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Polymer electrolyte membranes from fluorinated polyisoprene-*block*-sulfonated polystyrene: Structural evolution with hydration and heating

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ABSTRACT

Small-angle neutron scattering (SANS) and ultra-small-angle X-ray scattering (USAXS) have been used to study the structural changes in fluorinated polyisoprene/sulfonated polystyrene (FISS) diblock copolymers as they evolved from the dry state to the water swollen state. A dilation of the nanometer-scale hydrophilic domains has been observed as hydration increased, with greater dilation occurring in the more highly sulfonated samples or upon hydration at higher temperatures. Furthermore, a decrease in the order in these phase separated structures is observed upon swelling. The glass transition temperatures of the fluorinated blocks have been observed to decrease upon hydration of these materials, and at the highest hydration levels, differential scanning calorimetry (DSC) has shown the presence of tightly bound water. A precipitous drop in the mechanical integrity of the 50% sulfonated materials is also observed upon exceeding the glass transition temperature (T_g), as measured by dynamic mechanical analysis (DMA).

1. Introduction

Ionomers have increasing utility in various areas of research and industry such as batteries, fuel cells, electrolysis cells, ion exchange membranes, sensors, electrochemical capacitors, modified electrodes, and even golf balls [1]. Ionomers typically are comprised of a hydrophilic acid-bearing phase embedded in a hydrophobic phase. The hydrophilic phases are known to form due to aggregation of the acid groups into multiplets or larger clusters [2–4]. Nafion™, which is the most used ionomer material in proton exchange membrane (PEM) applications, is composed of a hydrophobic fluoropolymer backbone and hydrophilic fluorosulfonic acid-bearing side chains [5]. Other PEM materials range from fluoropolymer to aromatic to hydrocarbon backboned materials, bearing pendant acid groups in one configuration or another [6].

The clusters formed by the acid groups at the end of the side chains are essential in facilitating ionic conductivity by absorbing water which dissociates the protons, forming hydronium ions which may hop from one acid site to the next during transport [7] or, alternatively, protons may migrate directly through the aqueous phase or hop across hydrogen bonds of adjacent molecules. Thus, the quantity, shape, size, and connectivity of these ionic aggregates dictate the observed transport properties of such materials.

When block copolymers of suchionomers are made, typically in the diblock, triblock, or graft copolymer architectures [8], an extra level of morphological complexity is introduced, which yields a hierarchical structure. As in normal block copolymers, nanometer-scale phase separation occurs between the blocks, creating separate hydrophobic and hydrophilic domains with morphologies that can be similar to those observed for neutral block copolymers. The acid groups in the hydrophilic domains further form clusters at a smaller length scale [9,10].

Swelling or dilation of ionomers upon increasing water or methanol content and heating to service temperature is also an important factor affecting conductivity and mechanical integrity. Block copolymer ionomers with one block being a fluoropolymer have been shown to exhibit enhanced network formation and mechanical integrity, especially when hydrated [11]. Backbone stiffness and the nature of the counterions associated with the acid sites are known to affect the degree of water uptake, and hence, swelling [6,12]. The structure of Nafion™ has been shown to undergo evolution and phase inversion in order to conserve specific surface as water content increases [13].

Previously, we reported the synthesis of well-defined block copolymer ionomers comprised of a fluorinated hydrophobic block

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Table 1
D spacing for fluorinated polyisoprene-*block*-sulfonated polystyrene (FISS) obtained by USAXS.

Sample	Dry samples, USAXS at room temperature		Hydrated samples, SANS		
	D spacing of block (nm)[a]	D spacing of cluster (nm)	D spacing of block, 23 °C (nm)	D spacing of cluster, 23 °C (nm)	D spacing of block, 60 °C (nm)
AC28	20.3 (20.2)	4.7	19.8		9.5
CS23	20.3 (19.2)	4.7			
AC50	22.7		26.5	3.2	35.5
CS50	23.7 (22.2)	3.2	27.8	5.8	Disintegrates

[a] Values in parentheses are from SANS.

and a partially sulfonated hydrophilic block by means of post-polymerization modification of the common near-monodisperse polystyrene-*block*-polyisoprene (PS-PI) diblock copolymer [14]. The structures of membranes fabricated from these materials, as well as their transport properties (i.e. proton conductivity and methanol permeability) to assess their viability for low temperature direct methanol fuel cell applications [15]. With a view to understanding the swelling induced structural evolution of our fluorinated polyisoprene-*block*-sulfonated polystyrene (FISS) ionomers from the dry membrane to their swollen state, in this work we have investigated their structure using ultra-small-angle x-ray scattering (USAXS) and small-angle neutron scattering (SANS) under conditions mimicking fuel cell usage. Furthermore we have looked at the state of water in these systems, and the effect of swelling on thermal transitions using differential scanning calorimetry (DSC). Finally, thermal and mechanical transitions were studied using dynamic mechanical analysis (DMA).

2. Experimental section

2.1. Materials

The synthesis and characterization of fluorinated polyisoprene-*block*-sulfonated polystyrene (FISS) materials have been described in detail elsewhere [14]. The precursor poly(styrene)-*block*-poly(isoprene) (PS-PI) diblock copolymer used in this work was anionically polymerized, having characteristics: $M_w = 31{,}200$, PDI = 1.05, 27 mol% PS. The samples were quantitatively fluorinated and sulfonated to 23, 28, and 50 mol%, as determined by ^{1}H NMR. Some of these samples were neutralized to the cesium salt form, and the balance was left in the acid form. The cesium form facilitates contrast in X-ray scattering experiments, in addition to exhibiting different transport properties. The cesium salts are noted as CSXX where XX is the mole% sulfonation. The acid forms are denoted by ACXX, where again XX is the mole% sulfonation. For example, a sample coded AC50 would refer to the acid form of the material, sulfonated to 50 mol% of the styrene units in the PS block. Nafion™ 112 was generously donated by Atofina Chemicals Inc., and was pretreated to the acid form according to a procedure reported elsewhere [16].

2.2. Preparation of membranes

Freeze dried FISS samples were dissolved in a mixture of toluene/N-methylformamide (THF/NMF:85/15 (w/w)) with a concentration ranging from 12 to 15 wt%. The NMF was used as a polar co-solvent. These solutions were then cast onto glass plates for a day in the fume hood at room temperature for rapid casting of kinetically trapped disordered morphologies. Subsequently, they were placed in an oven for 1 day at 60 °C, and finally in the oven at 60 °C under vacuum for a day to remove most of the residual solvent. The acid-form samples were further reactivated by soaking

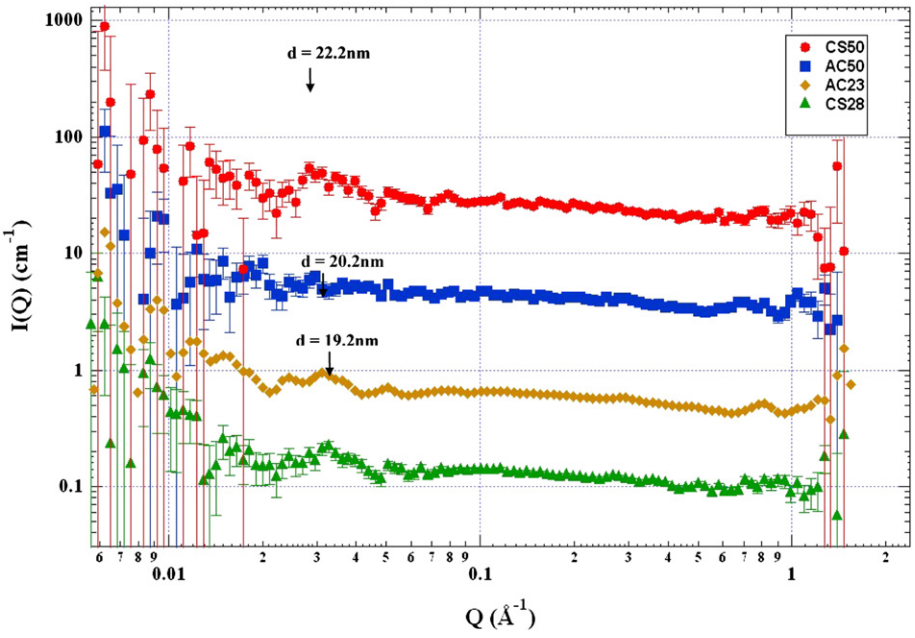

Fig. 1. SANS profiles from fluorinated polyisoprene-*block*-sulfonated polystyrene, dry at 23 °C.