Imidazolium sulfonate-containing pentablock copolymer–ionic liquid membranes for electroactive actuators†

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Block copolymer–ionic liquid composite materials emerge as promising candidates for electromechanical transducer applications. Herein, a novel imidazolium sulfonate-containing pentablock copolymer–ionic liquid composite was prepared and fabricated into thermally stable electroactive actuators, which exhibit effective actuation response under a low applied potential of 4 V.

Electromechanical polymeric transducers have received significant attention recently for many emerging applications, including electromechanical actuators, sensors, electro-active coatings, and artificial muscles. Desirable physical properties for polymeric membranes in electromechanical transducers include high ionic conductivity, tunable modulus versus temperature behavior, efficient response at relatively low voltages (<5 V), and facile fabrication processes.1 However, only a few families of polymeric materials fully satisfy these requirements, and in most instances, anionic ionomers with random placement of sulfonates and carboxylates are leading candidates. Moreover, sulfonic acid containing polymers suffer from poor thermal stability due to low temperature degradation reactions.2 There remains a unique opportunity for the design of multiphase block copolymers wherein the nanoscale morphology presents (1) an imidazolium sulfonate, polar phase for ion-conductivity in the presence of added electrolyte, and (2) a nonpolar phase that imparts acceptable thermomechanical performance.

Block copolymer–ionic liquid composite membranes have emerged as promising candidates for electromechanical transducer applications. Due to microphase separation of different immiscible sequences, block copolymers self-assemble into nanostructured materials and exhibit a combination of multiple properties.3 Tailoring sequence length, molecular weight distribution, and chemical composition of each block generates various nanostructured materials for applications in water purification, fuel cell membranes, energy harvesting, and energy storage.4,6 Spontak et al. recently described the fabrication of electroactive membranes using non-neutralized sulfonic acid-containing pentablock copolymers swollen with high levels of ethylene glycol and glycerol (~450 and ~500 wt%, respectively).7 However, the critical morphological and dynamic mechanical properties of the membranes were not described. In order to achieve effective actuation response (high free displacement and blocked force) at low applied potentials (<4 V), block copolymer-diluent materials with well-defined nanostructured morphology and good mechanical properties are necessary. Our research group has demonstrated the potential synergy of charged copolymers with imidazolium and phosphonium ionic liquids (ILs), which are defined as salts with melting temperatures below 100 °C. The introduction of ionic liquids into charged copolymer membranes improves the performance of electromechanical polymeric transducers due to their negligible volatility, high ionic conductivity, and high electrochemical and thermal stabilities.8,9 Therefore, a combination of block copolymers and ILs affords a unique platform to develop tunable membranes for electromechanical transducers. More interestingly, charged block copolymers enable preferential incorporation of ILs into the IL-compatible phase to form an organized IL dispersion in the polymeric matrix, leading to high ionic conductivity.9,10 However, block copolymer–IL composite membranes, which simultaneously possess high ionic conductivity and excellent mechanical strength, are rarely reported in the literature.

Recent studies revealed that imidazolium-containing polymers showed promise as electromechanical transducers due to their reasonably high ionic conductivity, acceptable affinity to ionic liquids, and tailored structures and morphologies.11,12 Long et al. developed a series of N-vinylimidazolium- and vinylbenzylimidazole-based homopolymers with tailored ionic conductivity and thermal properties.13 Gibson et al. investigated imidazolium-containing polyesters for high ionic conductive materials.14 However, most recent studies focused on imidazole-containing homopolymers, random copolymers, and diblock copolymers. In order to achieve desired mechanical properties, triblock (ABA) and multiblock copolymers are particularly interesting candidates. Herein, we described a facile strategy to prepare imidazolium-containing pentablock copolymers from NexarTM, which is a commercially available sulfonated pentablock copolymer from Kraton Polymers LLC.15 Combination of living anionic polymerization with a selective sulfonation strategy affords NexarTM well-defined pentablock architectures containing a selectively sulfonated polystyrene central block with an ion exchange capacity (IEC) at 2.0 (Fig. 1, acid form). IEC is defined as the...
milliequivalents of sulfonic acid per gram of polymer (mequiv. per g). Nexar™ serves as a precursor for novel imidazolium-containing sulfonated pentablock ABCBA copolymers through facile and quantitative neutralization of sulfonic acid sites with various N-alkyl imidazoles (Fig. 1). Modified Nexar™ contains a hydrophilic, imidazolium polystyrene sulfonate central (C) block that enables incorporation of ionic liquids for ion transport, hydrogelated polystyrene (B) blocks that impart membrane flexibility and elasticity, and hydrophobic poly(tert-butyl styrene) (A) blocks that serve as physical crosslinks to provide mechanical strength in the presence of ILs.

Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) revealed the microphase-separated morphologies of imidazolium-neutralized Nexar™ with 1-ethylimidazolium cations (KP-SO₃[EtIm]+). Fig. 2a shows the FESEM image of KP-SO₃[EtIm]+ cast from a dilute cyclohexane solution (1 mg mL⁻¹) onto a silicon wafer. FESEM demonstrated that KP-SO₃[EtIm]+ formed uniformly dispersed spherical domains at the nanoscale (~30 nm), which presumably resulted from the micellar structures of KP-SO₃[EtIm]+ in cyclohexane. Winey et al. previously characterized the solution morphology of the sulfonic acid form of Nexar™ in cyclohexane and demonstrated spherical micellar structures using transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). These earlier efforts demonstrated that the polystyrene sulfonate central block formed a dense core of spherical micelles, and hydrogenated polystyrene and poly(tert-butyl styrene) blocks formed soft coronas. AFM confirmed that KP-SO₃[EtIm]+ solid membranes displayed well-defined microphase-separated morphology (Fig. 2b). Lighter regions in AFM images represent hard phases, and darker regions represent soft phases. In light of the micellar structures observed in FESEM, the spherical structures, which are uniformly distributed in the AFM phase image, arise from the polystyrene sulfonate central blocks. In a similar fashion to Winey et al., the bulk morphology of KP-SO₃[EtIm]+ films was strongly related to solution morphology. Future complementary morphological characterization will fully understand the microphase separation behavior of these imidazolium-containing pentablock polymers.

Swelling KP-SO₃[EtIm]+ films with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIm TfO) (Fig. 3a) generated pentablock copolymer–ionic liquid composite membranes.‡ 1Ls impart enhanced conductivity without volatilization, which is necessary for the fabrication of robust electroactive devices. IL uptake was determined according to the following equation: wt% uptake = (m - m₀)/m₀, where m₀ is the initial film mass and m is the swollen film mass. Fig. 3b shows the swelling behavior of KP-SO₃[EtIm]+ membranes in EMIm TfO as a function of time. EMIm TfO gradually swelled into the membrane with time and reached a maximum uptake near 35 wt %. Previous studies in our laboratories indicated that the IL swelling behavior of polymer membranes strongly depended on polymer structure, ionic liquid type, sample dimensions, and swelling conditions.** Mechanical property characterization using dynamic mechanical analysis (DMA) revealed that KP-SO₃[EtIm]+–EMIm TfO composite membranes displayed well-defined rubbery plateaus with high storage moduli near 700 MPa. A high modulus is critical for generating larger force during actuation. All samples showed two distinct thermal transitions due to a microphase-separated morphology (Fig. 3c). Thermal transitions near ~35 °C and 110 °C corresponded to hydrogenated polystyrene and poly(tert-butyl styrene), respectively, which were independent of ionic liquid uptake (Fig. 3d). This observation indicated that EMIm TfO preferentially located in the imidazolium-containing polystyrene sulfonate phase. Moreover, KP-SO₃[EtIm]+–EMIm TfO composite membranes showed reduced rubbery plateau moduli relative to ionic liquid-free KP-SO₃[EtIm]+ membranes due to plasticization.

Fabrication of electromechanical actuators with KP-SO₃[EtIm]+–EMIm TfO composite membranes employed a layer-by-layer, direct assembly method. A KP-SO₃[EtIm]+–EMIm TfO composite membrane of 40 μm thickness was placed between a 30-layer conductive network composite (CNC) layer and a 3 nm anionic gold nanoparticle layer. A layer-by-layer method affords uniform CNC coatings on ionomeric membranes with precisely controlled thickness at the nanoscale. Fig. 4a illustrates the structure of an electromechanical actuator, which includes a central, ionomeric membrane, CNC layers, and gold electrode layers. The actuator mechanically deforms (actuates) upon an applied potential. Fig. 4(b1–b4) shows the actuation performance under an applied potential of 4 V under ambient conditions (23 °C, ~43% relative humidity). The data confirm that the device deformed effectively upon an applied potential of 4 V. Fig. 4c shows the actuator curvature of the device as a function of time. The actuator containing KP-SO₃[EtIm]+–EMIm TfO composite membranes bent toward the anode and reached a maximum curvature of 0.26 mm⁻¹ at 20 s. The device under continued applied potential decayed back to the original position at t = 46 s and further bent to the cathode side with a final curvature of 0.67 mm⁻¹ at t = 120 s. This actuation mechanism was described in the earlier literature, which is unique from typical back-relaxation behavior. Zhang et al. proposed a two-carrier model to explain this phenomenon, where both cations and anions were mobile and accumulated on electrodes during bending. However, mobile cations

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and anions accumulated on electrodes at different rates due to different ion sizes and mobility, resulting in different bending directions at different times. However, this model does not fully explain the actuation behavior of KP-SO$_3$[EtIm]$^-$–EMIm TfO actuators, where volume of EMIm cations (7.8 × 5.8 × 3.3 Å$^3$) is larger than that of TfO$^-$ anions (4.4 × 4.4 × 3.3 Å$^3$), while the backward bending curvature is approximately two times higher than the forward bending curvature. The larger backward bending curvature is attributed to the formation of an anionic complex, which generates strain more effectively than single anions.

Madsen et al. further investigated the ionic association and diffusion of EMIm TfO in a Nafion® membrane using NMR. They demonstrated that EMIm cations moved sustainably faster than TfO$^-$ anions, which was presumably due to the formation of negatively charged triple ions. A fundamental understanding of the ion transport mechanism in a KP-SO$_3$[EtIm]$^-$–EMIm TfO actuator represents an important future effort for this novel class of actuators.

In summary, we described a facile materials strategy to fabricate electromechanical transducers from a pentablock copolymer–ionic liquid composite membrane. Imidazolium-containing pentablock copolymers were prepared from a commercially available sulfonated pentablock copolymer, and the ionic membranes possessed well-defined chemical compositions and microphase-separated morphologies. Combination of imidazolium-containing pentablock copolymers with EMIm TfO ionic liquids generated novel nanocomposite materials, which possessed good mechanical properties and exhibited actuation response with the application of a low applied potential (4 V). This study expands the class of multiphase copolymers that are suitable for electromechanical transducer applications. Fundamental understanding of the actuation behavior of pentablock copolymer–ionic liquid composite membranes will lead to optimal electroactive materials for electromechanical transducers in the future.

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Notes and references

‡ Material: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIm TIO) (>98%) and N-ethylimidazole (99%) were purchased from Aldrich and used as received. A sulfonated pentablock copolymer was synthesized and provided by Kraton Polymers LLC. The neutral block copolymer poly(tert-butyl styrene-b-styrene-b-hydrogenated isoprene-b-tert-butyl styrene) was synthesized through the sequential living anionic polymerization of tert-butyl styrene, isoprene, styrene, and tert-butyl styrene, and a subsequent hydrogenation of the isoprene blocks. The corresponding sulfonated pentablock copolymers were obtained butyl styrene, and a subsequent hydrogenation of the isoprene blocks. The corresponding sulfonated pentablock copolymers were obtained through a selective sulfonation of the styrene middle block.

Preparation of KP-SO$_3$[EtIm]$^+$ membranes: A sulfonated pentablock copolymer solution in cyclohexane (10 wt%) was added to a two-necked, round-bottomed flask equipped with a magnetic stir bar. A calculated amount of N-ethylimidazole (1:1 stoichiometry) was added dropwise to the flask under magnetic stirring (800 rpm). The solution was stirred at 23 °C for 24 h and directly cast on a Mylar/C$_{210}$ structure: gold–CNC–KP-SO$_3$[EtIm]+–CNC–gold. Finally, compression molded at 700 psi for 20 s between 50 nm thick gold layers. CNC layers serve as reservoirs for ionic liquid and meanwhile controlled thickness at the nanoscale through adjusting the number of electrostatic self-assembly, generating uniform coatings with well-controlled thickness at the nanoscale through adjusting the number of layers. CNC layers serve as reservoirs for ionic liquid and meanwhile reduce the sheet resistance. In the second step, the CNC-coated membrane was soaked in an EMIm TIO ionic liquid at 50 °C for 10 h and finally compression molded at 700 psi for 20 s between 50 nm thick gold foils to prepare the actuator. The resulting actuator device has a five-layer structure: gold–CNC–KP-SO$_3$[EtIm]+–CNC–gold. Characterization: Atomic force microscopy (AFM) was conducted on a Veeco MultiMode AFM using a tapping mode under ambient conditions. Field emission scanning electron microscopy (FESEM) was performed on a LEO (Zeiss) 1550 with a 4 mm working distance. Dynamic mechanical analysis (DMA) measurements were performed on a TA Instruments Q800 dynamic mechanical analyzer in the film tension mode at a frequency of 1 Hz and a temperature ramp of 3 °C min$^{-1}$ over the range –110 to 120 °C.