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Polymer electrolyte membranes from fluorinated polyisoprene-block-sulfonated polystyrene: Microdomain orientation by external field

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ABSTRACT

In this study, block copolymer ionomers of the cesium salt (20 mol %) of fluorinated polyisoprene-block-sulfonated polystyrene were spin cast into membranes and annealed under an electric field of ~40 V/μm at 130 °C for 24 h. The effect of this treatment was a 2.5 times increase in the ionic conductivity as measured by electrochemical impedance spectroscopy, under all humidity conditions measured. This can be attributed to the increased connectivity of the ionic domains of the block copolymers. This E-field alignment technique may thus find application in the fabrication of nanostructured polyelectrolytes with enhanced charge transport capacity.

1. Introduction

The use of external fields to orient the different components of polymeric systems has gained significant interest over the last decade. This technique involves the application of an external field to induce structural rearrangement of a material to achieve preferential texture in a desired direction. Different types of external fields have been employed including shear [1,2], electric fields [3–5], solvent evaporation [6,7], mechanical constraints [8,9], and magnetic fields [10]. These techniques commonly employ the interaction of the field with the anisotropic portions of the materials composed of different multi-component materials such as blends, block copolymers, or polymer-nanoparticle mixtures.

The purpose of such microdomain orientation is typically to enhance orientation-dependent properties, and thus these methods have found application in the fabrication of templating nanowire arrays [11,12], photonic crystals [13,14], and improved gaseous permeability [15]. The effective diffusion of small molecules through polymeric microdomains has been shown to vary inversely to the square of tortuosity [16], where tortuosity is a measure of the degree of twisting of the domains. In essence, a block copolymer with oriented domains has been shown to have much higher transport of a penetrant small molecule in the direction of orientation.

This same approach has been applied to the improvement of ionic conductivity. Studies by Weiss and co-workers [17,18] showed that a blend of sulfonated poly(ether ketone ketone) ionomer and neutral poly(etherimide) cast under an electric field (E-field), yielded a morphology with the ionic component oriented in the direction of the E-field (perpendicular to the plane of the membrane) and resulted in orders of magnitude increase in ionic conductivity. Also LiI:poly(ethylene oxide) (PEO)-based solid polymer electrolyte for batteries showed one order of magnitude increase in Li^{+} ion conductivity upon orientation of the PEO crystalline chains, by incorporation of magnetic particles and application of a magnetic field [19]. Furthermore, it has been predicted that an orientation of block copolymer ionomer domains in the direction of desired ionic conductivity would enhance their utility as polymer electrolyte fuel cell membranes [20].

Block copolymers are particularly well-suited for microdomain orientation by external fields due to their predictable formation of microstructures with anisotropic domains, such as lamellae or hexagonally packed cylinders. Much work has been done on the orientation of block copolymers using E-Fields. Most of the work

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has centered on polystyrene-*block*-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymers [3,5,21,22], and their complexes with lithium salts [23].

The driving force for the alignment of block microdomains is due to the dielectric constant difference between the dissimilar blocks. Recent experimental studies in the melt have suggested that disordering of the original lamellar morphology is followed by rotation of the smaller grains formed in the direction of the applied E-field [24,25], whereas studies from solution suggest the latter step is preceded by defect translation [26]. These suggested pathways have been corroborated by simulation [27,28].

Few studies have been reported on the orientation of ionomers by any external field [29,30]. This has been found to be a nontrivial task as the ionic aggregation of the charged sites severely limited chain mobility in nematic liquid crystal domains. Alternatively track-etched membranes with pores oriented normal to the plane of the membrane have been filled with ionomers, yielding significant increase in ionic conductivity as compared to isotropic membranes [31,32]. The work reported herein is focused on the orientation of block copolymer ionomer domains normal to the plane of membranes formed from them and investigation of the resultant effects on proton conductivity.

2. Experimental section

2.1. Materials

The synthesis and characterization of fluorinated polyisoprene-*block*-sulfonated polystyrene (FISS) materials have been described in detail elsewhere [33]. The precursor polystyrene-*block*-polyisoprene (PS-PI) diblock copolymer used in this work was anionically polymerized with molecular characteristics: Mw = 27,000, PDI = 1.05, 50 mol% PS. The fluorinated samples had the PS block sulfonated to 20 mol%, as determined by ^{1}H NMR, and subsequently 100% neutralized to the cesium salt form (see Scheme 1 for the structure). This sample will be referred to as FISS-CS20 hereafter. SEBS (Kraton G1650M; 30 wt% PS) was obtained from Kraton Polymers.

2.2. Preparation of membranes

Membranes from the FISS-CS20 samples were prepared by spin coating a 5 wt% solution in tetrahydrofuran (THF) onto a silicon substrate on which gold had been deposited. Spin speed was 1000 rpm and the solution was left to spin for 5 min. The resultant film was ~500 nm in thickness as determined by a Dektak profilometer. A piece of this membrane coated wafer was reserved as the as-cast sample.

2.3. E-Field alignment experiments

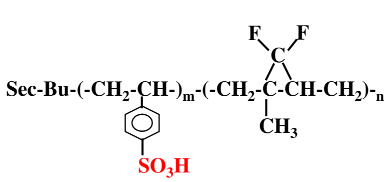
An aluminized Kapton film was used as the upper electrode, having a ~25 μm layer of crosslinked polydimethylsiloxane (PDMS) (Slygard) cured on the Kapton side. This layer was necessary to establish an intimate contact between the top electrode and the copolymer film, thus eliminating insulating air gaps. This sandwiched capacitor was placed in an oven under a nitrogen flow blanket and annealed at 130 °C for 24 h under an E-field strength of ~40 V/μm, as shown in Fig. 1. It is important that this alignment process take place above the Tg of the material (about 45 °C), which was reported previously [34], along with full DSC analysis. These samples show a Tg, but no other transitions such as melting or changes in cluster structure were observed in the thermograms. The E-field was typically applied before the oven was heated. The entire setup was quenched to room temperature before the applied E-field was removed. To prove the effectiveness of this setup, some preliminary work has also been done on rubbery di- and tri-block copolymers of polystyrene-block-polyisoprene, as well as polystyrene-block-polyethylene-co-butylene-block-polystyrene (SEBS), as shown in Fig. 2. Here the PS domains appear dark because of staining with ruthenium tetraoxide.

2.4. Transmission electron microscopy (TEM)

TEM was performed on samples of the protonated and cesium counterion materials. After removal of the Kapton and PDMS overlayers, a thin layer of gold, and then carbon was sputtered onto the surface of the sample membrane. The gold serves as a membrane edge marker, while the carbon serves as an epoxy diffusion barrier. Samples were embedded and cured in room temperature cure epoxy for 24 h. The membrane was then separated from the substrate by exposure to liquid nitrogen, and subsequently 50 nm thin sections of the sample were cut across the thickness of the membrane (E-field direction) using a Leica Ultracut UCT cryomicrotome at −120 °C. These were then collected on copper grids and stained with RuO_4 vapor for 1 h. This staining method is selective for the unsulfonated polystyrene domains. TEM images were obtained using a JEOL-2010 microscope operating at an accelerating voltage of 200 kV in the bright field mode.

2.5. Ionic conductivity

Ionic (cesium) conductivity of the membranes was measured by means of two-probe complex impedance spectroscopy techniques, which measure conductivity normal to the plane of the membrane. Pieces of both the as-cast and E-field treated samples still on the gold plated substrates were immersed in a chamber at 50% relative humidity (RH) for 24 h, and then rapidly sandwiched between another piece of gold coated silicon wafer (gold face touching membrane). A Solartron 1252A frequency response analyzer linked to an SI 1287 electrochemical interface was used within a frequency range of 0.1 and 300 kHz, and the value of the real intercept in the imaginary versus real impedance plot (Bode plot) in the high frequency range was taken as the bulk resistance of the membrane



Scheme. 1. Generalized structure of FISS block copolymer. The PI block is quantitatively fluorinated using difluorocarbene while only a portion of the PS units in the styrenic block bear the sulfonic acid group (shown in red). The H in the sufonic acid group may be exchanged for Cs.

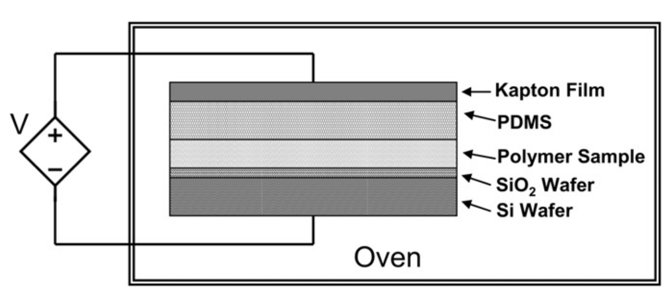


Fig. 1. Schematic of electric field alignment experimental setup.