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# Synthesis and Electric Field Actuation of an Ionic Liquid Polymer

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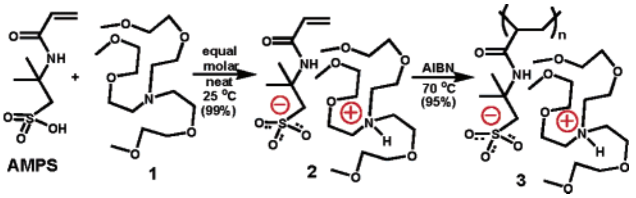
Polymerizable ionic liquids and their actuation in an electric field are a combination of material and properties with unique potential to display structural and fluid dynamics above that found for small molecule ionic liquids. Small molecule ionic liquids are generally monovalent organic salts with melting points or glass transitions below room temperature. They derive their liquid character from a selection of ionic structures which have very weak tendencies to coordinate with oppositely charged ions, low intermolecular forces and low symmetry. Their properties (immeasurably low volatility, nonflammability, very high polarity and solvating characteristics, high ionic conductivity, and a wide electrochemical potential window) are of substantial interest particularly with regard to applications as green solvents, analytical extraction solvents, and electrochemical supporting media.[1] Very recently it has been reported that water immiscible ionic liquids display significant electrowetting characteristics with an interesting dependence on the size of the cationic and anionic components.[2] Ionic liquids themselves provide an opportunity of producing a more stable actuating medium, eliminating such issues as solvent evaporation and degradation due to electrolysis, typically found in aqueous based electric field induced actuators.

In an ionic liquid polymer system, the cationic or anionic centers are constrained to repeat units in the polymer chain. As such, any molecular flow or diffusion requires a concerted motion of as many ionic centers as there are charged repeat units in the polymer chain. When subjected to an electric field, a polymeric system may respond in an enhanced or retarded manner relative to a small molecule ionic liquid, depending on whether the covalent linkage of cationic or anionic repeat units responds as a more highly charged single molecule or whether its macromolecular size inhibits molecular motion needed for a response. In this communication, we report an ionic liquid polymer system wherein a low molecular weight counterion promotes an ionic liquid character in both the monomer and polymer and an observation of electrowetting where the polymer displays a distinctive effect relative to that for the monomer.

Few examples of polymerizable ionic liquids have been reported. They are mostly based on the imidazolium ion functionalized with a polymerizable vinyl,[3] acrylic,[4] or styryl[5] moiety and have the physical form of a glass or sticky rubber. The oxyethylene ammonium counterion incorporated into the ionic liquid polymer system reported here promotes a liquid flow sufficient to observe the electrowetting actuation.

The formation of the monomeric ionic liquid salt and its polymerization is depicted in Scheme 1. The polymerizable component is the 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer which is a crystalline compound with a 192 °C melting point. It is converted to a liquid ammonium salt, **2**, by addition of an equimolar quantity of tris[2-(2-methoxyethoxy)ethyl]-amine, **1**. This tertiary amine was selected as one that would solvate the AMPS monomer without the need of a solvent and one whose oxyethylene substituents would shield the protonated ionic center from coordinating with the sulfonated anion, thereby depressing the melting point or glass transition to a very low temperature.

***Scheme 1.*** Reaction Scheme for AMPS Oxyethylene Ammonium Salt Monomer **2** and Polymer **3**



The glass transitions of the free amine **1** (−104 °C) and of the AMPS−ammonium salt **2** (−57 °C) presented in the differential scanning calorimetry (DSC) thermogram in Figure 1 demonstrate the remarkable capability of the oxyethylene-substituted amine to extend the liquid range of a salt to low temperatures. After the liquid ammonium sulfonate monomer formation is complete, a free radical initiator (2,2′-azobisisobutyronitrile, AIBN) is added and reacted at 70 °C. The monomer conversion is 95%, and the product is a clear acetone-soluble viscous liquid.

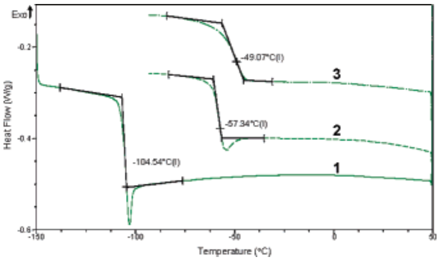


***Figure 1.*** Differential scanning calorimetry comparison of oxyethylene amine **1**, AMPS oxyethylene ammonium salt monomer **2**, and polymer **3** illustrating low $T_g$ upon salt formation in the monomer and polymer.

The spectroscopic characterization (IR, $^1$H and $^{13}$C NMR) is consistent with polymer structure, **3**, depicted in Scheme 1. The molecular weight is low but significant as indicated by an intrinsic viscosity measurement of 0.30 which is uncorrected for an observed polyelectrolyte coil expansion effect.[6] The glass transition temperature of ionic liquid polymer **3** is −47 °C as depicted in the Figure 1 thermogram. This is a remarkably modest increase from that of the unpolymerized monomer salt.

Electrowetting is an electrostatically driven surface effect where a liquid droplet's spreading on a hydrophobic surface is modulated by application of a voltage to the droplet and an underlying conducting substrate.[7] A schematic of this effect is illustrated in Figure 2. The droplet rests on a very thin low-dielectric insulating film (Teflon AF) which is supported on a conducting substrate and is contacted at the top by a very fine wire contact. Application of a voltage builds up a layer of charge on both sides of the interface with the dielectric film and decreases the interfacial energy.

The observed response is a spreading of the droplet and a changing of its curvature. The dependence of the droplet's contact

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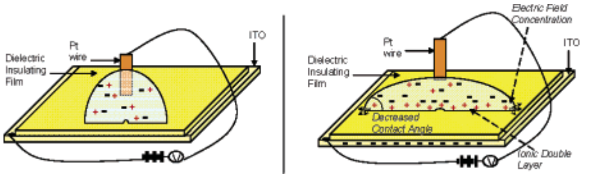

***Figure 2.*** Depiction of an electrowetting actuation electrode setup with (right) and without (left) an induced electric field.

angle, $\theta$, on the applied voltage, $V$, is described by the Young−Lippmann equation[8] as follows:

$$\cos\theta = \cos\theta_0 + \frac{1}{2\gamma}CV^2 = \cos\theta_0 + \frac{\epsilon\epsilon_0}{2\gamma t}V^2 \tag{1}$$

where $\theta_0$ is the contact angle at zero voltage, $C$ is the capacitance per unit area, $\gamma$ is the surface tension of the liquid, $\epsilon$ is the permittivity of the insulating dielectric, $\epsilon_0$ is the electric constant, and $t$ is the thickness of the dielectric layer. Surface tension measurements[9] of the monomer **2** and polymer **3** are 38.1 and 47.0 mJ/m$^2$, respectively. The contact angle measurements of the AMPS−ammonium salt monomer **2** and polymer **3** as a function of applied DC voltage are shown in Figure 3, and photographs of the ionic liquid polymer droplet at zero and maximum applied voltages in Figure 4 show a substantial contact angle change.

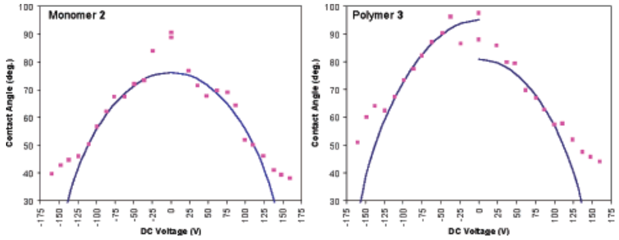

***Figure 3.*** Electrowetting curves of monomer **2** (left) and polymer **3** (right). Polarity corresponds to ITO electrode.

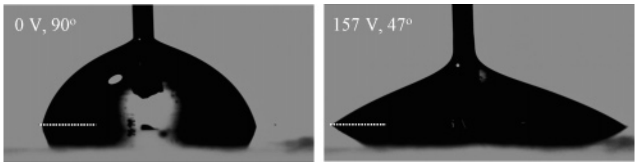

***Figure 4.*** Electrowetting AMPS oxyethylene ammonium salt polymer **3** as voltage increases from 0 V (left) to 157 V (right), wherein a large decrease in contact angle is clearly visible.

A parabolic best fit of the experimental contact angles to the voltage dependence of eq 1 is represented by the continuous line in Figure 3. Separate best fits were made for the negative and positive voltage regions of the curves. The electrowetting curve for the AMPS−ammonium sulfonate monomer, **2**, is similar to those reported for small molecule ionic liquids in both magnitude and shape.[2] No evolution of gas bubbles, discoloration, or degradation was observed between 0 and 157 V.

A monomer versus polymer comparison of contact angle data for the AMPS−ammonium salt system presents an interesting contrast. The polymer displays a larger contact angle at zero voltage, a similar magnitude of contact angle change over the voltage range, a departure from the Young−Lippmann equation at a lower voltage, a dissymmetry between the negative and the positive voltage sections of the electrowetting curve, and hysteresis over cyclic measurements (see Supporting Information).

These observed differences in electrowetting behavior correlate with the higher surface tension of the polymer and with the polyelectrolyte molecular structure. When no voltage is applied, the greater surface tension of the polymer is clearly consistent with the larger contact angle observed. When a voltage is applied, an electric field is concentrated across the Teflon AF interface and an ionic double layer of charge forms in the liquid at this interface. This decreases the surface tension at the solid−liquid interface and results in spreading of the liquid on the charged surface. A depiction is illustrated in Figure 2. The polymer differs from the monomer in that one of the charged components is a small cationic molecule and the other is a large anionic polyelectrolyte. When the substrate is charged, an oppositely charged component of the ionic liquid is adsorbed at the Teflon AF−ionic liquid interface. On reversal of polarity, a grouping of small molecule ions exchanges position with the polyelectrolyte. This disparity of molecular size correlates with the dissymmetry observed between the positive and negative sides of the electrowetting curve in Figure 3. While this correlation needs further study to quantify the polyelectrolyte molecular weight dependence, the effect of the molecular weight also appears to correlate with an observed hysteresis of the electrowetting curve when contact angle measurements are repeatedly cycled through the applied voltage range. Such behavior is consistent with a viscoelastic polymer.

This communication reports synthesis and electrowetting of a new ionic liquid monomer and polymer system. The uniqueness of the oxyethylene amine in the formation of the ammonium cationic species contributes to both the ionic and liquid nature of the monomer and polymer. Even more remarkable is the ability of this polymer to maintain its liquid nature as a macromolecule and to wet a substrate, showing preference for one polarity based upon the makeup of the ionic backbone of the polymer formed.

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**Supporting Information Available:** Details of the synthesis, characterization, and physical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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