled monolayer (SAM) of *n*-hexadecanethiolate-*d*₃₃ on Au was taken as a reference. Differential scanning calorimetry (DSC) was done using a TA Instruments Q1000 differential scanning calorimeter with a scan range of –90 to 130 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$. Electron

Table 1. Room Temperature (25 $^\circ\text{C}$) Ionic Conductivity of LPEI/PAA Composites

composite	relative humidity (%)	σ (S/cm)
(LPEI _{5.0} /PAA _{5.0}) ₃₀	0	8.5×10^{-12}
	17	2.8×10^{-11} ^a
	52	6.4×10^{-9} ^a
	100	1.0×10^{-5} ^a
(LPEI _{5.0} /PAA _{5.0}) ₃₀ OEGDA _{3.0}	0	7.2×10^{-11}
	22	5.0×10^{-6} ^b
	50	1.0×10^{-5} ^b
	22	9.5×10^{-5}

^a Reference 17. ^b Reference 18.

microscopy studies were accomplished using a JEOL 6320FV scanning electron microscope.

Ionic Conductivity Measurements. The ionic conductivities of the LPEI_{5.0}/PAA_{5.0} polyelectrolyte film and composite films treated in OEGDA at pH 3, denoted (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0}, were measured with a simple sandwich type cell consisting of ITO, the (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} composite film, and an Au electrode. Impedance spectroscopy was performed using a Solartron 1260 scanning from 10 MHz to 1 Hz. Due to noise at low frequencies and high impedances, the lowest frequency included in the analysis was variable and typically > 1 Hz. The signal amplitude was 100 mV with no bias; at this voltage, noise could be reduced. The results at an amplitude of 100 mV were compared with the 10 mV measurements to ensure there were no artifacts from increasing amplitude. The absence of any cell shorting in the circuit, even for rough samples, further substantiated that the evaporation-deposited Au did not penetrate the LBL film.

Results and Discussion

The assembly behavior of the LPEI_{5.0}/PAA_{5.0} LbL thin films is well described in our previous paper.¹⁷ In LPEI_{5.0}/PAA_{5.0} films, PAA ionization increases as LPEI ionization decreases with increasing pH. Morphology also changes with increased small ion screening of polyelectrolyte charge; weakly ionized polyions form thick, loopy conformations on the surface. At low pHs, LPEI chains are fully ionized and only PAA deposits thickly. The thickness of the LPEI/PAA system steadily increases up to a pH of 4 or 5, where both LPEI ($\text{p}K_a = 4\text{--}5$)¹⁷ and PAA ($\text{p}K_a = 4\text{--}5.5$)^{8,13} are partially ionized and thick, loopy layers of both polymers are formed upon adsorption. Thickness again decreases at higher pHs (over 6) as PAA gains further ionization and only LPEI deposits thickly. The ionic conductivity of typical electrostatic LBL films can be described as $nq\mu$, where n is the number of mobile ions, q is the ion charge, and μ is the ion mobility. To achieve a more conductive polymer electrolyte, a thick, loopy multilayer morphology was used in addition to taking advantage of the highly hydrophilic nature of LPEI and PAA. Therefore, the pH values of the LPEI and PAA solutions were maintained at 5.0 to produce thick, loopy polyelectrolyte films, which can bear a number of mobile species. The average thickness of a 60 bilayer LPEI_{5.0}/PAA_{5.0} film was 2.0 μm (average of ~ 33 nm per layer) with a root mean square (rms) surface roughness of 9.95 nm upon completion of LbL assembly and subsequent heat treatment. The thickness of a dried 60 bilayer (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} composite film increased from 2.0 μm to 5.5 μm after 20 min of soaking in an OEGDA aqueous solution at pH 3.0. Ionic conductivity also reached its maximum value after 20 min of immersion in the OEGDA solution.

The ionic conductivities of a variety of LPEI_{5.0}/PAA_{5.0} composites with and without OEGDA treatment and their dependence on relative humidity are shown in Table 1. Even though the LPEI_{5.0}/PAA_{5.0} film exhibited thicker and

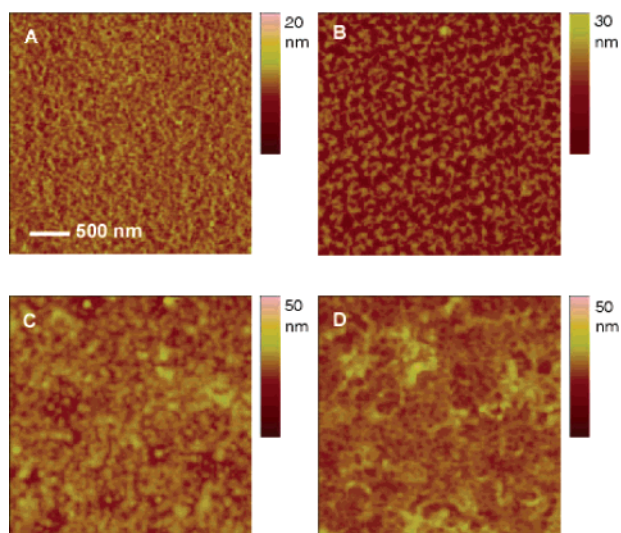


Figure 2. AFM surface profiles of (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} at immersion times of (a) 0, (b) 5, (c) 10, and (d) 20 min.

loopier morphology compared to films constructed at pH levels where the polyelectrolyte chains are fully charged, the ionic conductivity of LPEI_{5.0}/PAA_{5.0} is only high at high RH, or when fully saturated with water. However, as we have observed in previous studies on electrolyte layers for photovoltaic cells, upon the introduction of OEGDA into the LPEI_{5.0}/PAA_{5.0} polyelectrolyte film, the ionic conductivity of the composite was greatly increased at a lower RH.

To further understand this phenomenon, we have investigated this thin film system using grazing-angle FTIR, DSC, atomic force microscopy (AFM), scanning electron microscopy (SEM), and impedance spectroscopy. These investigations suggest that treatment in an aqueous OEGDA solution at a pH of 2–3 induces a porous transition in the weak polyelectrolyte system, facilitating the introduction of the oligomer molecules within the film. This study marks the first report of a porous polyelectrolyte film as a solid-state electrolyte with the unique incorporation of a third-party oligomer to increase chain mobility and ionic conductivity.

Tapping mode AFM was used to observe the surface topography of the films as a function of immersion time and to investigate the nature of the morphology change in the construction of the (LPEI_{5.0}/PAA_{5.0})/OEGDA composite. Figure 2 shows the AFM surface profiles of a (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} composite film at various immersion times. The immersion times in the OEGDA solution were 0 (i.e., without OEGDA), 5, 10, and 20 min.

Prior to soaking the LBL film in the OEGDA solution (0 min), the surface of the film was relatively smooth, with an rms roughness of 9.95 nm. Once immersed into the OEGDA (pH 3.0) solution, the LPEI_{5.0}/PAA_{5.0} film was swollen due to the absorption of water and OEGDA. After 5 min, the surface became rough and appeared porous; the rms roughness increased to 14.45 nm. After 10 min, the surface morphology became rougher, and minimal changes were observed in the surface topography between 10 and 20 min.

Mendelsohn et al. have reported that microporous polymer thin films can be created from polyelectrolyte multilayer films of poly(allylamine hydrochloride) (PAH) and PAA, (PAH_{7.5}/PAA_{3.5}), by a simple aqueous treatment.⁸ They demonstrated that a pH-induced ionic-bond-breaking and reformation mechanism in the PAH/PAA system enabled a morphological reorganization introducing

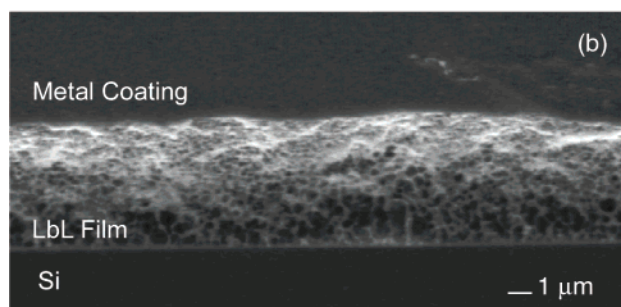
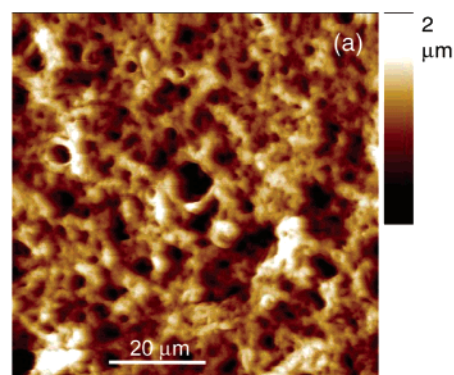


Figure 3. (a) AFM micrograph and (b) cross-sectional SEM micrograph of (LPEI_{5.0}/PAA_{5.0})₂₅ treated in water at pH 2.0.

porosity into the film. As-assembled PAH/PAA films exhibited a nonporous film structure. Once the PAH/PAA films were treated with pH 2.5 aqueous solution, they exhibited microporous morphology. Rubner and co-workers have also created reversible nanoporous films from phase separated PAH/PAA multilayer films treated at pH 1.8.²¹ The pH behavior of the LPEI_{5.0}/PAA_{5.0} system is consistent with that observed for PAH_{7.5}/PAA_{3.5}. In our case, the LPEI_{5.0}/PAA_{5.0} film was immersed into an aqueous OEGDA solution at a pH range of 2.0–3.0. This pH range was chosen on the basis of the observation of maximal ionic conductivity under these conditions.¹⁸ The multilayer system, assembled at pH 5.0 for both LPEI and PAA, was constructed under conditions of partial ionization for both polyions; the transition of PAA acid groups and subsequent bond breaking and reformation.

To compare the structural differences between LPEI/PAA films treated in OEGDA and those treated in water, as well as to confirm a porous transition in this film system, we treated LPEI_{5.0}/PAA_{5.0} films in pH 2.0 aqueous solutions. Figure 3a shows an AFM image of the top surface of a (LPEI_{5.0}/PAA_{5.0})₂₅ film that was treated for <1 min in a pH 2.0 aqueous solution. It reveals a microporous structure, with pore sizes ranging from submicron to tens of microns. This microporous structure is a result of the protonation of the acid groups of PAA that lead to rearrangement of the ionic bonds between LPEI and PAA.⁸ Figure 3b shows a cross-sectional SEM micrograph that demonstrates this porous structure is found through the entire thickness of the film. The film is porous to the extent that a significant amount of the surface metal coating necessary to image the film in SEM has penetrated into the bulk of the film. This porous transition is seen as one

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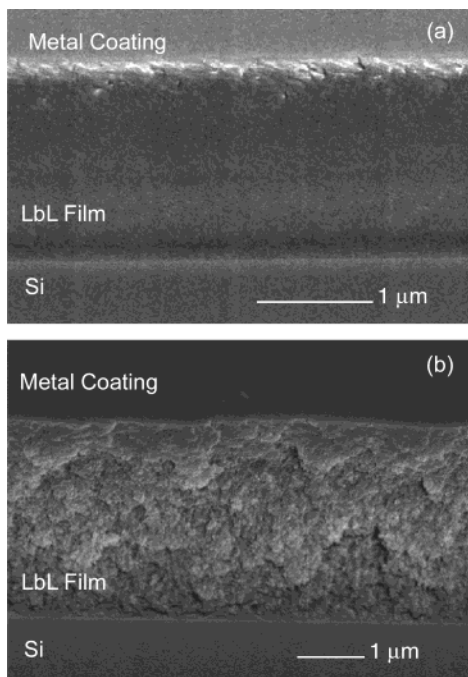


Figure 4. Cross-sectional SEM micrographs of (LPEI_{5.0}/PAA_{5.0})₂₅ film (a) before and (b) after OEGDA_{3.0} treatment.

of the necessary steps for maximum inclusion of the OEGDA molecules into the composite film.

Examination of the OEGDA treated samples using cross-sectional SEM did not indicate the presence of a completely open pore network, as was observed in low pH water treatment. The main structural difference between the films treated in OEGDA is the fact that the OEGDA remains within the composite film after drying and acts to increase chain mobility and ionic conductivity. Furthermore, the OEGDA solution is responsible for three important steps in the electrolyte construction: (1) the porous transition due to the low pH of the OEGDA solution, (2) the uptake of OEGDA by the polyelectrolyte matrix, and (3) the uptake of the mobile ionic species that are added to the OEGDA solution. This postprocessing routine for forming polymer electrolytes has broad flexibility for the introduction of other interesting guest species within a pH sensitive polyelectrolyte matrix.

Figure 4 presents electron micrographs of a (LPEI_{5.0}/PAA_{5.0})₂₅ film before and after OEGDA treatment at pH 3.0. Before treatment in OEGDA (Figure 4a), the polyelectrolyte film is dense with little discernible internal structure. There is a clear transition observed after OEGDA treatment, as shown in Figure 4b. The film thickness is increased 2 to 3-fold, and a more open layer structure is shown due to the treatment at pH 3.0. Similar structural changes were observed with OEGDA treatment at pH 2.0.

To further investigate the nature of the morphology change in Figure 4b, GA-FTIR was used as a tool to confirm the intercalation of OEGDA into the completed LbL thin film. Figure 5 shows GA-FTIR spectra of a (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} film. The GA-FTIR spectra illustrate the existence of OEGDA within the LBL film after immersion in the OEGDA solution, as indicated by a large peak at around 1145 cm⁻¹ for the C–O–C stretching mode of the oligoethylene glycol chain. The peak intensity increases with immersion time, corresponding to an increase in the amount of OEGDA introduced into the LPEI/PAA film with exposure time to the OEGDA solution at pH 3. Moreover, the peaks at around 1680 cm⁻¹ are character-

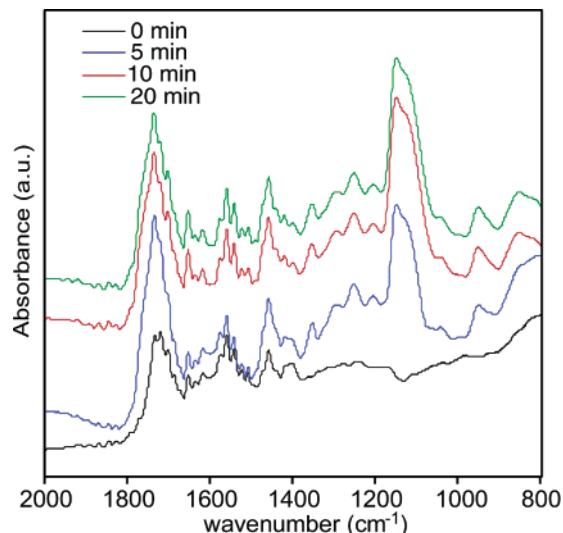


Figure 5. GA-FTIR spectra of the (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} composite with various immersion times into OEGDA solution at pH 3.0.

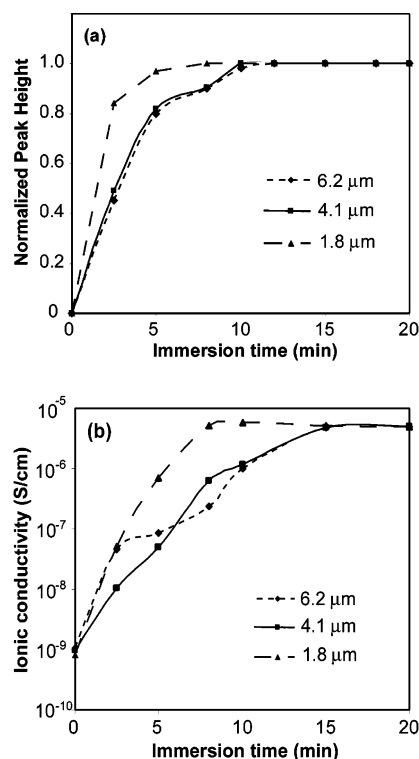


Figure 6. (a) Immersion time dependence of the GA-FTIR peak intensities of the C–O–C stretching mode of (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} film with different film thicknesses. (b) Immersion time dependence of the ionic conductivity of (LPEI_{5.0}/PAA_{5.0})/OEGDA_{3.0} film with different film thicknesses. The lines were added only to aid the eye.

istic of the amide group, CONH, and exist in all spectra. These peaks indicate the formation of covalent bonds between the secondary amine group of the LPEI and the acid group of the PAA within the film due to the thermal treatment at 120 °C used to dry the films prior to immersion in the OEGDA solution. These covalent bonds help stabilize the LPEI_{5.0}/PAA_{5.0} film and maintain its mechanical integrity, under acidic conditions and OEGDA inclusion. Figure 6a shows the dependence of the C–O–C stretching mode peak intensity on immersion time for LPEI_{5.0}/PAA_{5.0} films of different thicknesses. The peak intensity is normalized with the 20 min sample. All

samples show saturation by 10 min, although the thinner film (1.8 μm) clearly saturates faster, at about 3–5 min. The saturation behavior and the time/thickness dependence suggest a diffusion limited process for the absorption of OEGDA throughout the film.

Figure 6b shows the dependence of ionic conductivity on immersion time for the LPEI_{5.0}/PAA_{5.0} samples with different thicknesses. All samples in Figure 6b also exhibit saturation at around 10 min, again with the 1.8 μm sample saturating slightly faster. In addition, an elemental analysis of the ionically conductive samples proves the existence of iodide after doping with LiI (C, 26.12; H, 4.03; N, 3.08; I, 38.11), indicating penetration of the conducting ionic species as well as the OEGDA from solution into the film. The gradual rearrangement to a more open film structure correlates well with the observation of increased ionic conductivity, thus suggesting the importance of the role of porosity in the increase of OEGDA uptake by the LbL film. The ionic conductivity maximum value is probably indicative of a film structure such that percolation of the aqueous OEGDA ionic solution is achieved. Water absorption from the OEGDA solution was also confirmed by FTIR and DSC measurements. We have reported previously that water acted as an excellent plasticizer for LBL polyelectrolyte multilayer film.¹⁷ We contend that the OEGDA acts partially as a humectant, increasing the amount of water in the composite at atmospheric humidity, leading to increased flexibility of the oligomer segments within the LbL composite, accompanied by a large increase in ionic conductivity.

Multilayer composites were also characterized by DSC, with and without OEGDA treatment at pH 3.0. The first scans of both the treated and untreated composites (not shown) exhibit a large endothermic peak near 95 °C attributed to the presence of water within the composites under ambient conditions. Figure 7 shows the second scan of both the LPEI_{5.0}/PAA_{5.0} and (LPEI_{5.0}/PAA_{5.0})OEGDA_{3.0} composites. While the untreated composite shows few interesting features in the DSC, the composite treated with OEGDA clearly exhibited a glass transition, crystallization peak, and melting peak of -54.5 , -26.0 , and 13.5 °C, respectively. These features can be attributed to the OEGDA present in the film, since they did not appear in the untreated assembly. At room temperature, OEGDA, which is essentially small oligomer chains of poly(ethylene oxide), is in a molten state within the assembly. This molten OEGDA enhances the ionic conductivity because of its increased flexibility and the capability of the poly(ethylene oxide) segments to move ions through the LbL matrix. The LbL matrix functions to give this third-party oligomeric species an ionically conductive environment with suitable thin film mechanical properties.

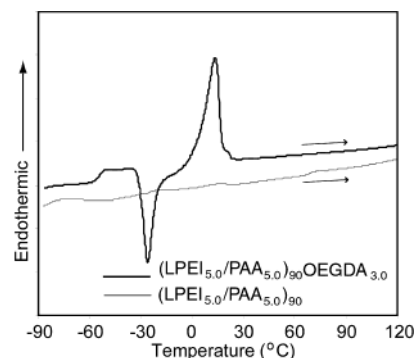


Figure 7. Differential scanning calorimetry plots of (LPEI_{5.0}/PAA_{5.0})₉₀ (lighter plot) and (LPEI_{5.0}/PAA_{5.0})₉₀OEGDA_{3.0} (darker plot) multilayer composites. The second DSC scan of each sample is presented. The OEGDA treated composite exhibits features at -54.5 , -26.0 , and 13.5 °C corresponding to the glass transition, crystallization peak, and melting peak, respectively, of the OEGDA oligomer within the LbL multilayer.

Conclusion

A novel solid-state polymer electrolyte, (LPEI_{5.0}/PAA_{5.0})/OEGDA, was reported. Using various analysis techniques, the LPEI_{5.0}/PAA_{5.0} polyelectrolyte multilayer film was shown to have a porous structure after immersion into OEGDA solution at pH 3.0. The GA-FTIR and DSC studies showed the existence of molten OEGDA and water inside of the LPEI_{5.0}/PAA_{5.0} film. The treatment in low pH aqueous solutions with or without OEGDA shows a porosity transition that has previously been demonstrated for hydrophobic polyelectrolytes, whereas in this case we have shown it occurs for a polyelectrolyte pair that includes the hydrophilic polymer LPEI, which has shown promising ionic conductivity properties in previous studies in our laboratory. The high ionic conductivity of (LPEI_{5.0}/PAA_{5.0})/OEGDA was shown to result from the combination of plasticization by water and flexible OEGDA oligomer segments incorporated in the film through this porous transition. Ongoing work in our laboratory on this (LPEI_{5.0}/PAA_{5.0})/OEGDA composite film, and films made from other combinations of LbL films and plasticizers, will be applied to many important current research areas including batteries, sensors, and electrochromics.

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