SAXS Analysis of the Thermal Relaxation Behavior of Oriented Perfluorosulfonate Ionomer Membranes

Forrest A. Landis¹, Robert B. Moore², Kirt A. Page² and Charles C. Han¹

¹Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

²Department of Polymer Science, The University of Southern Mississippi, Hattiesburg, MS 39406

INTRODUCTION

Perfluorosulfonate ionomers (PFSI) are a class of fluorocarbon polymers which contain a small amount of an ionic functional monomer which has been incorporated into the polymer backbone via copolymerization.¹ Due to the difference in polarity between the relatively nonpolar fluorocarbon matrix and the highly polar ionic moieties of these ionic comonomers, the ionic groups will tend to phaseseparate and form nanometer-scale ionic aggregates.² These ion-rich aggregates have been modeled as inverse micelles where the center of the domain consists of several ion groups in a roughly spherical aggregate with the fluorocarbon chains immediately attached to the ion pairs emanating out radially from the ionic aggregate. These polymer chains which are pendant to the ionic aggregate can experience a significant decrease in their molecular mobility due to the anchoring effect of the ionic domains. The amount of the pendant backbone material around the ionic aggregate which experiences this reduction in mobility may be on the order of a persistence length of the fluorocarbon backbone.² When the concentration of ionic aggregates in the PFSI becomes large enough such that the regions containing the restricted mobility polymer chains can overlap and form a continuous phase, a second, higher temperature relaxation can be observed in the PFSI. This transition occurs at a higher temperature than the transition observed in a non-ionic, homopolymer analog of the PFSI.

In addition to causing the development of a higher temperature relaxation, the ionic aggregates act as thermally reversible, electrostatic cross-links within the fluorocarbon matrix when the PFSI is not in a hydrated state. These ionic cross-links have been shown to have a dramatic effect on the mechanical and viscoelastic properties of the PFSI. Specifically, the presence of the ionic cross-links in the material can increase the temperature at which the onset of viscous flow occurs in the membrane. Thermally induced viscous flow in a PFSI is characterized by an ion-hopping process where the thermal motions of the pendant fluorocarbon polymer chains cause an ion pair to hop from one ionic aggregate to an adjacent aggregate to relieve the internal stress.³ Previous studies involving the Nafion PFSI have shown that nature of the neutralizing cation can have a dramatic effect on the temperature at which the rate of the ion-hopping process becomes sufficient to allow for macroscale viscous flow to occur.^{4,5} Nafion which has been neutralized with a bulky alkylammonium counterion, such as tetrabutylammonium, will experience viscous flow at a temperature of almost 100 °C below that of Nafion neutralized with relatively small, alkali metal such as Na⁺.

In a prior study involving the small-angle scattering analysis (SAXS) of mechanically oriented Nafion membranes, it was shown that Nafion neutralized with tetrabutylammonium counterions resulted in an anisotropic scattering pattern that persisted upon removal of the stress.⁵ In this study, we use SAXS analysis to systematically characterize the thermal relaxation behavior of the oriented morphologies of Nafion membranes which have been neutralized with alkylammonium counterions of varying alkyl chain length. Moreover, we correlate the temperature at which the ion-hopping process allows for thermal relaxation of the oriented morphologies within the membranes to the changes in the Coulombic forces within ionic aggregates as the size and nature of the alkylammonium counterions are varied.

EXPERIMENTAL

Materials. Nafion 117 (1100 g/equivalent, sulfonic acid form), tetramethyl (TMA⁺), tetraethyl (TEA⁺), tetrapropyl (TPA⁺) and tetrabutyl (TBA⁺) ammonium hydroxide (1 mol/L in water) were obtained from Aldrich Chemical Co., Inc.

Preparation of Oriented PFSI Membranes. The acid form Nafion membranes were converted to the TMA⁺, TEA⁺, TPA⁺ and TBA⁺ neutralized forms using a previously detailed process.⁶ Oriented samples of Nafion were prepared by cutting the alkylammonium neutralized membranes into 5 mm wide strips and mounting each of these strips on a specially designed drawing apparatus. The drawing apparatus was designed to allow for the Nafion membranes to be drawn at a variety of temperatures due to the difference in flow characteristics of the Nafion membranes with the various alkylammonium counterions. The TMA⁺, TEA⁺, TPA⁺ and TBA⁺ neutralized Nafion membranes were drawn at 190 °C, 170 °C, 100 °C and 80 °C, respectively, to a draw ratio (L/L_o) of 3 as determined by the displacement of ink marks on the samples.

SAXS Analysis of Oriented PFSI Membranes. Time-resolved synchrotron small-angle X-ray scattering analysis was performed at the National Synchrotron Light Source Advanced Polymers Beamline (X27C) at the Brookhaven National Laboratory. The wavelength of the incident x-ray beam was 0.1366 nm and the sample-to-detector distance was 85 cm. A Mar CCD camera was used to collect 2D scattering profiles of the oriented Nafion samples. The standard uncertainty of the detector intensity has been calculated to be on the order of 2 %. The Nafion samples were heated in a sample chamber in the X-ray beam at 5 °C/min with an uncertainty of \pm 0.1 °C. and a scattering image was taken every minute from 50 °C to 300 °C. The collected scattering images were corrected for intensity and air scattering, and calibrated with a silver behenate standard using the Polar software developed by Stonybrook Technology and Applied Research, Inc.

RESULTS AND DISCUSSION

Figure 1 shows the SAXS profiles of an undrawn and drawn sample of TMA⁺-form Nafion at a variety of different temperatures. In the undrawn sample at 50 °C, a characteristic SAXS scattering pattern of the Nafion PFSI is observed. The main feature of this scattering pattern is a diffuse halo which has been attributed to interparticle scattering of incident X-ray photons originating from the constructive interference of waves emanating between the distinct ionic aggregates with fairly well-correlated inter-aggregate distances. As this material is heated to 300 °C, the scattering from the ionic domains decreases significantly in intensity such that only a faint halo is observed. When this material is cooled back to 100 °C, the scattering halo returns except now the ring is better defined suggesting a refinement in the spatial distribution of ion pairs and/or ionic aggregates during the heating process. The second set of images in Figure 1 is the scattering profile of an oriented TMA⁺-form Nafion sample during the same heating process. As in previous studies of ionomer deformation, an anisotropic scattering profile is observed indicating that a spatial redistribution and/or a deformation of the shape of the ionic domains has occurred during the drawing process. As this sample is heated to 150 °C, the orientation of the ionic domains persists; however, at 300 °C, the scattering pattern looks identical to the unoriented sample at the same temperature indicating that a significant amount of ion-hopping has occurred at this elevated temperature to cause the oriented ionic domains to relax. Upon cooling the sample back to 100 $^\circ\text{C},$ a slightly anisotropic scattering profile is still observed; however, the degree of orientation is greatly reduced relative to the oriented film before the heating process.

[°] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.



Figure 1. SAXS patterns of A) undrawn TMA⁺-form Nafion and B) TMA⁺-form Nafion at a draw ratio of 3 during the heating process. The draw direction is horizontal.

Due to the high intensity of the synchrotron X-ray beam, it is possible to rapidly obtain scattering patterns of the ionic relaxation process of oriented Nafion during the heating profile. Figure 2 shows the integrated intensity profiles of an oriented TEA⁺-form Nafion sample as it is heated. These profiles were obtained by integrating in a linear manner from the center of the scattering pattern along the meridional direction covering a scattering vector range from 0.2 nm⁻¹ to 4.5 nm⁻¹. It can be seen that the intensity of the scattering peak (at q = 2.0 nm^{-1}) ascribed to the ion domains begins to decrease as the sample is heated through a temperature range of 195 °C to 205 °C. This temperature range corresponds well with the higher temperature thermal relaxation observed in the dynamic mechanical analysis of Nafion, providing evidence that the onset of viscous flow in the ionomer does correlate with the thermally induced increase in the rate of the ion-hopping process.



Figure 2. Scattering profiles of oriented TEA⁺-form Nafion (draw ratio = 3) during the heating process.

As the Nafion counterion is varied from TMA⁺ to TBA⁺, the temperature at which the ionic domains relax back to an isotropic state decreases. Initially at 50 °C, all of the oriented Nafion samples show a similar scattering pattern to that observed for oriented TMA⁺-form Nafion (Figure 1). However, Figure 3 shows that at 150 °C, the ionic

domains of Nafion neutralized with the smaller counterions, TMA⁺ and TEA⁺, have undergone very little thermal relaxation. In contrast, TPA⁺ form Nafion has begun to relax back to an isotropic state, as indicated by the decrease in intensity and broadening of the ionomer peak, yet a small degree of orientation persists. Finally, Nafion neutralized with the largest alkylammonium counterion, TBA⁺, has already relaxed back to a completely isotropic state by the time the sample reaches 150 °C.



Figure 3. Scattering patterns of oriented Nafion (draw ratio = 3) neutralized with A) TMA^+ , B) TEA^+ , C) TPA^+ and D) TBA^+ counterions at 150°C.

CONCLUSIONS

By examining the scattering profiles of oriented Nafion PFSI's with a variety of alkylammonium counterions, we have determined that the temperature range where the oriented ionic aggregates relax back to an isotropic state is related to the nature of the alkylammonium counterions. Specifically, as the electrostatic interactions between the ion pairs is decreased by increasing the size of the alkylammonium counterion, a decrease in the temperature range at which the thermal relaxation of the ionic aggregates occurs is observed.

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