

EWOD-Driven Translational Movement of a Liquid Polyelectrolyte Droplet

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ABSTRACT: Controlled transportation of air- and electrochemically stable materials is of interest in many areas of science. Herein, we report the synthesis and characterization of an ionic liquid monomer and its corresponding polyelectrolyte. The translational movement of these ionic liquid droplets across a substrate using the mechanism of electrowetting on a dielectric (EWOD) is demonstrated with emphasis given to electrode design and selective switching in the device construction. Directional control of

a 2 mm sized polyelectrolyte droplet is shown to laterally move across the substrate surface on the order of 10s of minutes due to its increased viscosity, whereas its ionic liquid monomer also transverses but at a much faster pace on the order of 10s of seconds. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3865–3870, 2008

Key words: degree of polymerization (DP); ductile; radical polymerization; stimuli-sensitive polymers; synthesis

INTRODUCTION

One reason to transform an ionic liquid to a polymerized form is to combine their attractive properties (high-ionic conductivity, wide electrochemical potential window of stability, solvating characteristics, and nonflammability) with the mechanical properties of a processable polymeric matrix. Progress has been made in this direction particularly with imidazolium polymers^{1–4} and alkali metal sulfonate polymers.^{5,6} However, a different objective in this ionic liquid polymerization is to retain the liquid character of the ionic liquid monomer, i.e., to produce a liquid polyelectrolyte. To this end, we have reported a system based on an acid–base complex between a sulfonic acid functionalized polyacrylamide and an oxyethylene substituted amine (Scheme 1).⁷

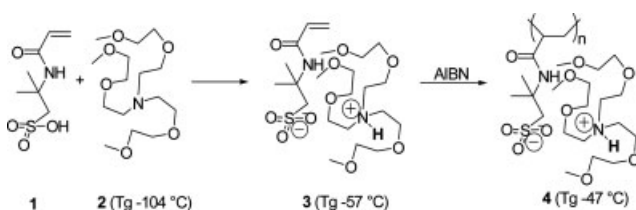
The oxyethylene amine, **2**, is responsible for the large T_g depression and liquid character of the polymerized salt. The fluid characteristics of this ionic liquid monomer, **3**, differ from that of the corresponding liquid polyelectrolyte, **4**, and correlate with an increased viscosity and surface tension. In an electrowetting experiment a droplet of the ionic liquid is placed on a flat conducting substrate covered by a very thin insulating film (a dielectric), and the droplet spreads and recovers when the substrate is charged

and discharged [Fig. 1(a)]. A particularly interesting feature of the liquid polyelectrolyte compared with the ionic liquid monomer is that the contact angle variation is larger and dependent on the polarity of the charge (i.e., greater wetting occurs when charge on the substrate is opposite that of the polyelectrolyte).⁷ This wetting effect is driven by the surface tension at the solid–liquid interface being modulated by a charging of the substrate. This effect is well known for aqueous salt solutions⁸ and has been studied for some ionic liquids⁹ and is referred to as electrowetting on a dielectric (EWOD).¹⁰ It currently finds application in using the droplet shape as a camera lens with an electrically controlled focal length.^{11,12}

In this work, we demonstrate a EWOD-driven translational movement of a droplet of this ionic liquid monomer and polymer system. The approach is derived from microfluidics-related research on aqueous salt solutions where lateral movements of a droplet is directionally controlled by an electrowetting mechanism.¹³ This is brought about by sectioning the conducting substrate into a series of individually chargeable electrodes; the dimension of which is slightly less than the droplet to be moved [Fig. 1(b)] and the spacing between such electrodes is minimized. The droplet is in simultaneous contact with three electrodes and migrates to the one that is charged. By charging every third electrode in a linear progression, the droplet can be made to follow such a track of electrodes. To our knowledge, this translational motion has not been observed for an ionic liquid substance before. Lab-on-a-chip applications are envisionable for this phenomenon. The

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Scheme 1 Synthesis of a polymerized ionic liquid.

details of this demonstration using the ionic liquid monomer and polyelectrolyte are described in this work.

EXPERIMENTAL

Materials

All reagents were purchased from the Aldrich Chemical Co. and used without further purification unless otherwise noted. Teflon AF was purchased from DuPont as a 6% solution in Fluorinert FC75, grade 1600, and used without further dilution. Dialysis tubing, SnakeskinTM with a molecular weight cutoff of 7,000, was purchased from Fisher Scientific. Glass slides coated with ITO ($\sim 1600\text{--}2400\text{ \AA}$) were purchased from δ -Technologies. Shipley's Microposit Photoresist S1813 and AZ Developer were used employing standard photolithographic techniques. A photoresist-coated chrome mask was purchased from Nanofilm, Inc. Transene's Chromium Mask Etchant was used in preparation of the mask. Drill bits, 350 μm size, were purchased from Drill Bit City. Single stranded insulated wire with a diameter of 250 μm was used and attached using a conductive epoxy kit from Web-Tronics. A 2-Pole, 6-Position Rotary Switch was purchased from Radio Shack.

Instrumentation

Intrinsic viscosity measurements, 5 *N* NaCl at 25°C, were conducted using a # 50 Ubbelohde viscometer and circulating temperature bath. An ABM High Resolution Mask Aligner was used to irradiate the photoresist. A VCA OptimaXE commercial contact angle

instrument fitted with a stage was used to capture translational movement. A KLA Profilometer was used to determine film thickness. An E-C Apparatus Corp. Power Supply, EC 105, provided DC voltage.

Synthesis of AMPS-ammonium salt monomer and polymer

A nitrogen purged 50 mL Schlenk flask was charged with freshly distilled tris[2-(2-methoxyethoxy)-ethyl]-amine (**2**) (1.56 g, 4.88 mmol), finely crushed 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (**1**) (1.00 g, 4.88 mmol), and methanol (2 mL). The reaction mixture was subsequently deoxygenated via the freeze-pump-thaw method (three times) and backfilled with nitrogen. Note: Total dissolution and solvent removal completes the formation of the AMPS-ammonium salt monomer (**3**), whereas the polymerization procedure was carried out immediately without removal of solvent.⁷ Polymerization: Upon warming to room temperature, 2,2'-azobisisobutyronitrile (AIBN) (8.0 mg, 0.05 mmol) was added to the reaction flask under a nitrogen atmosphere. The flask was then fitted with a water-cooled reflux condenser, vented to a bubbler, and heated to 65°C for 18 h. Upon cooling to ambient temperature, a 98% reaction conversion was determined by ¹H NMR, and the crude amber mixture was purified by dialysis in distilled water (1 L) for 24 h. Removal of excess water and solvent under vacuum yielded ionic liquid polymer (**4**) (1.74 g, 67%) as a light amber oil.⁷

Fabrication of segmented electrode device

To produce a mask, an electrode pattern (MS PaintTM, MS PowerPointTM) printed on a laser transparency sheet was transferred to a photoresist coated mask via a mask aligner (12 s). The photoresist was developed (60 s), dried under nitrogen, etched, rinsed with 2% H₂SO₄ and distilled with water, and dried.

ITO-coated glass slides were cleansed with soap, rinsed with distilled water and methanol, and then

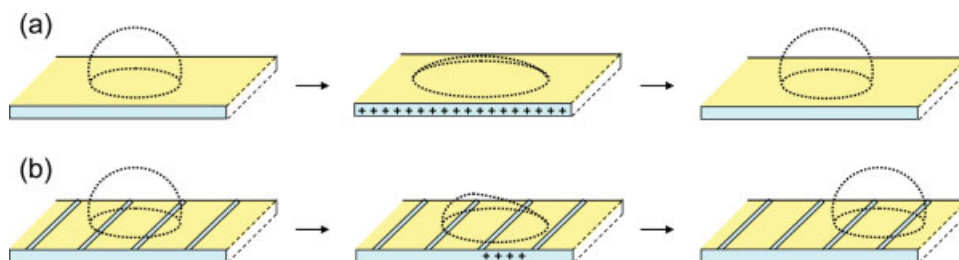


Figure 1 Electrowetting effect. Sketch of droplet (a) spreading and (b) translational movement in response to charging of the substrate. Counter electrode and thin film dielectric are not shown for clarity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

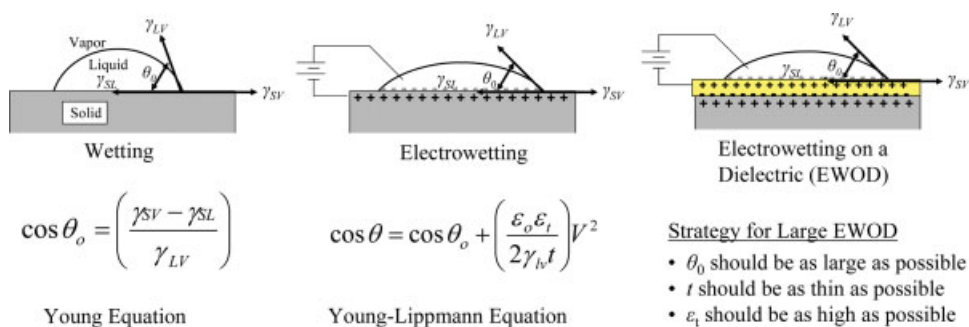


Figure 2 The wetting behavior of a droplet on a conductive substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dried. The slides were spin coated with the photoresist (300 rpm for 5 s then 2000 rpm for 1 min) and heated at 120°C for 2 min. After cooling, the slides were transferred to the mask aligner, where the mask was placed on top of the ITO-photoresist surface and irradiated for 2 s. The slides were transferred to a recrystallization dish containing the developer, shaken (10 s), and rinsed with distilled water and dried. The ITO etching solution made fresh on site and consisted of 10 mL HCl, 2.5 mL HNO₃, 1 drop Triton X, and 37.5 mL distilled water. The slides were immersed in the ITO etching solution, gently shaken for 10 min at 55°C, and immediately washed with distilled water. Before removal of the photoresist, 350 μm holes were drilled through the ITO glass slide where electrical leads could be attached at specified points. The slides were cleaned with acetone and wiped gently to ensure removal of the photoresist. Masking tape was used to protect areas where a dielectric layer was not desired; thereby yielding a thin spin-coated layer of the dielectric film on top of the zig-zag patterned electrodes only. The slide was spin coated with Teflon AF at 2000 rpm for 30 s and heat treated in an oven at 80°C for 18 h which produced an insulating film thickness of 1.29 μm. The masking tape was removed and insulated wire was fed carefully through the drilled holes, forced into an intimate contact with the ITO surface, and secured with conductive epoxy. These wires which came together at three common points were then connected to the switch. A 90-μm thin gold wire, serving as the one bare electrode required for electrowetting, was laid across the ITO electrode-dielectric surface and held in place with masking tape.

To facilitate the switching of voltage to every third zig-zag electrode, a 2-pole, 6-position rotary switch was converted to a 1-pole, 12-position rotary switch; hence, each position represented one electrode. Every third position was then linked together by insulated conductive wire, secured with solder, and connected to the three common leads from the ITO

slide. Finally, both the switch and the gold wire were connected to a DC voltage source to complete the electrode device.

RESULTS AND DISCUSSION

Mechanism of EWOD-translated motion

The wetting phenomena of electrolyte droplets, in addition to ionic liquid monomer **3** and liquid polyelectrolyte **4**, can be manipulated or directed toward the translational movement of these droplets across a surface. The wetting behavior, better known as contact angle θ_o of a droplet and described by Young's equation,¹⁴ is the thermodynamic equilibrium of surface tension or interfacial energy between three phases: γ_{LV} is the liquid-vapor interface; γ_{SL} is the solid-liquid interface; and γ_{SV} is the solid-vapor interface (Fig. 2).

If a small potential is applied, the contact angle decreases and the droplet further wets or spreads over a conductive surface, i.e., electrowetting. Although effectively changing the wetting behavior, there lies a threshold in which further wetting of the droplet at higher voltages is prevented due to electrolysis or degradation at the droplet-electrode interface. This threshold can be deferred with the addition of a dielectric layer, thereby limiting current flow through the droplet foregoing electrolysis. This type of wetting behavior, EWOD or the modulation of surface tension at the solid-liquid interface by charging of the substrate, is the mechanism by which ionic liquid monomer **3** and corresponding liquid polyelectrolyte **4** is transported across a surface in a desired path. Strategies for obtaining a large EWOD effect are as follows: have an initial contact angle at zero voltage, θ_o , as large as possible; a dielectric thickness, t , as thin as possible; and a dielectric constant, ϵ_t , as high as possible. Changes in contact angle can be predicted at known voltages by referring to the Young-Lippmann equation,^{14,15} where ϵ_o is the vacuum permittivity constant, $8.85 \times$

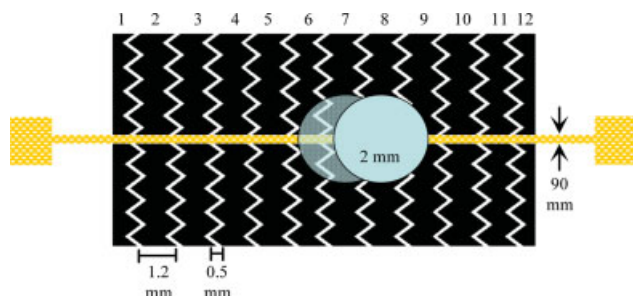


Figure 3 Dimensions for a 12-patterned electrode design in a zig-zag shape, contacting gold electrode, and droplet are displayed. Dielectric omitted for clarity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$; ϵ_t is the dielectric constant of Teflon AF, 1.89; γ_{lv} is the surface tension of the ionic liquid monomer 3 (38.1 mJ/m^2) or polymer 4 (47.0 mJ/m^2)^{7,16}; and t is the thickness of the Teflon AF film, $1.29 \text{ }\mu\text{m}$. As voltage is applied, surface tension at the solid-liquid interface decreases, thus making possible the movement of monomer 3 or polymer 4 toward or onto its neighboring electrode.

Segmented electrode configuration and design

Electrodes carefully spaced and turned on and off in an appropriate manner can be fabricated to facilitate electrowetting-based transport of materials as seen in aqueous electrolytes.¹⁷⁻¹⁹ Important features that contribute to this type of transport are electrode size, shape, and configuration. Through prior work, it was shown that droplets of ionic liquid monomer 3 or polymer 4 with a diameter of 2 mm effectively wet a thin-film dielectric-coated electrode surface via

EWOD when $<160 \text{ V}$ was applied.⁷ Therefore, the upper limit of electrode size in this study was based upon this droplet and were constructed at 1.2 mm.

However, electrode shape, like size, is just as important for maximizing coverage of the electrode to achieve faster movement of the droplet as demonstrated by both Fair¹⁷ and Kim,¹⁹ where a zig-zag or comb-shaped electrode was used in the EWOD driven translational movement of aqueous electrolyte droplets. Hence, as displayed in Figure 3, a zig-zag shaped electrode was used in constituting a 12-electrode pattern.

The zig-zag design of the electrode theoretically allows two electrodes to lay in the same plane as if the electrodes were placed parallel or linear to each other. If parallel or linear-shaped electrodes were configured, the droplet could get stuck between electrodes; coming to a complete stop, without overlapping a neighboring electrode which is required for forward progress. For this reason, as the droplet moves from one zig-zag-shaped electrode to a neighboring zig-zag-shaped electrode, the droplet undoubtedly is already in place and waiting for the switching on of the next electrode, either when behind or in front of the droplet depending on which electrode is purposely switched on. To effectively carry out this design while maintaining low voltage, electrode spacing was kept to a minimum of 0.5 mm; limited only by the template chosen.

One bare counter contacting electrode is necessary for translational motion of the ionic liquid droplets to occur. Therefore, a chemically inert gold wire with a diameter of 90 μm was chosen to lie delicately on top of the thin dielectric layer. (Fig. 4) The smaller the wire's diameter the less likely the droplet will wick up the bare electrode, thereby maintaining a mostly circular not oblong hemisphere.

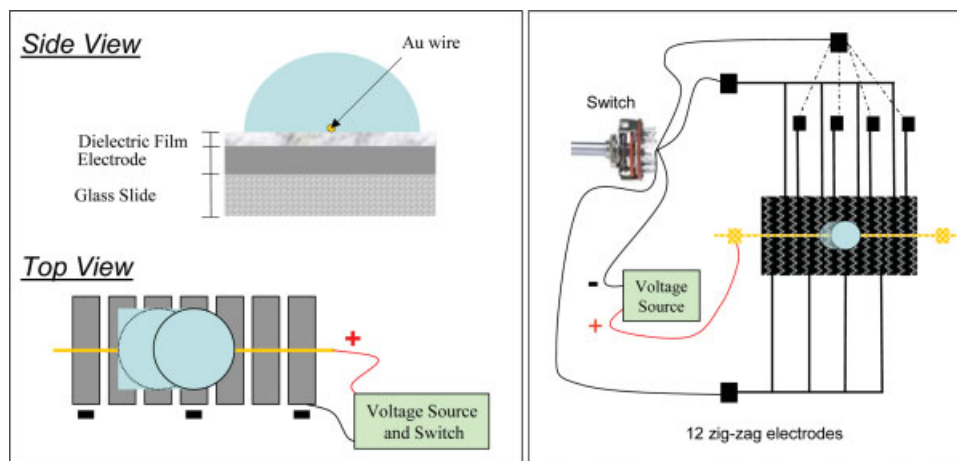


Figure 4 Left: A simplified view of the electrode device constructed with ionic liquid droplet on top. Right: The complete device highlighting the zig-zag electrode pattern. Dielectric omitted for clarity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

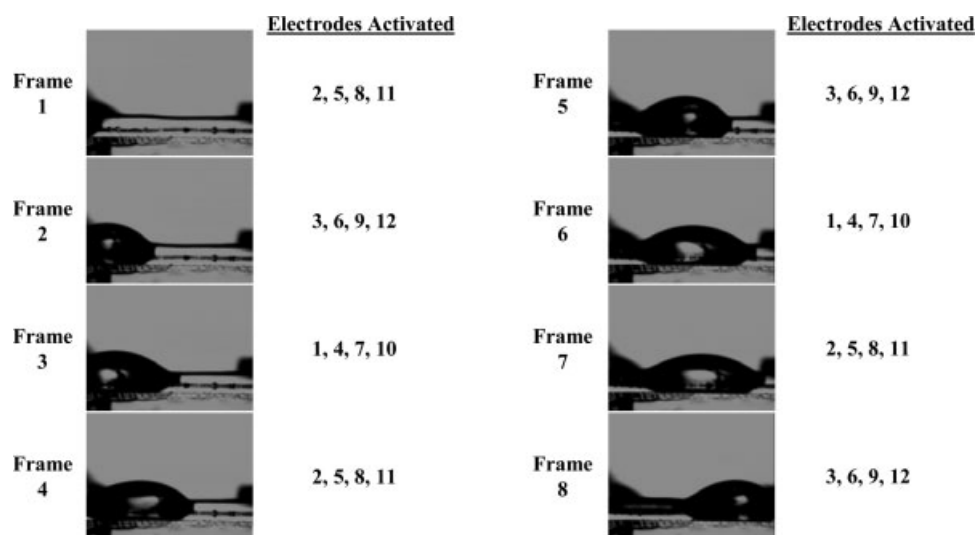


Figure 5 An example translational motion of an ionic liquid polymer as seen over eight frames through the charging of every third electrode.

Monomer and polymer systems used in demonstration

Ionic liquid monomer **3** and liquid polyelectrolyte **4** were synthesized by modification of an earlier reported procedure⁷ with methanol added as a solvent in this work. The polymer (a viscous clear amber oil) was purified using the dialysis procedure as described in the Experimental section. This process did not result in loss of the oxyethylene amine counterion as confirmed by NMR and IR spectroscopies. In addition to the spectroscopic characterization previously reported,⁷ polyelectrolyte **4** was characterized by intrinsic viscosity. The resulting value of $[\eta] = 0.35$ dL/g has a corresponding M_v of 69,000 D (DP \sim 130) if the Mark-Houwink parameters for a tetrabutylammonium-poly(AMPS) analog are employed.¹³ As both monomer **3** and polymer **4** were isolated as *neat* liquids, no solvent was required for these droplets to demonstrate EWOD.

Operation of device with droplet manipulation

For directional control, a three-electrode configuration was employed. Activated electrodes are indicated in Figure 5 as lateral movements of the droplet, beginning on the left side and progressing to the right over eight continuous frames. This permits one to decisively charge every third electrode without having to worry about the droplet reversing direction. With this three-electrode design, the droplet encompasses or touches three electrodes at any one time. Hence, with a droplet size of 2 mm, a maximum electrode size of 1.2 mm with 0.5 mm spacing was used with the understanding of as long as a minuscule amount of the droplet overlaps three electrodes, directional control would occur.

Comparison of monomer—Polymer ionic liquid droplets

As expected, upon polymerization there was an increase in viscosity of the ionic liquid polymer; hence, the longer time it takes to traverse the electrode surface—on the order of 10s of minutes. Nevertheless, the benefit of a polymerized ionic liquid **4** is entrapment of the counterion due to the polymer network thereby producing a material that is still liquid in nature and less affected by volatile evaporation or loss of the ionically bound counter ion. On the contrary, the less viscous ionic liquid monomer **3** crossed the electrodes surface at a much faster pace—on the order of 10s of seconds.

SUMMARY

Polyelectrolyte **4** successfully retained the liquid quality found in its ionic liquid monomer. Choosing oxyethylene amine as the counter ion depressed the T_g and is solely responsible for maintaining the liquid nature in this polyelectrolyte. Because of the fluid characteristics of ionic liquid monomer **3** and polymer **4**, droplets of these materials were shown to transport across a predetermined path with the tailoring of such parameters as electrode shape, size, and configuration. The utilization of surface tension reduction at the dielectric solid–liquid interface, brought about the construction of a device where the sectioning of a conducting substrate into a series of individually chargeable electrodes transpired; the dimension of which is slightly less than the droplet itself and the spacing between such electrodes is minimized. The droplet simultaneous is in contact with three electrodes and migrates to the one that is charged. By charging every third electrode, the droplet can be made to follow

such a track of electrodes. As expected, upon polymerization there was an increase in viscosity of the ionic liquid polymer; hence, the longer time it takes to traverse the electrode surfaces versus the less viscous ionic liquid monomer.

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