

# Polymerized Ionic Liquid Films in Strong Electric Fields: Ion Transport and Nanopatterning

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## ABSTRACT

We have recently studied local ion transport and structural changes in thin films of an imidazolium based polymerized ionic liquid (PIL) using an integrated experiment-theory approach. We find that experimental data for the kinetics of charging and steady state current-voltage relations could be explained by taking into account the dissociation of ion-pairs under an applied electric field (known as the Wien effect). Onsager's theory of the Wien effect coupled with the Poisson-Nernst-Planck (PNP) formalism for the ion transport is found to be in excellent agreement with the experimental results. We also demonstrated that by means of atomic force microscopy (AFM) one can form topographical features on the surface of PIL-based thin films with a significantly lower electric potential and power consumption as compared to non-conductive polymer materials. Furthermore, by tuning the applied voltage and ambient air humidity, reproducible control over the dimensions of the structures formed is achieved.

**Keywords:** Wien effect, polymerized ionic liquids, ion transport, nanopatterning, Poisson-Nernst-Planck

## 1 INTRODUCTION

Polymerized ionic liquids (PILs) [1-2] are promising materials for various solid-state electronic applications such as dye-sensitized solar cells, lithium batteries, actuators, field-effect transistors, light emitting electrochemical cells, and electrochromic devices. However, fundamental understanding of interconnection between ionic transport and mechanical properties in PILs is far from complete. To date, we lack experimental studies and predictive theory describing important aspects/processes of PILs. In particular, delocalization of charges and the larger sizes of ions in PILs lead to novel engagement between

conductivity and structural properties, which can be significantly different from those observed in conventional polyelectrolytes like poly(styrene sulfonate). For example, a recent study [3] has demonstrated that conductivity in PILs is strongly decoupled from structural dynamics contrary to the classical theory of ion transport.

In this work, we have studied [4-5] interconnections between ion transport and structural changes in thin films of an imidazolium based PIL using an atomic force microscope (AFM) tip and applying a direct current (DC) electric field. The effects of moisture were studied by controlling ambient air relative humidity (RH). Theoretical calculations were done to develop a fundamental understanding of the mechanism of ion transport and pattern formation near the surface of the films.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Experiments were done using 300 nm thin films prepared by spin-coating poly(1-ethyl-3-vinylimidazolium bis(trifluoromethylsulfonyl) imide) (poly-EtVImNTf<sub>2</sub>) onto a gold coated electrode after dissolving in 2-butanone at concentration of 6 mg/ml. The poly-EtVImNTf<sub>2</sub> has a bulk glass transition temperature of  $T_g = 52.9$  °C and its chemical formula along with a schematic of the experimental set up is presented in Figure 1.

### 2.2 Experiments

Measurements were performed on a Multimode 8 (Bruker) AFM interfaced with a National Instrument DAQ card controlled via LabView and Matlab software. The IVz spectroscopic mode in the scanning probe microscopy (SPM) was used to monitor electric current and mechanical

properties of the sample as a function of the applied electric field. In the IVz mode, a 1-step DC bias waveform is applied to the conductive AFM tip in contact with the film, whereas current is read off of the bottom electrode and the z-position of the tip is recorded simultaneously (cf. Figure 1 (b)). We studied ion transport and structure of the PIL samples with a positively-biased AFM tip, so that it repelled the positively charged polymeric backbones, allowing us to ignore issues related to polymer adsorption. Measurements were performed at each location of a pre-defined spatial grid. To avoid excessive current, a 2 GΩ protective resistor was connected in series with the sample and current amplifier (Femto DLPCA-200). Cantilevers with Cr/Pt conductive coatings (Budget Sensors) were used.

The AFM platform was equipped with a heating stage and an environmental chamber allowing for fine regulation of temperature and relative humidity of the ambient gas. Prior to the measurements, the sample was pre-conditioned at 100 °C in dry synthetic air flow for half an hour to desorb surface water. Subsequent cooling and measurements were also performed in a constant flow of dry air. We note that the volume probed using AFM depends on the radius of curvature of the tip apex and contact area between the tip and the film. Both of these parameters were controlled in the experiments: the radius of the tip was ~ 20-25 nm and the contact area was controlled by the setpoint. The spread in the contact area was judged from the variation of the cantilever's contact resonance frequency and it was found that changes in the contact area do not exceed 10-20 %. The data presented were averaged over different grid points, and data taken on different dates were found to be consistent with each other.

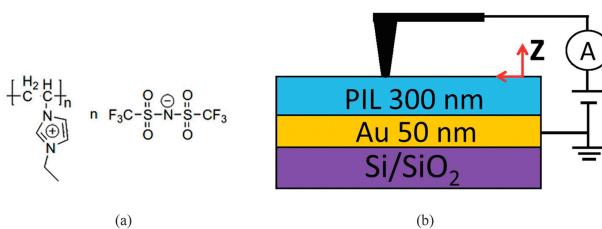


Figure 1 (a) Chemical formula of the PIL studied in this work; (b) schematic representation of the AFM setup to read off current response and z-change to a step DC bias waveform applied in a pre-defined location. Reproduced from Ref. [4] with permissions.

The nanopatterning study presented in this work was produced on a Cypher AFM (Asylum Research and Oxford Instruments Company, Santa Barbara). The custom lithography software was written in Igor Pro (WaveMetrics, Inc.) used to control tip position and bias application. At each point on the image the tip was engaged to the surface and a short 250 ms pulse of a +6 V amplitude was applied

to the tip. Then the tip was retracted and moved to the next position.

### 2.3 Theory

The kinetics of charging as well as steady state relations between ionic current and applied voltage in films of PILs were studied using a novel extension of the Poisson-Nernst-Planck (PNP) formalism [4,6] by incorporating the effect of ion-pair dissociation in the presence of an applied electric field. The latter effect is included by merging Onsager's theory [7] of the Wien effect with the PNP formalism. The general treatment for the ion transport using such a formalism in a two component system is presented elsewhere [4] along with the details of comparison with the experiments.

## 3 RESULTS

In order to study the *local* effects of applied voltage on mechanical response and ionic transport in PILs, we first minimized the presence of moisture. The relative humidity of air was maintained at ~ 0 % using environmental cell. In order to understand correlations between the electrical properties and resulting changes in mechanical properties, we performed measurements of the electric current and penetration depth ("z-changes") as a function of time in the presence of the electric field. Six different voltage values (4,5,6,10,15 and 20 V) were used. Experimental results obtained from these measurements was compared with theoretical predictions of the Wien-Onsager theory based extension of the PNP model (called the PNP-Wien-Onsager model). In second set of experiments, relative humidity of the ambient air was varied and its effects on structural changes in the presence of applied electric field were studied in the context of nanopatterning.

### 3.1 Ion Transport: Steady State

It was found [4] that the steady-state current and the maximum current resulting from application of one-step bias increases with an increase in the applied voltage. However, the steady state current was found to increase in a non-linear manner highlighting a non-ohmic nature at high voltages (Figure 2). A possible explanation of the non-ohmic behavior is physical damage to the structural integrity of polymer thin film induced by the electric field. For example, it was reported [8] earlier that application of a strong electric field initiates dielectric breakdown in thin polymer films of neutral poly (methyl methacrylate) (PMMA), which leads to an increase in conductivity by ten orders of magnitude (from  $10^{-14}$  S/m to  $10^{-4}$  S/m). To understand the effects of electric field on conductive properties, we first estimated ionic conductivity ignoring any non-linear effects. Later, the non-linear effects were included in our analysis using the PNP-Wien-Onsager

model. Using Ohm's law (i.e., linear relation between current and voltage), the conductivity of sample was estimated to be  $\sigma = I_\infty L/V \sim 2.6 \cdot 10^{-6} \text{ S/m}$  for 4 V, where L (=300 nm) is the sample thickness;  $I_\infty$  is the steady state value of the current per unit area at voltage V so that the net current =  $I_\infty S$ , S being the sample area limited by the tip diameter. For 15 V, the conductivity was found to be  $1.2 \cdot 10^{-5} \text{ S/m}$ . These values feature a change by one order of magnitude in conductive properties of material below and above a threshold voltage along with the observed mechanical changes in the form of holes (Figure 3). Noting the reversible nature of the current-voltage measurements and the fact that the current measured by the SPM was small (pA range), we suggested that the increase in conductivity under applied voltages is not a result of an irreversible structural damage to the film but rather is indicative of significant ion motion occurring on the PILs surface and an increase in the amount of free ions. We hypothesized that strong electric field facilitates formation of the free ions shifting the charge density of materials and resulting in local depression of glass transition temperature, which subsequently leads to weaker mechanical properties and increased ion mobility [4]. Our hypothesis is substantiated by excellent agreement between the PNP-Wien-Onsager model and experimental data as shown in Figure 2.

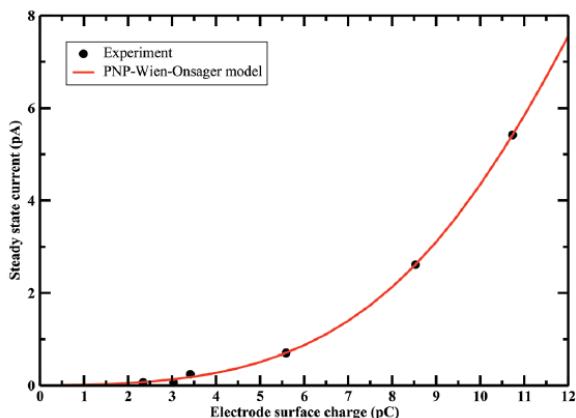


Figure 2: Comparison between theory and experiments for the steady state current is shown here and an excellent agreement between the two is found. The electrode surface charge for an applied voltage was estimated using the data on kinetics of charging as presented in Ref. [4]. Reproduced from Ref. [4] with permissions.

The agreement between the theory and experiments allows us to more confidently predict [4] structural properties of the PIL films such as the observed significant softening of the PIL films beyond certain threshold voltages and formation of holes under an AFM tip, through which electric field was applied.

### 3.2 Nanopatterning

The softening and formation of holes *beyond a threshold voltage* was used to pattern [5] the films (Figure 3) using the AFM tip. In particular, we demonstrated [5] that by means of AFM one can form topographical features on the surface of PolyIL-based thin films with a significantly lower electric potential and power consumption as compared to non-conductive polymer materials. Furthermore, by tuning the applied voltage and ambient air humidity, control over dimensions of the formed structures was reproducibly achieved.

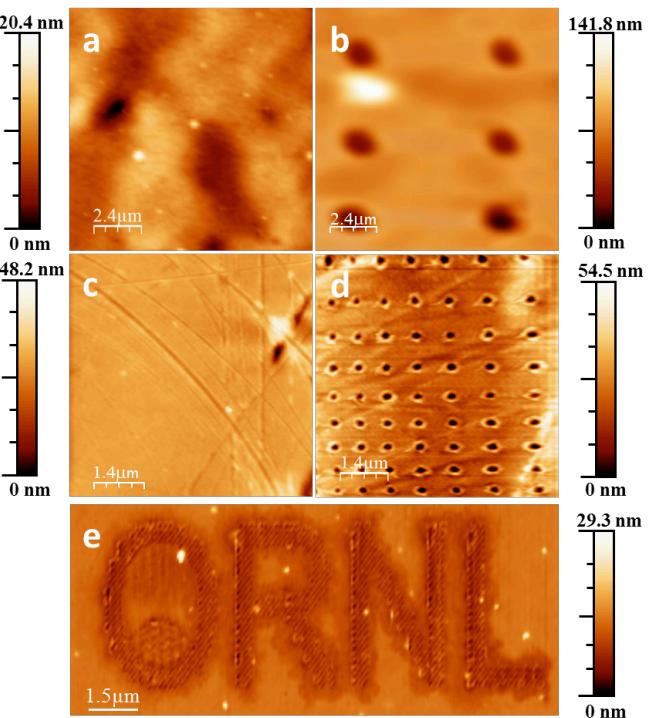


Figure 3: AFM topographic images of the 120 nm-thick PIL film after application of triangular voltage pulses with amplitudes of 10 V (a) and 20 V (b) at 0% RH, and with amplitudes 2 V (c) and 6 V (d) at 40% RH. (e) Example of patterning produced with pulses of +6 V amplitude applied to the tip for 250 ms at each point in the pattern. The distance between the points is ca. 100 nm. Reproduced from Ref. [5] with permissions.

We hypothesize that ions unbind at certain threshold voltage, and that it is dependent on humidity. Due to the nature of the sample, ion dissociation results in formation of mobile anions and significantly fewer mobile cations. In the absence of water this dissociation requires a rather large activation energy of  $\sim 3.5 \text{ eV}$ , which correlates well with our experimental observation of the high threshold voltage

at 0% RH. At a high humidity, water molecules begin to form a solvation shell around bound ion pairs near the sample surface. This leads to a reduction of the activation energy for ion dissociation by providing a solvating environment characterized by a high dielectric constant. The dissociated anions then move towards the interface with the positively charged tip due to the attractive electrostatic forces and form an interfacial layer. The time required for the ions to electromigrate to the interface depends on the local viscosity and electric field. Indeed, we have observed [5] the presence of a characteristic delay time between application of potential and actual changes of the mechanical properties. The delay time is well-resolved upon application of the step voltage to a thicker film (300 nm). The time delay depends on the relative humidity; for instance, at 11% RH and 10 V it is  $\sim$ 2.5 s, while it becomes undetectable at higher humidity [5]. If we attribute this delay to the ion migration to the interface, then the roughly estimated mobility of  $10^{-16}$ - $10^{-17}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> cannot be ascribed to migration of H<sup>+</sup> or OH<sup>-</sup> ions with a mobility of 10<sup>-9</sup> m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the polymer melts, but rather to migration of bulky anions of the PIL. Higher humidity leads not only to a better ion solvation, but also to a reduced local viscosity due to the general effect of plasticization; so, ions diffuse faster in the PIL. As ions arrive at the interface, an uncompensated dense electrical charge starts to buildup. When the cumulative charge density reaches a critical value it experiences an instability similar to electrohydrodynamic instabilities reported for non-conductive polymers [9] that stimulates softening of the polymer interface. Similar charge-induced softening in electric field has been previously reported for the interface between the crystalline and superfluid <sup>4</sup>He, where formation of ripplons was observed [10]. In our case, this effect is not limited to the interface and can propagate inside the material since the concentration of ionic species in the polymer is very high. Also, the proposed scenario of softening explains why the tip has to be positively biased to induce hole formation: it has to be attractive for the mobile anions. When the tip is negatively charged it will only attract the dissociated cationic chains of the PIL, which are too bulky and move too slowly to induce hole formation. Furthermore, the dynamics of hole growth after the softening under the tip can be qualitatively understood using theoretical analysis of the fastest growing mode in the electrohydrodynamic instability [9]. The complete mechanism of softening and details of hydrodynamic analysis of hole formations are likely more complicated than suggested by our simple models and requires extensive theoretical and experimental developments to elucidate possible electrohydrodynamic instabilities in multicomponent system containing charged polymers and water.

#### 4 CONCLUSIONS

In conclusion, we have studied local ion transport and structural changes in films of an imidazolium based

polymerized ionic liquid, poly(1-ethyl-3-vinylimidazolium bis(trifluoromethylsulfonyl) imide) at room temperature. The kinetics of charging and steady state current were studied using AFM in combination with theory. Comparisons between the experiments and Onsager's theory of the electric field dependence of the dissociation constant coupled with the Poisson-Nernst-Planck (PNP) formalism reveals that the dissociation of ion-pairs resulting from the presence of an applied electric field dictates the ion transport and structural changes. In addition, we have found that films containing PILs become softer under application of DC field. We observed formation of holes when the applied voltage exceeded a certain threshold value. By tuning the strength of electric field and environment conditions, we demonstrate that one can form topographical features on the surface of a PIL in a reproducible manner with a good control over dimensions of the structures formed. The pattern formation for the ion-containing PIL occurs at a significantly lower strength of electric field and electric power as compared to the non-conductive polymer materials. Although the mechanism of the pattern formation is complex and additional experiments are required to fully unveil contributions of Faradaic processes as well as processes associated with ionization of water, the underlying PILs softening is undoubtedly dominated by the ion dissociation and electromigration in the polymer as opposed to Joule heating [5]. These observations have promising implications for practical application of nanopatterning, where flexibility in pattern design and good control over the pattern lateral characteristics are necessary.

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