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Influence of the Sample Preparation Method on the Ultra-Small-Angle X-ray Scattering of Lightly Sulfonated Polystyrenes

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Ionomers are polymers with a small mole fraction of ionic groups covalently bonded to the polymer backbone. Small-angle X-ray scattering (SAXS) patterns of ionomers have two significant features, a peak at $q = 1–2\ \mathrm{nm}^{-1}$ ($q = 4\pi\ \sin(\theta/\lambda)$) and an upturn as $q \to 0$.[1] Transmission electron microscopy[2,3] and SAXS[4,5] have shown that the peak arises from interparticle interference of dispersed ionic rich aggregates. The acid forms of most ionomers (neutralizing cation = H^+) do not exhibit a peak but do show the upturn. The effect of the sample preparation method,[6] thermal history,[7] and plasticizer[8–10] on the SAXS peak has been investigated. However, few studies have examined the upturn.

One investigation which did examine the upturn was an anomalous small-angle X-ray scattering study of lightly sulfonated polystyrene neutralized with Ni^{2+}.[11] This study showed that the upturn was due to an inhomogeneous distribution of ionic repeat units rather than voids or impurities. Two theories have been proposed to explain the cause of the upturn. The first attributes the upturn to an inhomogeneous distribution of dissolved ionic groups in the polymer matrix, while the second attributes the upturn to an inhomogeneous distribution of ionic aggregates. Studies which followed the development of the SAXS peak with temperature in Mn(SPS)[12] and halato-telechelic polybutadiene ionomers[13] found that the intensity of the peak scaled inversely with the intensity of the upturn. Previous investigations of the upturn have been severely limited by the q range available with conventional Kratky or pinhole collimating optics.

This investigation benefits from a recently constructed Bonse–Hart camera. Although the principle of a Bonse–Hart camera was developed over 25 years ago,[14] very few cameras have been fabricated because of the difficulties in producing a goniometer with the necessary accuracy as well as the difficulty in producing perfectly matched crystals. This newly constructed apparatus can reliably measure scattering at a q value of $0.001\ \mathrm{nm}^{-1}$, which corresponds to a Bragg spacing of approximately 60 000 Å. This camera has been used to study the upturn in lightly sulfonated polystyrenes.

Experimental Section. Sulfonated polystyrenes were kindly supplied by R. D. Lundberg of Exxon Chemical Co. Two materials were studied, acid materials where the molar degree of sulfonate substitution was 5.6% and a sodium neutralized material where the molar degree of substitution was 6.1%. Both materials were produced from the same base polystyrene (Styron 666: $M_n = 106\,000$, $M_w = 288\,000$ by GPC) according to the usual method.[15] Samples were cast onto mercury from a 1 wt % solution using the mixed solvent toluene/methanol (90/10, v/v). The evaporation rate of the solvent was controlled so that the samples were dry to the touch in approximately 24 h. Samples were then dried for 1 week in a 70 °C vacuum oven. Elemental analysis showed that the resultant mercury content was less than 100 ppm in all cases. Samples were also compression molded so that the effect of the sample preparation method could be studied. The acid form was compression molded at 150 °C and 9000 psi while the sodium ionomer was compression molded at 200 °C and 9000 psi. In both cases the samples were allowed to slowly cool to room temperature under pressure. The thickness (t) of the compression-molded samples was controlled such that $\mu t \sim 1$ (μ is the X-ray absorption coefficient), while μt for the solution-cast samples were approximately 0.4.

Spectra were collected on a Bonse–Hart camera constructed at Kyoto University. Cu $K\alpha_1$ X-rays were produced by a Rigaku Rotaflex RU-200 rotating-anode generator. Two matched silicon crystals are used to create the Bragg condition necessary for the Bonse–Hart camera. Multiple reflections from the crystals isolate Cu $K\alpha$ X-rays and provide the extremely precise collimation required to measure scattered intensities at extremely low angles with extremely high resolution. A proportional counter is used to detect the scattered X-rays. Because of the many orders of magnitude shift in the scattered intensities with scattering angle, attenuators are placed in front of the first crystal if necessary so as not to exceed the dynamic range of the detector. The apparatus is fully described elsewhere.[16] Because the experimental apparatus fulfilled the necessary conditions,[17] data were desmeared according to the infinite line approximation.[18]

Results and Discussion. Background-subtracted, desmeared USAXS curves of the four samples studied are shown in Figure 1A. Relative intensities are shown rather than absolute intensities because of the lack of a suitable calibration material in the q range of interest. No interparticle interference peak is seen in these spectra because of the limited q range investigated. The qualitative shapes of the curves are identical for all four samples, which suggests that the cause of the upturn is the same for both the acid form and the sodium form. SAXS spectra of the compression-molded materials taken with a Kratky camera shown in Figure 1B have a substantial peak between 1 and 2 nm^{-1} for the sodium-neutralized material but not for the acid material. Although SAXS spectra for these particular solution-cast samples were not collected, other solution-cast samples from the same materials showed a peak for the sodium sample and no clear peak for the acid sample. A simple comparison of desmeared SAXS and USAXS patterns was not possible because the q ranges did not overlap.

Two models can be easily applied to the USAXS pattern. The first is Guinier's law, which implicitly assumes a particle morphology. Guinier's law is written in the following form:

$$I(q) = n^2\theta^{-q^2{R_g}^2/3} \tag{1}$$

where n is a constant and R_g is the radius of gyration of the particle. Guinier's law is strictly valid for isolated, monodisperse, and isodiametric particles and is an approximation at low q; however, it has been found to describe a number of experimental curves quite accurately.[18] From eq 1, a plot of ln I vs q^2 should be linear with the slope

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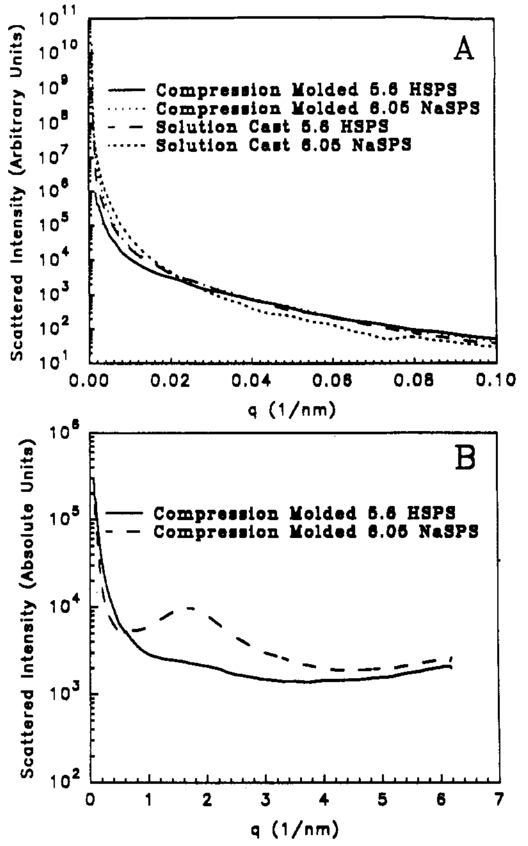

Figure 1. Scattering patterns for lightly sulfonated polystyrenes. (A) USAXS spectra collected on a Bonse–Hart camera. (B) SAXS spectra for compression-molded materials collected on a Kratky camera.

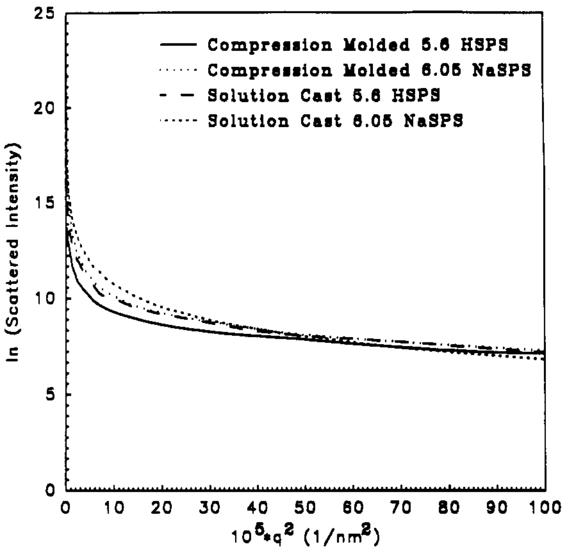

Figure 2. Guinier plots derived from Figure 1A.

proportional to R_g^2. Guinier plots are shown in Figure 2. As can be seen by inspection, Guinier's law does not describe any of the four curves accurately.

The Debye–Bueche model assumes that scattering arises from a two-phase system with sharp interfaces, where both the sizes and shapes of the phases are random. This model corresponds to an exponential decay of the electron density correlation function. The relevant expression from this model follows:

$$I(q) = \frac{K^2}{(1 + c^2q^2)^2} \qquad (2)$$

where K depends on the system in question and c is called the correlation length. The correlation length is a measure of the size scale of the electron density heterogeneity.[19] A plot of $I^{-1/2}$ vs q^2 should be linear, and the correlation length c can be extracted from the ratio of the slope to the intercept. Debye plots are shown in Figures 3 and 4. Three of the curves clearly show concave downward curvature; which agrees with the observations of Register et al.[11] and is inconsistent with three intraparticle interference models as also discussed in this same reference. USAXS curves of the solution-cast sodium neutralized material are described reasonably well by the Debye–Bueche relationship; however, careful examination does show a slight downward curvature which is more evident upon examination of the smeared data (not shown). If it is assumed that the Debye–Bueche model does describe the morphology of the solution-cast ionomer, then a lower limit on the correlation length can be calculated. Since the intercept is essentially zero, a particular value for the correlation length cannot be computed. By estimating an upper limit on the intercept from Figure 4 as 0.001, 2000 Å was calculated as the lower limit on the correlation length. Given the error on estimating the intercept, a similar calculation using the closed form expression for infiniteline collimation[20] on the smeared data was carried

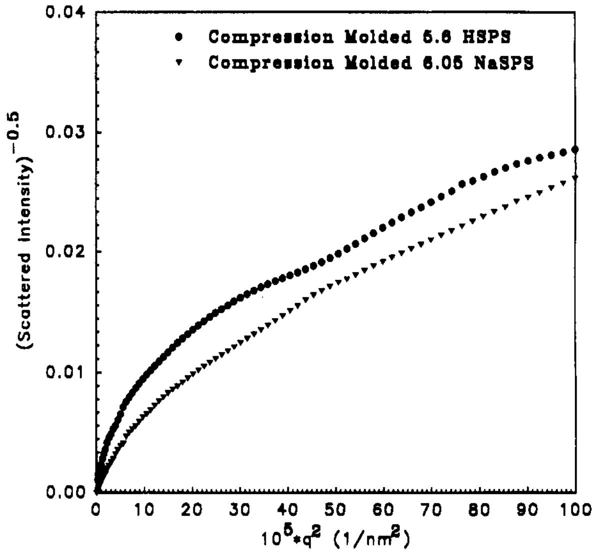

Figure 3. Debye–Bueche plot for compression-molded lightly sulfonated polystyrenes from Figure 1A.

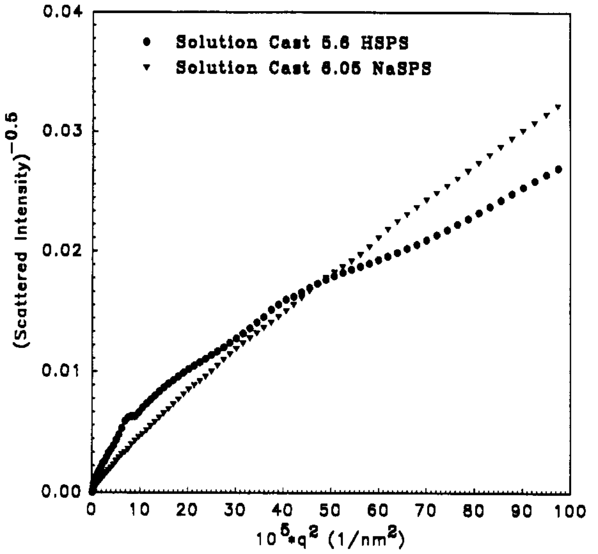

Figure 4. Debye–Bueche plot for solution-cast lightly sulfonated polystyrenes derived from Figure 1A.

out yielding approximately the same result.

In a recent publication,[20] a Bonse–Hart camera was used to measure the scattering pattern to $q = 0.01$ nm^{-1} of compression-molded 7.4 mol % sulfonated polystyrene, both the zinc and the acid form. These authors found that background scattering and scattering from the acid were nearly identical, an observation not found in this study nor in other studies in the literature.[7,11,21] Guinier's approximation failed for the zinc-neutralized material. A Debye–Bueche fit showed slight downward curvature but was nearly a straight line. The correlation length calculated from this analysis was 900 Å. The ratio of the correlation lengths calculated from a SAXS study of compression-molded sodium- and zinc-neutralized samples of 4.5 mol % SPS was approximately 1.7,[21] so the correlation length calculated from the previous USAXS study is not necessarily inconsistent with the results presented in this study.

In conclusion, USAXS patterns of the acid form and sodium-neutralized form of lightly sulfonated polystyrene show the same qualitative shape at low q, even though SAXS patterns of the two materials are very different. Guinier's law did not describe any of the four curves accurately while in only one instance did the Debye–Bueche law approximately fit the data and a lower limit on the correlation length was calculated as 2000 Å.

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