Co-Poly(ionic liquid) Films via Anion Exchange for the Continuous Tunability of Ion Transport and Wettability

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ABSTRACT: This manuscript details a novel and simple approach to achieve surface-tethered co-poly(ionic liquid) (coPIL) films through the exchange of the resident anion of a poly(ionic liquid) (PIL) film with two or more anions. Initially, surface-tethered PIL films were prepared by the surface-initiated ring-opening metathesis polymerization of the ionic liquid monomer 3-[(bicyclo[2.2.1]hept-5-en-2-yl)methyl]-1,2-dimethylimidazol-3-ium hexafluorophosphate ([N1-dMIm][PF6]) whose PF6− anion was easily interchanged with aqueous solutions containing a binary mixture of the PF6− anion, along with perchlorate (ClO4−) or bis-(fluorosulfonyl)imide (FSI−) anions. The binary mole fraction of each anion in the film was determined from the infrared spectra of the coPIL films. The thermodynamically driven anion selectivity for exchange from the liquid phase into the coPIL films was determined to follow the order ClO4− < PF6− < FSI−. The aqueous wettability of p[N1-dMIm] coPIL films containing both the PF6− and ClO4− anions (p[N1-dMIm][PF6][ClO4]) was quantified by contact angle goniometry with the observation that the surface showed an enrichment in the ClO4− anion compared to the average binary anion mole fraction of ClO4− in the film ($\theta_{ClO4}$). The rate of ion transport through the p[N1-dMIm][PF6][ClO4] coPIL films, quantified by electrochemical impedance spectroscopy, linearly depends on the binary anion mole fraction of ClO4− in solution ($\chi_{ClO4}$), enabling continuous tunability by over three orders of magnitude for ion conductivity in the coPIL films.

1. INTRODUCTION

Poly(ionic liquids) (PILs) comprise a polymeric backbone with an IL species in each of the repeat units, enabling the tuning of the material properties in discrete quantities by anion or cation exchange.1–5 PILs have been utilized for multiple applications including energy harvesting and storage, sensing, drug and gene delivery, separations, catalysis, polymer electrolytes, sorbents, dispersants, smart materials, and responsive materials.1,2,5–9 A co-poly(ionic liquid) (coPIL) is a polymer that is composed of repeating units with differing molecular structure where one or more repeats contain an IL species. A coPIL affords additional degrees of freedom for the modulation of material properties due to the combination of multiple ionic and/or nonionic moieties in the polymer to yield random and block coPILs.3,6,11–15 Copolymerization of an IL monomer with a nonionic monomer results in coPILs with a dilute charge character through the reduced concentration of ionic moieties along the polymer backbone.3,6,11–15 CoPILs with opposite charges on the backbone17,18 or those with a uniform polymer backbone and differing counterions,19–21 obtained by the copolymerization of an anionic monomer with a cationic monomer or by the copolymerization of monomers having the same polymerizable moieties but differing counterions, respectively, can lead to coPILs with enhanced ionic conductivities.3,5 In all the previously mentioned approaches, the synthetic burdens intrinsic in the formation of different monomer units, as well as the inherent challenges in determining the optimal polymerization conditions for coPIL formation, must be overcome.

In this article, we report a straightforward approach to achieve surface-tethered coPIL films via anion exchange. Initially, surface-immobilized PIL films on planar gold substrates were prepared by the surface-initiated ring-opening metathesis polymerization (ROMP) of 3-[(bicyclo[2.2.1]hept-5-en-2-yl)methyl]-1,2-dimethylimidazol-3-ium hexafluorophosphate ([N1-dMIm][PF6]), whose PF6− anion can be easily exchanged to alter film properties in discrete quantities.2 In our approach, surface-immobilized p[N1-dMIm][PF6] films are immersed in aqueous solutions containing a binary mixture of anions to exchange with the resident PF6− anion to achieve random surface-tethered coPILs via a novel and rapid route. This route to coPILs is advantageous as compared to traditional copolymerization strategies in that it only requires...
the synthesis of one monomeric unit to achieve random coPIL films. The composition of the random coPIL films can easily be controlled in a continuous manner by varying the binary mole fraction of each anion in solution prior to anion exchange. The formation of random coPILs via anion exchange is a reversible process allowing for the regeneration of the PIL homopolymer by anion exchange. By simply exposing the coPIL film to a solution containing the anion of the homopolymer, we are able to reverse the formation of the coPIL. In this way, the intrinsic advantages of PILs are retained and enhanced by the ability to easily prepare coPIL films from the PIL homopolymers. Further, use of surface-tethered films facilitates an easy separation of the coPIL films from the anion exchange solution while enabling large anion-induced changes in film and surface properties.

Based on our recent work, p[N1-dMIm] films containing the PF$_6^-$ and ClO$_4^-$ anions exhibit dramatically different film properties, which motivated our choice of these anions in this work. In particular, p[N1-dMIm][PF6] films exhibit an advancing water contact angle of 61 ± 2° and a film conductivity of 0.008 ± 0.001 μS/cm, whereas p[N1-dMIm][ClO4] films exhibit an advancing water contact angle of 35 ± 3° and a film conductivity of 13.6 ± 0.8 μS/cm. Therefore, a p[N1-dMIm][PF6][ClO4] film can provide a versatile test bed to elucidate the effects of anion composition on both wettability and ionic conduction. Our recent work enabled us to discretely vary film properties based on the selection of anion. Here, the focus is on coPIL films by using mixtures of two anions for the continuous tunability of film properties between the extremes of the two homopolymers. Achieving continuous tunability over three orders of magnitude for a thin film for the first time demonstrates a significant advance in control over our prior discrete approach based on single anion exchange.

2. RESULTS AND DISCUSSION

2.1. p[N1-dMIm] CoPIL Film. Polymerization of the IL monomer 3-{[(bicyclo[2.2.1]hept-5-en-2-yl)methyl]-1,2-dimethylimidazol-3-ium hexafluorophosphate ([N1-dMIm][PF6]) at a concentration of 0.1 M in 1,2-dichloroethane (DCE) for 15 min leads to a surface-tethered p[N1-dMIm][PF6] film with a thickness of 650 ± 30 nm. The successful anion exchange of the resident PF$_6^-$ anion by exposure to an aqueous solution containing a mixture of the potassium salts of PF$_6^-$ and ClO$_4^-$, to form a p[N1-dMIm][PF6][ClO4] coPIL film, is evidenced by the IR spectra in Figure 1. The IR spectrum for the p[N1-dMIm][PF6] film displays both the P–F stretching peak at 855 cm$^{-1}$ and the Cl–O stretching peak at 1106 cm$^{-1}$. The IR spectrum for the p[N1-dMIm][PF6] film in Figure 1. The data lie below the x = y line. For example, exchange of p[N1-dMIm][PF6] films in a x$_{ClO4^-}$ = 0.5 aqueous binary anion solution results in a p[N1-dMIm][PF6][ClO4] coPIL film with x$_{ClO4^-}$ = 0.13 ± 0.02. The results for the anion exchange from p[N1-dMIm][PF6] films are not statistically different from those for the anion exchange from p[N1-dMIm][ClO4] films, indicating that the conditions for anion exchange were sufficient to achieve equilibrium (see the Supporting Information).

In order to express the partitioning preference of the PF$_6^-$ and ClO$_4^-$ anions from the liquid phase into the solid phase, an equilibrium constant was derived using the chemical potential of each anion in the liquid and solid phase. For the exchange reaction involving ions a and b

\[ x_a + y_a \rightleftharpoons x_b + y_b \]

the chemical potentials of the species in liquid (μ$_{i,l}$) and solid (μ$_{i,s}$) can be described by

\[ \mu_i^l = \mu_i^{a,l} + RT \ln(x_i) \]

\[ \mu_i^s = \mu_i^{a,s} + RT \ln(y_i) \]

to give

\[ \alpha = K_{eq} = \frac{x_y y_b}{y_x x_b} = e^{-\Delta\mu_i^s/RT} \]

where \( \Delta\mu_i^s = \Delta\mu_i^a + \Delta\mu_i^b \). Rearranging eq 4, we obtain

\[ y_a = x_a (1 - x_b) \alpha \]

where \( \alpha \) can be thought of as the selectivity of the anion b for the solid phase compared to that for anion a. Equation 5 was used to fit the data shown in Figure 2a yielding \( \alpha = 7 \pm 1 \) and the data shown in Figure 2b yielding \( \alpha = 6 \pm 1 \). These values of \( \alpha \) demonstrate a selectivity for the film for PF$_6^-$ as compared to ClO$_4^-$, as well as an attainment of equilibrium due to the same value of \( \alpha \) determined using the different PIL homopolymers.

To further investigate the effect of the anion on coPIL formation, we studied coPIL films with PF$_6^-$ and FSI$^-$ anions. The binary mole fractions of (FSI$^-$ and PF$_6^-$) in the p[N1-dMIm][PF6][FSI] coPIL film were determined as described in...
but a strong partitioning toward the curve is a
coPIL
in addition to the aqueous solubility of PILs, the
dMIm][PF6][ClO4]
dMIm][PF6][FSI] coPIL
exhibit high selectivity for FSI
line. For example, anion exchange of p[N1-dMIm][PF6]
PF6
surface wettability of the p[N 1-dMIm][PF6][ClO4] coPIL
fraction of FSI
contact angle (θ) as a function of the binary anion mole fraction of ClO4
Figure 3. The p[N1-dMIm] films

each value was determined by obtaining the average and standard
deviation of at least three independently prepared films. Solid curves are fits of the data with eq 5. The dashed line is the x = y line.

Figure 3. Binary anion mole fraction of FSI− in the film (yFSI−) as a function of the binary anion mole fraction of FSI− in solution (xFSI−) for p[N1-dMIm][PF6][FSI] coPIL films prepared by anion exchange. Each value was determined by obtaining the average and standard deviation of at least three independently prepared films. The solid curve is a fit of the data with eq 5.

Figure 2. Binary anion mole fraction of ClO4− in the film (yClO4−) as a function of the binary anion mole fraction of ClO4− in solution (xClO4−) for p[N1-dMIm][PF6][ClO4] coPIL films. (a) p[N1-dMIm][PF6][ClO4] coPIL films prepared from p[N1-dMIm][PF6] films. (b) p[N1-dMIm][PF6][ClO4] coPIL films prepared from p[N1-dMIm][ClO4] films. Each value was determined by obtaining the average and standard deviation of at least three independently prepared films. Solid curves are fits of the data with eq 5. The dashed line is the x = y line.

The PF6− anion has a strong partitioning toward the aqueous environment for the p[N1-dMIm][PF6][FSI] films but a strong partitioning toward the film for the p[N1-dMIm][PF6][ClO4] films. This leads to a ranking of the relative free energy stabilization in the solid phase as ClO4− > PF6− > FSI−.

2.2. Contact Angle. Considering the fact that the anion affects the surface wettability of surface-tethered ILs with water,25 in addition to the aqueous solubility of PILs,26 the surface wettability of the p[N1-dMIm][PF6][ClO4] coPIL films was assessed by contact angle goniometry as shown in Figure 4. We have previously shown that the advancing water contact angle (θa) of a p[N1-dMIm][PF6] film (61 ± 2°) is greater than the θa of a p[N1-dMIm][ClO4] film (35 ± 3°), which we attribute to the stronger interaction of water with ClO4−, as compared to PF6−, to stabilize the water/polymer interface. For surfaces with microscopic heterogeneity, the Cassie equation (eq 6) provides a prediction of the measured contact angle (θ) from those of the homogenous surfaces (θ)23.

\[
\cos \theta = \sum f_i \cos \theta_i
\]

where fi is the fraction of the surface covered by component i. In Figure 4, the dashed line represents the Cassie relationship for a p[N1-dMIm][PF6][ClO4] coPIL film. The θa for the p[N1-dMIm][PF6][ClO4] film, however, lies below the Cassie line, indicating an enrichment of the surface in the ClO4− anion, compared to the average binary anion mole fraction of ClO4− in the film (yClO4−). For example, yClO4− = 0.5 results in a θa that is statistically the same as that for a pure ClO4− film. Given that the interface is thermodynamically distinct from bulk, the minimization of interfacial free energy between the polymer film and the aqueous phase results in a surface enrichment of the ClO4− anion.
2.3. \(\text{p[N}_{1}\text{-dMIm}][\text{PF}_6][\text{ClO}_4]\) CoPIL Film Ion Transport.

We have previously shown that the film anion governs the ion transport resistance of \(\text{p[N}_{1}\text{-dMIm}]\) films with no impact from the electrolyte cation.\(^2\) The ion transport resistance of the \(\text{p[N}_{1}\text{-dMIm}]\) films was shown to follow the order \(\text{ClO}_4^- \ll \text{FSI}^- \ll \text{NTf}_2^- < \text{PF}_6^-\).\(^2\) \(\text{p[N}_{1}\text{-dMIm}][\text{PF}_6][\text{ClO}_4]\) ion transport was investigated by utilizing electrochemical impedance spectroscopy (EIS). In EIS, a low amplitude sinusoidal potential (\(E_{ac}\)) perturbation of varying frequency is applied around the equilibrium potential of the working electrode.\(^2\)\(^4\) The \(E_{ac}\) drives the motion of ions (ionic conductivity) through the film as mediated by the exchange of ions between the liquid and solid phases. EIS was conducted in the presence of an aqueous electrolyte solution consisting of a mixture of the potassium salts of PF\(_6^-\) and ClO\(_4^-\) anions at a total anion concentration of 0.1 M. The \(x_{\text{ClO}_4^-}\) for the electrolyte solution was equal to the \(x_{\text{ClO}_4^-}\) for the binary anion exchange solution utilized in the formation of the coPIL films to avoid net ion exchange during collection of the EIS spectra. Figure 5 shows representative Bode plots of EIS spectra for \(\text{p[N}_{1}\text{-dMIm}][\text{PF}_6][\text{ClO}_4]\) films with varying binary film anion mole fractions of ClO\(_4^-\) (\(\gamma_{\text{ClO}_4^-}\)). A 0.1 M aqueous electrolyte solution prepared using KPF\(_6\) and KClO\(_4\) salts and consisting of the same \(x_{\text{ClO}_4^-}\) used to prepare the coPIL film, was used to collect the spectra. The fits of the spectra to the equivalent circuit in Scheme 1 are displayed as solid curves.

![Electrochemical impedance spectra in the Bode format for p[N\(_{1}\) dMIm] [PF\(_6\)] [ClO\(_4\)] \(\gamma_{\text{ClO}_4^-} = 0\), p[N\(_{1}\) dMIm] [ClO\(_4\)] \(\gamma_{\text{ClO}_4^-} = 1\), and p[N\(_{1}\) dMIm] [PF\(_6\)] [ClO\(_4\)] films with varying binary film anion mole fractions of ClO\(_4^-\) \(\gamma_{\text{ClO}_4^-}\). A 0.1 M aqueous electrolyte solution prepared using KPF\(_6\) and KClO\(_4\) salts and consisting of the same \(x_{\text{ClO}_4^-}\) used to prepare the coPIL film, was used to collect the spectra. The fits of the spectra to the equivalent circuit in Scheme 1 are displayed as solid curves.

**Figure 5.** Electrochemical impedance spectra in the Bode format for \(\text{p[N}_{1}\text{-dMIm}][\text{PF}_6][\text{ClO}_4]\) \(\gamma_{\text{ClO}_4^-} = 0\), \(\gamma_{\text{ClO}_4^-} = 1\), and \(\gamma_{\text{ClO}_4^-} = 0\) and \(\gamma_{\text{ClO}_4^-} = 1\) films. This difference in resistance is attributed to the difference in the interaction of the PF\(_6^-\) and ClO\(_4^-\) anions with the aqueous environment and the film. Molecular dynamics simulations of a 1-butyl-3-methylimidazolium hexafluorophosphate ([C\(_4\)-MIm][PF\(_6\)]) IL show that the butyl group reorients in the presence of water to preferentially interact with the IL bulk, and because of a weak interaction between the F atoms of the PF\(_6^-\) anion and H atoms of water, no appreciable miscibility with water was observed.\(^2\)\(^5\) However, ClO\(_4^-\) anions have a negligible impact on the hydrogen bond (H-bond) network in bulk water because of the transitional character of the water–perchlorate H-bond, which mirrors the dynamic, labile H-bond networks observed for liquid water, resulting in a strong

**Table 1. Effect of the Binary Anion Mole Fraction of ClO\(_4^-\) in the p[N\(_{1}\) dMIm] [PF\(_6\)] [ClO\(_4\)] coPIL Films on the Film Resistance (\(R_f\)), Conductivity (\(\kappa_f\)), and Capacitance (\(C_f\)) Values**

| \(\gamma_{\text{ClO}_4^-}\) | \(R_f\) (\(\Omega\cdot\text{cm}^2\)) | \(\kappa_f\) (\(\mu\text{S/cm}\)) | \(C_f\) (\(\mu\text{F/cm}^2\)) |
|-----------------|-------------------|-----------------|-----------------|
| 0               | 5.89 ± 0.07       | 0.011 ± 0.001   | 0.17 ± 0.01     |
| 0.13 ± 0.02     | 3.43 ± 0.04       | 0.019 ± 0.001   | 0.18 ± 0.01     |
| 0.54 ± 0.01     | 0.43 ± 0.01       | 0.193 ± 0.010   | 0.23 ± 0.04     |
| 0.72 ± 0.05     | 0.19 ± 0.01       | 0.335 ± 0.017   | 0.23 ± 0.06     |
| 1\(^a\)         | \((4.34 ± 0.04) \times 10^{-3}\) | \(≥ 13.6 ± 0.8\) | \(≥ 13.6 ± 0.8\) |

\(^a\)The maximum film resistance for the \(\text{p[N}_{1}\text{-dMIm}][\text{ClO}_4]\) film was estimated as being no larger than the \(R_f\) (4.34 ± 0.04 \(\Omega\cdot\text{cm}^2\)) for EIS spectra of a \(\text{p[N}_{1}\text{-dMIm}][\text{ClO}_4]\) film in a 0.5 M Ca(ClO\(_4\))\(_2\) electrolyte solution.\(^2\)
interaction between the ClO$_4^-$ anion and water molecules.$^{26,27}$ As the PF$_6^-$ anions in solution migrate toward the working electrode because of changes in potential, an exchange of PF$_6^-$ anions from the solution phase to the film phase occurs. As a result of the weak interaction between the PF$_6^-$ anions and water, the thermodynamic equilibrium lies toward the ClO$_4^-$ anion. For example, for a coPIL film prepared from a solution with $x_{\text{ClO}_4^-} = 0.5$, the solution contains equal mole fractions of ClO$_4^-$ and PF$_6^-$ anions. However, because the ClO$_4^-$ anions contribute very little to the $R_t$ but yet still participate in anion exchange with the film, the $R_t$ of the coPIL film is determined by the continuous anion exchange of the PF$_6^-$ anions with the film, resulting in half the value of the $R_t$ measured for a pure PF$_6^-$ solution ($x_{\text{ClO}_4^-} = 0$). Figure 6 demonstrates the ability to continuously tune the ion transport of the coPIL films by controlling the composition of their environment. This environmentally responsive film resistance could be useful in the design of dynamic and ion-sensitive films.

### 3. EXPERIMENTAL SECTION

#### 3.1. Materials.

Chromium-coated tungsten rods were purchased from R.D. Mathis, gold shot (99.99%) was acquired from J&J Materials, and silicon (100) wafers were obtained from WRS Materials. A Millipore Elix filtration system was used to produce deionized water ($\geq 10.0$ MΩ).

The following chemicals were purchased from Sigma-Aldrich and used without further modification: 3-bromopyridine, 4-mercapto-1-butanol (95%), dicyclopentadiene (98%), Grubbs catalyst second generation [(H$_2$IMes) (PCy$_3$)(Cl)$_2$Ru = CHPh], and trans-3,6-endomethylene-1,2,3,6-tetrahydrophthalamoyl chloride (NBDAC). The following chemicals were purchased from Fisher Scientific and used without further modification: allyl bromide (99%), 1,2-dichloroethane (DCE), 1,2-dimethylimidazole (98%, dMIm), ethanol (200 Proof), methylene chloride (DCM), potassium bis[(fluorosulfonyl)imide (KFSI), potassium hexafluorophosphate (KPF$_6$), and potassium perchlorate (KClO$_4$).

Grubbs third generation catalyst ([[(H$_2$IMes) (3-Br-ppy)$_2$](Cl)$_2$Ru = CHPh]) was synthesized as described by Love et al.$^{30}$ 3-[(bicyclo[2.2.1]hept-5-en-2-yl)methyl]-1,2-dimethylimidazol-3-ium hexafluorophosphate ([N$_1$-dMIm]·[PF$_6$]) was synthesized as described by Njoroge et al.$^2$

#### 3.2. Polymerization on Gold Substrates.

Silicon (100) wafers, rinsed with water and ethanol and dried in a stream of nitrogen, were used to prepare gold-coated silicon wafers by sequentially depositing thin films of chromium (100 Å) and gold (1250 Å) through thermal evaporation in a diffusion-pumped chamber (CVC-PSM66 evaporator) at a base pressure of $\leq 4 \times 10^{-6}$ Torr and a rate of 1–2 Å s$^{-1}$. 1.2 cm $\times$ 4 cm gold-coated silicon substrates obtained by cutting the gold-coated wafers were placed in a 1 mM ethanolic solution of 4-mercapto-1-butanol for a minimum of 1 h to yield a chemisorbed hydroxyl-terminated self-assembled monolayer. Subsequently, the films were rinsed with ethanol, water, and ethanol and dried in a stream of nitrogen, after which they were exposed to a 5 mM solution of NBDAC in DCM for a minimum of 30 min to yield the acylation product of a surfacet-
tethered norbornenyl group. The NBDAC films were rinsed with DCM, ethanol, water, and ethanol and dried in a stream of nitrogen.

The norbornenyl-modified substrates were then exposed to a 5 mM solution of Grubbs third generation catalyst in DCM for 12 min, rendering them active for ROMP. The ROMP-active substrates were quickly rinsed with DCE and immediately placed in a 0.1 M [N_{1}-dMIm][PF_{6}] solution in DCE for up to 15 min. The substrates were subsequently rinsed with DCM, ethanol, water, and ethanol and dried in a stream of nitrogen.

3.3. Anion Exchange. Aqueous solutions (0.2 M) containing the pure salts of the desired anions were prepared and combined volumetrically to achieve a 0.2 M binary mixture of the anion salts at the desired mole fraction in the exchange solution. The anion exchange of p[N_{1}-dMIm] films containing a resident anion was accomplished by immersing the film in the exchange solution for a minimum of 2 h. The substrates were subsequently rinsed with water and ethanol and dried in a stream of nitrogen.

3.4. Characterization. Fourier transform infrared (FTIR) spectra of the surface-tethered films were collected using polarization modulation-infrared absorption spectroscopy (PM-IRRAS). PM-IRRAS was performed using a Bruker TENSOR 27 FTIR spectrometer equipped with a PEM-90 photoelastic modulator (Hinds Instruments) and a liquid nitrogen cooled mercury-cadmium-telluride detector with a nondichroic BaF_{2} window. The source beam employed a half-wavelength (λ/2) retardation modulated at a frequency of 50 kHz and set at 85° incident to the sample surface. Spectra were collected over 5 min (360 scans) at a resolution of 4 cm\(^{-1}\).

The thickness of the surface-tethered films was determined by performing profilometry on three 1 mm long scans per sample across a hand-made scratch defect used to establish a baseline for polymer growth. Profilometric thicknesses were determined using a Veeco Dektak 150 stylus profilometer. Measurements were performed using a stylus with a 12.5 μm radius, applying 29.4 μN of force and operating in the hills and valleys detection mode. The scan duration was varied to collect the height data every 0.028 μm. Each scan was plane-fitted using the instrument software. Reported values represent the averages and standard deviations of at least three independently prepared films.

Advancing and receding water contact angles were measured on both sides of approximately 5 μL drops with the syringe in the probe droplet during measurements on the thin film surface, using a Ramé-Hart manual contact angle goniometer with a microliter syringe. The reported values and ranges represent the averages and standard deviations from three measurements per sample of at least three independently prepared samples.

Ion transport in the thin films was determined by performing EIS. An electrochemical cell was constructed consisting of the gold-coated silicon substrate coated with the film to be studied as the working electrode, a gold-coated silicon substrate as the counter electrode, a Ag/AgCl/KCl (3 M) reference electrode, and a 0.1 M aqueous solution of the film anion potassium salts as the electrolyte. To limit the testing area to 1 cm\(^{2}\) of each sample, a sample holder of a Flat Cell (Princeton Applied Research, model K0235) was utilized. The spectra were acquired using a Gamry Instruments Reference 600 potentiostat interfaced to a personal computer. The electrochemical cell was perturbed with a 5 mV rms ac voltage applied at the open circuit potential, which was varied in frequency from 10\(^{5}\) to 10\(^{-2}\) Hz using 10 points per decade. The two-time-constant equivalent circuit model consisting of a solution resistance (R_s), a film capacitance (C_f) and resistance (R_f), and an interfacial capacitance (C_i) and resistance (R_i) shown in Scheme 1 was used to fit the spectra using the Gamry EChem Analyst software package.

4. CONCLUSIONS

Random coPIL films were prepared by the simple anion exchange of p[N_{1}-dMIm] films with aqueous solutions consisting of PF_{6}− anions and either ClO_{4}− or FSI− anions. These films exhibit a thermodynamically determined selectivity, with PF_{6}− anions more selective for the film compared to ClO_{4}− anions, but less selective than FSI− anions. The surface wettability for p[N_{1}-dMIm]PF_{6}[ClO_{4}] films shows that the concentration of the ClO_{4}− anion on the surface is higher than that in the bulk. The film resistance (R_f) to ion conduction for p[N_{1}-dMIm]PF_{6}[ClO_{4}] films is linearly dependent on the binary anion mole fraction of PF_{6}− in solution (x_{PF_{6}−}) as the R_f of the ClO_{4}− anion is too small to be measured. This trend in R_f is consistent with the much greater thermodynamic tendency for PF_{6}− to occupy sites in the film. In this way, a key characteristic of the film, R_f can be continuously tuned between the extremes of the two homopolymers by simply changing the film ionic environment. The ability to easily form random coPIL films that exhibit a continuum of tuned properties between those of the homopolymers greatly increases the utility of PIL films.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02165.

Determination of the binary anion film mole fraction of PF_{6}− (y_{PF_{6}−}) and ClO_{4}− (y_{ClO_{4}−}) for p[N_{1}-dMIm][PF_{6}][ClO_{4}] films, determination of the binary anion film mole fraction of PF_{6}− (y_{PF_{6}−}) and FSI− (y_{FSI−}) for p[N_{1}-dMIm][PF_{6}][FSI] films, selectivity plots for the binary anion exchange of p[N_{1}-dMIm][PF_{6}][ClO_{4}] films, phase angle plots for the EIS spectra collected for p[N_{1}-dMIm][PF_{6}][ClO_{4}] coPIL films, and the values of the interfacial fitting parameters of the EIS spectra in Figure 5 (PDF).

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Notes

The authors declare no competing financial interest.

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