Anisotropic Ionic Conductivity in Uniaxially Oriented Perfluorosulfonate Ionomers

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Introduction

Orientation of polymers, as well as the preparation and characterization of ordered polymeric architectures, has been the focus of recent research efforts.[1] For example, previous studies have shown that the electrical conductivity of conjugated polymers may be enhanced by molecular-level orientation.[2] In addition, a variety of liquid-crystalline polymeric (LCP) systems containing mesogenic units within the main chains[3] or as pendent side chains[4] may be processed in an ordered state for the purpose of imparting anisotropic properties (i.e., in applications such as ultrahigh-strength fibers and electrooptic devices).

Recently, Dang and co-workers[5] showed that rigid-rod, liquid-crystalline polymers may be functionalized with sulfonate groups to produce molecularly ordered, ionically conductive materials. Furthermore, thin films cast from sheared solutions of these polymers were found to exhibit anisotropic ionic conductivity. In these LCP systems, the conductive pathway persists and is apparently arranged by the self-assembly of the mesogenic units prior to film formation and "locked-in" by the high-T_g polymeric matrix. While this study has demonstrated that anisotropic ionic conductivity is possible via molecular orientation of high-T_g, LCP systems, this persistent behavior (i.e., anisotropic conductivity in the absence of an external orientational stress) has not been observed in more traditional ionically conductive polymers.

Perfluorosulfonate ionomers (PFSIs, e.g., Nafion) have been used as solid polymer electrolytes (SPEs) in a variety of industrial electrolytic processes.[6] The efficient cation conduction and permselectivity of these ionomers has been attributed to the material's unique supramolecular structure.[7-9] On the basis of wide- and small-angle X-ray scattering studies,[8-10] the morphology of PFSIs has been found to include crystalline tetrafluoroethylene segments of the backbone and relatively large (ca. 40 Å in diameter) ionic aggregates of the side-chain sulfonate groups. We have previously shown that the ionic aggregates in PFSIs act as multifunctional electrostatic cross-links which can be weakened by neutralizing the ionomer with tetrabutylammonium (TBA^+) counterions.[10] Of specific importance to this investigation, these diminished Coulombic interactions increase the melt-flow character of the polymer relative to that observed with PFSIs containing alkali-metal cations (i.e., the cations typically used in SPE applications).[10] This change in melt-flow behavior allows for permanent deformation (i.e., chain flow) when the membranes are subjected to uniaxial stress. In contrast, the strong electrostatic cross-links in PFSIs containing small inorganic ions yield an elastic behavior that would tend to restore the isotropic morphology after removal of the extensional stress.[10]

Previous studies of ionomer deformation[8,11-15] have shown that uniaxial extension alters the spatial distribution of ion pairs and aggregates and/or affects the general shape of the ionic domains. Thus, in agreement with these fundamental results, it is reasonable to expect that changes in the bulk properties of PFSIs may be realized if uniaxial extension has a consequential effect on the nanoscale organization of the ionic domains. In this communication, we report a procedure for altering the morphology of PFSI membranes that yields a material exhibiting anisotropic ionic conductivity.

Experimental Section

Preparation and Orientation of Melt-Processed Films. The PFSI membranes (Nafion 117, 1100 EW, from E. I. DuPont de Nemours & Co.) were precleaned in refluxing 8 M HNO_3, washed with deionized water, and then neutralized with a stoichiometric amount of tetrabutylammonium hydroxide (Aldrich). A dry, melt-processable powder of TBA^+-form Nafion was prepared by first dissolving the neutralized membranes in a mixed solvent of methanol, propanol, and water (30:30:40 by volume) in a Parr high-pressure reactor at 250 °C. The hydrophobic PFSI was then precipitated from solution by "steam-stripping" in boiling water.[10] The resultant TBA^+-form Nafion was dried, ground into a fine powder, and then pressed into membranes (ca. 0.2 mm in thickness) on a heated Carver laboratory press at ca. 250 °C.

Small samples of approximately 2 cm^2 were cut from the pressed films and stretched at ca. 200 °C, to extensional ratios (λ_b = final length/initial length) ranging from 1.0 to 5.4. These oriented films were then air-cooled to room temperature and removed from the stretching device. Note that during the high-temperature deformation, the lateral dimension of the samples tapered slightly; in an attempt to select for regions containing the highest degree of uniaxial orientation (for a given extensional ratio) all morphology and property analyses were performed on segments which were cut from the center of the stretched region.

Samples prepared for the conductivity measurements were pressed between polished steel plates to obtain very smooth

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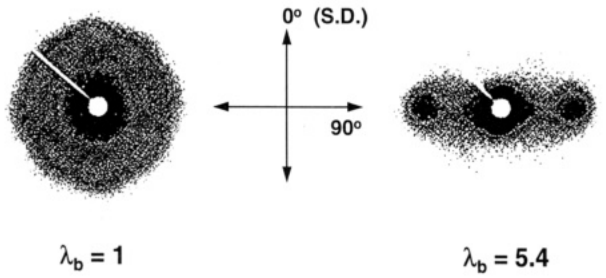

Figure 1. Two-dimensional SAXS patterns of melt-pressed and uniaxially oriented TBA$^+$-form Nafion (λ_b = stretched length/initial length). The stretched direction (S.D.) is aligned with the azimuthal angle $\mu = 0°$.

surfaces. These films were stretched, at ca. 200 °C, to an extensional ratio of 3.2 and then converted to the Na$^+$ form. In the Na$^+$ form, PFSIs imbibe water (which enhances charge mobility) and become efficient ionic conductors. The TBA$^+$-to-Na$^+$ form conversion was accomplished by first stirring the films in 4 M H_2SO_4 in methanol for 12 h (this step converts the films to the acid form) followed by neutralization in aqueous NaOH. Due to significant differences in solvent swelling between the TBA$^+$ and Na$^+$ form PFSIs, the uniaxial dimension of the oriented films was maintained by use of a Kel-F clamp during the complete conversion process. After removal from the clamp, no changes in the dimensions of the converted membranes (e.g., retraction) were observed.

Characterization. Surface conductivity measurements were conducted on hydrated, Na$^+$ form films using a Hewlett-Packard 4192A-LF AC impedance analyzer at 5 Hz with a bias of 1 V. All measurements were performed on free-standing membranes (i.e., extensional stress was removed prior to analysis). The surface conductivity probe consisted of an array of interdigitated, parallel gold fingers, separated by a distance of 0.33 mm. To evaluate the anisotropic conductivity, the probe was positioned onto the hydrated films (with a constant pressure) such that the gaps between the gold-finger electrodes were aligned in directions either parallel or perpendicular to the direction of orientation. To obtain a pair of measurements, the probe alignment was rotated between the parallel and perpendicular directions. The anisotropic conductivity results reported here represent an average of 13 pairs of measurements at different positions on the surfaces of the PFSI films.

Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) data were obtained using a Siemens XPD-700P polymer diffraction system equipped with a two-dimensional, position-sensitive area detector. The sample-to-detector distances for the SAXS and WAXD studies were 49 and 10 cm, respectively. All samples were free-standing, and the SAXS/WAXD data were collected in the transmission mode.

Results and Discussion

Morphology of Oriented PFSIs. Figure 1 compares the two-dimensional SAXS patterns for TBA$^+$-form Nafion in the as-processed and uniaxially oriented states. For the unoriented sample ($\lambda_b = 1$), the isotropic SAXS data show a faint outer ring of maximum intensity at a scattering angle that corresponds to a Bragg spacing of ca. 5.0 nm. This SAXS maximum has been attributed to scattering from the ionic aggregates with a distribution of correlation lengths related to interaggregate dimensions.[8,16] As the film is stretched (λ_b = 5.4), anisotropy develops in the scattering pattern. On the basis of previous SAXS studies of oriented ionomers[14,15] and our recent results from infrared dichroism[17] and dielectric relaxation studies,[18] this anisotropic scattering may be attributed to an elongation of the ionic domains in the direction of uniaxial extension.

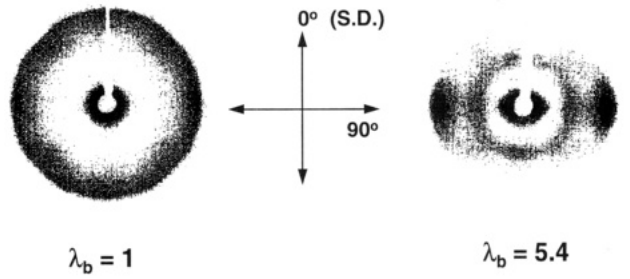

Figure 2. Two-dimensional WAXD patterns of melt-pressed and uniaxially oriented TBA$^+$ form Nafion (stretched length-initial length). The stretched direction (S.D.) is aligned with the azimuthal angle $\mu = 0°$.

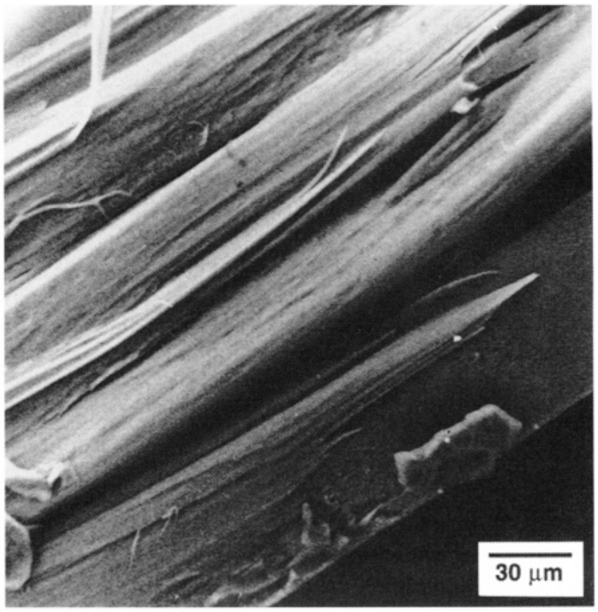

Figure 3. Scanning electron micrograph of a freeze-fractured surface of a highly oriented, TBA$^+$ form Nafion membrane (λ_b = ca. 6).

The effect of uniaxial extension on the WAXD profiles shown in Figure 2 is similar to that observed with SAXS; however, the diffuse ring from the unoriented sample in Figure 2 is attributed to a weak crystalline reflection, at $2\theta = 18°$, which is superimposed as a shoulder on a broad amorphous halo (ca. $2\theta = 12°-22°$).[8,11] As the sample is uniaxially extended to λ_b = 5.4, these data show that both the amorphous and crystalline domains are "locked" into an orientation aligned with the direction of extension. As further evidence of this chain orientation, scanning electron microscopy of a freeze-fractured, oriented sample (Figure 3) reveals fibrillar-like texture in the stretched direction. This persistent texture suggests matrix chain orientation and is consistent with the nature of poly(tetrafluoroethylene) which tends to form fibrils upon stretching.[19]

Anisotropic Conductivity of Oriented PFSIs. Once the ionomer is uniaxially extended, it may be converted from the TBA$^+$ form to one containing small

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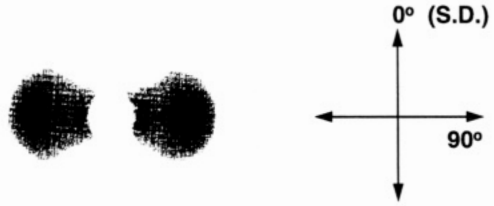

Figure 4. Two-dimensional SAXS pattern of a uniaxially oriented Nafion membrane in the Na^+ form ($\lambda_b = 3.2$). The sample was oriented in the TBA^+ form and then converted to the Na^+ form prior to SAXS analysis. The stretched direction (S.D.) is aligned with the azimuthal angle $\mu = 0°$.

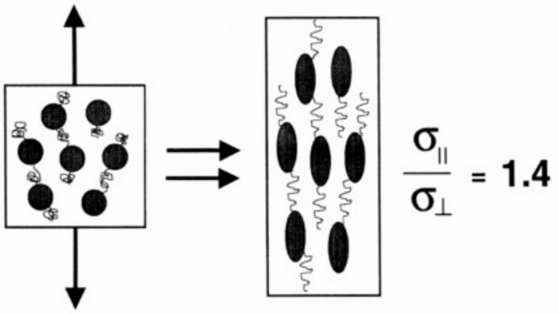

Figure 5. Schematic representation of the effect of uniaxial orientation on the postulated morphology and observed surface conductivity of extended Nafion membranes.

inorganic ions (e.g., Li^+, Na^+, K^+). The anisotropic SAXS data in Figure 4 demonstrate that the oriented morphology of the stretched samples can be maintained when the membranes are converted to the Na^+ form. While the qualitative appearance of the SAXS pattern in Figure 4 is comparable to that shown in Figure 1 (i.e., both patterns are anisotropic), it is interesting to note that the peaks of maximum intensity for the Na^+ sample (Figure 4) are slightly broader and occur at lower scattering angles relative to those of the TBA^+ sample. These observations indicate a moderate relaxation in the degree of orientation and a change in the scattering dimensions upon conversion to the Na^+ form. To better understand these differences, we are currently investigating the systematic effects of orientation and conversion on PFSI morphology.

Figure 5 schematically illustrates the proposed morphological changes that occur upon uniaxial extension; the shaded structures represent the ionic domains (i.e., clusters[7,8]) and the coils represent the polymer chains between ionic aggregates. Note that in the actual membranes, the phase boundaries between the ionic and matrix domains are not as discrete as illustrated in Figure 5; the matrix phase has been proposed to contain side chain ether linkages and residual sulfonate groups.[9]

After uniaxial extension, surface conductivity measurements made parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the axis of orientation show that ionic conductivity in the direction parallel to the stretching direction was 40% greater than the conductivity in the perpendicular direction (i.e., $\sigma_{\parallel}/\sigma_{\perp} = 1.4$). Since mobile cations must traverse both the ionic and matrix domains during bulk conduction at low frequency, it is reasonable to expect that this anisotropic conductivity has a contribution from oriented ionic aggregates and oriented matrix polymer chains. In contrast, it is important to note that *isotropic* conductivity was observed in the unoriented, melt-processed and unoriented, as-received membranes.

Conclusions

Uniaxial extension of TBA^+ form PFSI membranes at elevated temperatures results in a material with an oriented morphology which persists after the samples are removed from the extensional stress. This oriented morphology is proposed to consist of elongated ionic domains and oriented polymer chains. Surface conductivity measurements from the oriented Na^+ form membranes show that ionic conductivity in the direction parallel to the stretching direction was 40% greater than the conductivity in the perpendicular direction. This anisotropic behavior suggests that intra- and interaggregate ionic transport is enhanced in the parallel direction relative to transport in the perpendicular direction. Thus, in agreement with previous morphology and transport models for PFSIs,[7-9] the potential energy barrier for ion transport in these uniaxially extended membranes is envisioned as being lowest when traversing the elongated ionic domains[7] and minimized when interaggregate transport occurs along a direction of the preferential chain orientation.

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