Investigating the Electromechanical Response Mechanism of Ionic Block Copolymers

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ABSTRACT

One of the rapidly developing frontiers in research and engineering applications is focused on the rational design of materials that have targeted functionalities and tunable responses to external stimuli. Such materials stand to revolutionize how structural components are designed for applications including flexible electronics, biomimetic devices, nanofluidics, as well as separation chemistry. A chief obstacle to achieving this capability is the lack of a fundamental understanding of how chemical structure and morphology give rise to macromolecular properties. With this in mind, our research explores how polymer structure, counterion species, and film morphology affects the electromechanical response of materials when exposed to external electric fields. We report here the development of an AB ionic diblock copolymer Poly($1BDIMAPF_6$-*b*-styrene) (hereafter, 1-BDIMA/PS) where an imidazolium ring paired with a PF_6 counter-anion in the ionic B block imparts electromechanical responsiveness, while polystyrene provides structural support as the A block. As a thin (~30 nm) film on a Si substrate, 1-BDIMA/PS adopts a semi-lamellar structure as confirmed by neutron reflectometry (NR) and TOF-SIMS. Additionally, when 1-BDIMA/PS is prepared as a thick (~100 µm) membrane sandwiched between two gold leaf electrodes, the film actuates under low applied potentials (< 1 V). Preliminary simulations on coarse-grained models of a similar system also confirm counter-ion mobility under applied electric fields. Collectively, these results indicate that 1-BDIMA/PS is not only an excellent candidate for future electromechanical responsiveness studies, but that the sensitivity of NR to scattering length density as well as sub-nanometer changes in thickness make it a promising tool for investigating polymer and counterion mobility under applied fields in the future.

Keywords: actuators, ionic polymers, neutron reflectometry

1 INTRODUCTION

The electromechanical response of ionic polymers to an applied electric field places charged systems in a position to be of immense use in a number of applications including flexible electronics, biomimetic devices, and nanofluidics [1],[2]. While the use of common ionic polymers such as Nafion as actuators has been thoroughly studied [3], the literature lacks a complete knowledge of the complex interplay of an electromechanical response and the chemical structure, morphology, and ion mobility of these charged systems. The actuating behavior of ionic polymer systems results from deformation due to electric/Maxwell stress (electrostatics of ion distribution) as well as viscous/hydrodynamic stress (properties of the polymer structure and chemical identity) [4],[5]. A fundamental understanding of how each of these parameters affects the electromechanical response would allow for the rational design of ionic polymer systems that give rise to specific functionality. To this end, we have developed an AB ionic diblock copolymer system to explore the factors described above.

We have utilized RAFT polymerization to synthesize the AB block copolymer Poly(1BDIMA-*b*-styrene), hereafter 1-BDIMA/PS, where the ionic B block contains charged imidazolium groups to impart electromechanical responsiveness and a polystyrene A block providing structural integrity to the film. The flexibility of this system allows not only the possibility for exchange of the counter-anions associated with the imidazolium ring, but by tuning the lengths of each block, it is possible to target a variety of thin film morphologies. Additionally, we have utilized fully deuterated styrene in the polymerization, which provides significant contrast to the hydrogenated ionic block when collecting neutron reflectivity profiles.

For the studies described here, the copolymer system has been prepared with a 70:30 ratio of ionic to polystyrene blocks, as confirmed by 13C NMR, with a PF_6 counter-anion. TOF-SIMS and neutron reflectometry (NR) measurements have indicated that thin films (~30 nm) prepared on Si substrates adopt a semi-lamellar morphology with an ionic block rich layer at the silicon-polymer interface and a mixed ionic/polystyrene layer at the polymer-air surface. The presence of the ionic block throughout the film depth provides a continuous path for ion movement, a trait that should benefit the electro-responsiveness of the material. Actuating behavior of the 1-BDIMA/PS system was confirmed by preparing a thick (~100 µm) membrane of the copolymer sandwiched between two gold leafs. Upon applying a potential of 1 V, the device bent towards the anode with an actuation curvature (inverse radius) of 0.16 mm^{-1}, consistent with migration of the counter-anions towards the cathode [6]. Additionally, simulations done on a similar system to the

polymer confirm the migration of counter-ions when exposed to an electric field. These results demonstrate that the 1-BDIMA/PS copolymer system is not only an excellent candidate for future electromechanical response studies, but that TOF-SIMS and NR would be ideal tools for determining how counter-anion and polymer motion contribute to the electro-responsiveness of this promising class of materials.

2 MATERIALS AND METHODS

2.1 Preparation of 1-BDIMA/PS

Poly(1BDIMAPF$_6$) macroCTA and Poly(1BDIMAPF$_6$-b-styrene) diblock copolymers were prepared by dissolving monomer, CTA and initiator in acetonitrile and degassed by purging the reaction mixture with Argon. The polymerization was performed at 65 °C and upon termination with air, the polymer was precipitated into ethyl acetate to yield a light brown solid. To identify the ratio of ionic to polystyrene blocks, 13C NMR was used to quantify signals arising from the deuterated styrene and imidazolium ring. The copolymer was determined to have a 2.5:1 molar ratio of ionic to polystyrene blocks.

2.2 Thin Film Analysis

Si wafers used as the supporting substrates for the thin polymer films were sonicated in acetone, isopropanol, and methanol (Fisher Scientific) for 5 min each before being dried under Ar (g). Wafers were then immersed in a piranha solution (1:3 30% hydrogen peroxide/concentrated sulfuric acid – *Caution, explosive in the presence of organic contaminants*) for 30 min, then rinsed with high-purity water (> 18 MΩ cm) and subsequently dried under Ar (g). Solutions of 3% wt/v of 1-BDIMA/PS dissolved in dimethylformamide (Fisher Scientific) were then spin-coated onto the clean Si substrates. The films were covered and annealed at room temperature in a fume hood for 18 hrs, then under vacuum at 120 C for 24 hrs. Ellipsometry (J.A. Woollam MC2000U) was used to determine thicknesses of the resulting films using an incident angle of 75° with respect to surface normal and data profiles were fit using a Cauchy model for the polymer layers.

To probe the thin film morphology as a function of depth, TOF-SIMS (TOF.SIMS.5 IonTOF) was used to measure the spin-coated polymer on 500 μm thick 1 cm^2 Si wafers (Silicon Quest Intl.). Regions 500 x 500 μm were sputtered with a low energy Ar ion-cluster gun (4 nA current, at 5 keV) while a primary Bi gun (30 nA current, at 30 keV) with a 5 μm spatial resolution and 0.005 Da spectral resolution probed a 200 x 200 μm area. In positive ion detection mode, D^+, H_2^+, and Si^+ were used to track the deuterated polystyrene block, hydrogenated ionic block, and the substrate surface, respectively. Data was processed using SurfaceLab (IonTOF) software and depth profiles were normalized to maxima.

NR measurements were done on the Liquids Reflectometer (BL-4B) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Si substrates used in these experiments (University Wafer) were 51 mm in diameter and 5 mm thick. Reflectivity was collected using a wavelength (λ) band of 2.5 Å < λ < 16.7 Å and discrete incident angles (θ) between 0.6 – 2.71°, achieving a wavevector transfer (q_z, Eq. 1) range of 0.008 - 0.2 Å^{-1}. Seven (λ, θ) settings were collected where incident

$$q_z = 4\pi/sin\theta \qquad (1)$$

beam slits maintained a constant dQ/Q resolution of 0.023 so that each dataset can be absolutely normalized into a single reflectivity curve. The resulting reflectivity is dependent on the structure and composition of the film normal to the surface and can be fit by a slab-model approach using layers of varying thickness, roughness, and scattering length density (SLD), where the SLD is the product of a material's chemical composition and it's mass density. Modeling of the reflectivity profiles was done using Motofit [7], where fitting used the thickness determined by ellipsometry as an initial constraint. The thickness, roughness, and SLD of each layer were varied to fit the reflectivity while minimizing a χ^2 error function and retaining feasible physical properties of the layers.

2.3 Molecular Dynamics

We adopted the Kremer-Grest (KG) bead-spring model to depict the diblock copolymer, for which the monomer beads interact through a Weeks-Chandler-Andersen (WCA) potential and were bonded with a finitely extensible nonlinear elastic (FENE) potential along the chain [8]. The detailed force field setting can be found elsewhere [8],[9]. While the 1-BDIMA/PS system has a 70:30 composition, initial modeling focused on characterizing a purely lamellar system and so a symmetric charged-neutral diblock copolymer, which formed a lamellar structure from phase separation was considered. Each copolymer chain consisted of 50 coarse-grained beads, with half being the charged block. The degree of ionization of the charged block was taken to be 20% so that one in every five beads along the charged block had a charge of +1e, e being the charge of an electron. Equal number of counter-ions (charge of -1e) were introduced to ensure global electroneutrality. Neutral beads of the copolymer possessed a fixed dipole moment, which was adjusted according to the chemical species of the monomer. Non-bonded beads and particles in the system interacted through short-range WCA repulsion and long-range electrostatic interactions. Simulations were performed using the LAMMPS molecular dynamics simulator [10],[11].

We first studied the self-assembly in a bulk system with a Langevin thermostat and a Nosé-Hoover barostat. Following the standard procedures described in Refs [8],[9], we determined the commensurate domain spacing

for the lamellar phase of the charged-neutral diblock copolymer melt (with polymer bead number density of 0.85). The domain spacing was set as the film thickness which was then bounded by two planar electrodes. The number density of the polymer beads in thin film is maintained the same as in the bulk case. An electric field was applied and using Langevin dynamics simulations, we examined the morphological response and charge distribution of the confined thin film system.

2.4 Macroscale Actuation

Membranes for actuator assemblies were prepared by casting 700 μL of a 30% wt/v solution of 1-BDIMA/PS in dimethylformamide into a Teflon mold 14 mm wide and 33 mm long. The solvent was allowed to evaporate for 72 hrs while covered on the bench top, and then 24 hrs covered in a fume hood. The membrane was then annealed at 120 C for 24 hrs. After cooling, the membrane was removed from the mold and pressed between two sheets of gold leaf (L.A. Gold Leaf, 24K, 120 nm) using 750 lbs of force for 30 sec. The resulting film was then cut into ~1.5 x 10 mm strips and tested on a custom-built station where curved segments of copper wire were used to clamp the membrane at one end, allowing free movement at the other. The clamping copper wires in contact with the gold leaf on either side of the membrane were also used as electrodes to apply a potential of 1 V (HP 6205B DC power supply) while movement was recorded using a camera. Measurements of the actuation were done using the image processing software Gwyddion, and actuation

$$I = 2r \sin \left(\theta / 2 \right) \qquad (2)$$

curvature (reported as inverse radius) was calculated from Eq. 2, where I is the chord length of the arc, θ is the arc angle, and r is the radius of the curve.

3 RESULTS AND DISCUSSION

3.1 Thin Film Morphology

To probe the film morphology TOF-SIMS was used to monitor the distribution of D^+, H_2^+, and Si^+ species throughout the film depth in positive ion detection mode (Figure 1). As the polystyrene block of 1-BDIMA was completely deuterated and the ionic block was fully hydrogenated, these species serve as unique markers for where these blocks lie normal to the substrate surface. Based on the intensity of D^+, the polystyrene block is largely present at the air-polymer interface and its presence drops off quickly. Signal from the H_2^+ ion indicates that the ionic block is co-present with the polystyrene at the air interface, but its signal continues to increase with the depth of the film, reaching a maximum near the Si interface.
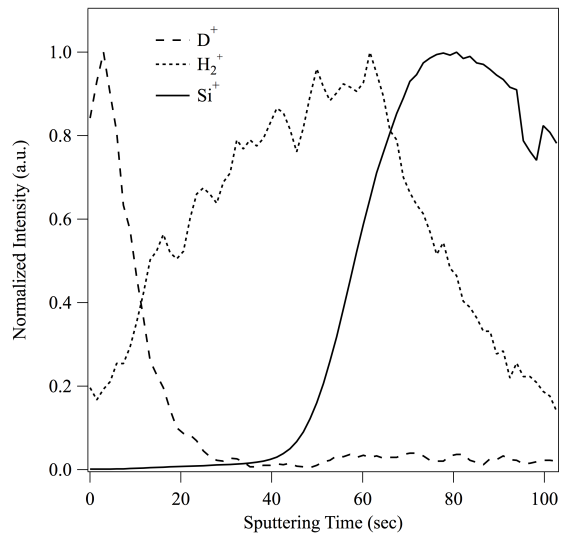

Figure 1: TOF-SIMS results showing normalized intensity of D^+, H_2^+, and Si^+ species as a function of sputtering time (film depth).
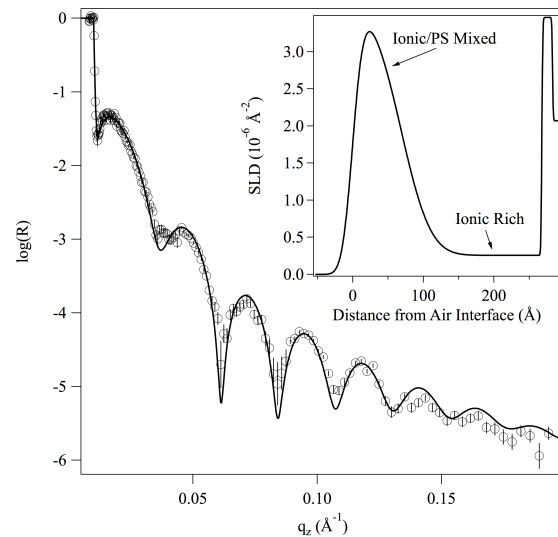

Figure 2: Neutron reflectivity data (points) along with the model fit (solid line) with an inset showing how the SLD varies as a function of distance from the air interface. The ionic block of the polymer segregates to the SiO_x surface, while a mixed ionic and polystyrene (PS) region exists at the air interface.

Initial ellipsometry measurements of the thin films yielded thicknesses of ~30 nm, and so these values were used as a starting point to fit the NR data. This constraint was consistent with an initial thickness estimate based on the Kiessig fringe spacing in the neutron reflectivity profile which suggested a total film thickness of ~25 nm. The resulting model for the reflectivity data is shown in Figure 2, where the inset shows how the SLD varies with the depth of the film. The main features of the inset indicate that the ionic portion of the polymer (SLD 0.25×10^{-6} Å^{-2}) segregates at the SiO_x interface, while a mixed layer of

polystyrene and ionic blocks (SLD of 3.66 x 10^{-6} Å^{-2}) exists at the air interface. For reference, the SLD of fully deuterated polystyrene is 6.46 x 10^{-6} Å^{-2} [12]. This morphology is consistent with phase diagrams of diblock copolymers with similar block ratios reported in the literature [13]. The NR and TOF-SIMS results both show that the ionic block of the copolymer is present throughout the film thickness, providing a continuous conducting path for ion movement that is beneficial to the electro-responsiveness of the material.

3.2   Diblock Simulations

The morphology of the polymer and the counter-ion distribution was monitored as a function of the electric field. For no electric field the charged polymer beads and the counter-ions are found to be near each other as shown in Figure 3, whereas strong partitioning between charged polymer beads and counter-ions was observed when an electric field of 14 LJ (~ 100 MV/cm) units was applied across the electrodes.
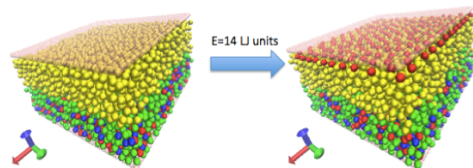

Figure 3: Morphology of the polymers and counter-ions as a function of applied electric field. Red beads are counter-ions, yellow beads belong to the neutral block, blue beads are the charged beads on the polymer and green beads are dipolar beads on the charged block.

3.3   Device Actuation

To confirm the electro-responsive nature of the copolymer, a 1 V potential was applied to a membrane of 1-BDIMA/PS sandwiched between two gold leafs. When applying a 1 V potential, the device bends with an actuation curvature of 0.16 mm^{-1}. While the magnitude of actuation curvature of this device is not as significant as other values in the literature [6], it is important to note that the membrane here was prepared without any addition of ionic liquid, which has been reported to enhance actuation [14].

4   CONCLUSION

We have developed an electro-responsive ionic diblock copolymer (1-BDIMA/PS) that adopts a semi-lamellar morphology as a thin film as confirmed by TOF-SIMS and NR. Both measurements indicate that the ionic block is present throughout the film thickness, providing an uninterrupted channel that should facilitate ion movement, thus improving the electro-responsiveness of the material. When prepared as an actuator, the device bends when a 1 V potential is applied with an actuation curvature of 0.16 mm^{-}

1. Initial simulations on a lamellar copolymer have also indicated counter-ion mobility when exposed to an electric field. Collectively, these results demonstrate the potential for the 1-BDIMA/PS copolymer to be used as a platform for systematically investigating the factors that drive the electromechanical response of ionic materials. Future research will focus on using neutron reflectometry to observe polymer and counter-anion mobility during *in situ* electric field measurements and expanding simulations to more accurately model experimental conditions.

REFERENCES

[1]   Shahinpoor, M.; Bar-Cohen, Y.; Simpson, J. O.; Smith, J. Smart Mater. Struct. 7, R15, 1998.
[2]   Hu, J.; Meng, H.; Li, G.; Ibekwe, S. I. Smart Mater. Struct. 21, 53001, 2012.
[3]   Duncan, A. J.; Leo, D. J.; Long, T. E. Macromolecules 41, 7765, 2008.
[4]   Zhenyi, M.; Scheinbeim, J. I.; Lee, J. W.; Newman, B. A. J. Polym. Sci. Part B Polym. Phys. 32, 2721, 1994.
[5]   Michel, S.; Zhang, X. Q.; Wissler, M.; Löwe, C.; Kovacs, G. Polym. Int. 59, 391, 2010.
[6]   Jangu, C.; Wang, J. H. H.; Wang, D.; Sharick, S.; Heflin, J. R.; Winey, K. I.; Colby, R. H.; Long, T. E. Macromol. Chem. Phys. 215, 1319, 2014.
[7]   Nelson, A. J. Appl. Crystallogr. 39, 273, 2006.
[8]   Grest, G. S.; Lacasse, M. D.; Kremer, K.; Gupta, a M. J. Chem. Phys. 105, 10583, 1996.
[9]   Seo, Y.; Brown, J. R.; Hall, L. M. Macromolecules 48, 4974, 2015.
[10]   Plimpton, S. J. Comput. Phys. 117, 1, 1995.
[11]   http://lammps.sandia.gov.
[12]   Mitamura, K.; Yamada, N. L.; Sagehashi, H.; Torikai, N.; Arita, H.; Terada, M.; Kobayashi, M.; Sato, S.; Seto, H.; Goko, S.; Furusaka, M.; Oda, T.; Hino, M.; Jinnai, H.; Takahara, A. Polym. J. 45, 100, 2012.
[13]   Mai, Y.; Eisenberg, A. Chem. Soc. Rev. 41, 5969, 2012.
[14]   Liu, Y.; Lu, C.; Twigg, S.; Ghaffari, M.; Lin, J.; Winograd, N.; Zhang, Q. M. Sci. Rep. 3, 973, 2013.