Small-Angle X-ray Scattering Investigation of Temperature Influences on Microstructures of an Ionomer

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Introduction

Ionomer morphology has received extensive studies due to its interesting characteristics in the molecular aggregation of ionic groups. The strong scattering peak in the small-angle X-ray scattering (SAXS) profile has been accounted for by several models.[1-3] From the multiphase relaxation point of view, Eisenberg et al.[4] proposed that the ionic multiplets were the basic unit of aggregation. The ionic aggregates were surrounded by a spherical region of polymer backbones of restricted mobility. Some overlap of the restricted regions of the ionic phases could be characterized by a high-temperature relaxation relative to the one for the surrounding matrix. The electron density inhomogeneity in a length scale comparable to the average distance between two adjacent multiplets leads to an ionic peak in the SAXS profile. The SAXS profiles of ionomers at different temperatures depended on the counterions and the method of sample preparation.[5-9]

In this paper we report SAXS measurements of an ionomer which has undergone different thermal treatment. Extra care was taken in correcting the thermal expansion which was responsible for the primary change in the SAXS profile at different temperatures. We used an approach developed by Fischer[10] and Gehrke et al.[11] The modified Porod law[12] and the inverse Fourier transform were used to evaluate the microstructure parameters.

Experimental Section

The 7.4 mol % zinc salt of sulfonated polystyrene (ZnSPS) was prepared from polystyrene ($M_w = 1.05 \times 10^5$, $M_w/M_n = 1.01$). The sample film of 0.5 mm in thickness was melt compression-molded at 200 °C and annealed in a vacuum oven at 85 ° for 48 h. SAXS experiments were performed at the X3-A2 State University of New York (SUNY) Beam Line, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), using a Bonse–Hart camera[13] and a modified Kratky camera.[14] A Braun linear position-sensitive detector coupled with the Kratky camera had a channel-to-channel distance of 46 μm and the sample-to-detector distance was 254 mm, covering a scattering vector q ($=(4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle and the wavelength $\lambda = 0.154$ nm) which could vary from 0.1 to 5 nm^{-1}. The SAXS profiles were corrected for background, sample absorption, beam intensity decay, detector uniformity, and thermal density fluctuations. Temperature was controlled to ±1 °C.

Results and Discussion

Figure 1 shows SAXS profiles for ZnSPS at various temperatures. The ionic peak became weaker with increasing temperature. The interdomain distance was estimated, to a first-order approximation, from the peak position (q_{max}) using the Bragg law ($L = 2\pi/q_{max}$) and was denoted as $L_{q_{max}}$ in Table I. $L_{q_{max}}$ decreased only slightly from 2.9 to 2.6 nm with increasing temperature from room temperature to over 259 °C. The invariant which quantitatively describes the scattering power of the medium is given by

$$Q = 2\pi^2 V \delta\rho^2 \phi(1-\phi) = \int_0^\infty q^2 I(q)\, dq$$

with ϕ and V being, respectively, the volume fraction of one of the two phases and the scattering volume and $\Delta\rho$ ($=\rho_1 - \rho_2$) the difference in the electron density of the two phases. Generally, $\Delta\rho$ changes with temperature due to the difference in the thermal coefficient of expansion of the two phases. Thus, if ϕ remains constant, the invarient becomes a function of temperature and follows[10,11]

$$\left[\frac{Q(T)}{Q(T_0)}\right]^{1/2} = 1 + \frac{\alpha_1 - \alpha_2}{\Delta\rho(T_0)}(T - T_0)$$

where $\alpha_1 = d\rho_1/dT$, $\alpha_2 = d\rho_2/dT$, and T_0 is a reference temperature. On the basis of this equation, $(Q(T)/Q(25\ °C))^{1/2}$ was plotted against T in Figure 2. In spite of the insufficient data points in the present study, the data below ~250 °C seem to suggest three distinct slopes which suggest the changes in the thermal expansion coefficient difference, $\alpha_1 - \alpha_2$, between the two phases provided that ϕ remains constant. Thus, if the linear behavior were true, two glass transitions can be identified in this plot, i.e., the glass transition of the polystyrene matrix at ~100 °C and the glass transition of, *presumably*, ionic domains at ~170 °C. The result is in qualitative agreement with the dynamic viscoelastic measurements of ionomers, in which two glass transition temperatures were observed.[15] It should be noted that the second transition temperature (~170 °C) was ~30 °C lower than that obtained from the dynamic viscoelastic measurements. The reasons might be due to (a) different sample histories and preparations, (b) different instrumental methods, and, more importantly, (c) different heating rates. In our case the heating rate could be considered slow because the SAXS profile at each temperature was recorded after a 15-min thermal equilibration time at that temperature. Thus, a lower T_g would be expected, since we could not expect a true equilibrium in morphology by thermal equilibration at low temperatures over relatively short time periods. The apparent linear behavior in Figure 2 does seem to suggest that, below ~250 °C, the change in the SAXS profiles upon heating could be attributed primarily to the difference in the thermal expansions between the two phases rather than to microstructure changes. When the temperature was above ~250 °C, the square root of the normalized invariant decreased sharply and deviated substantially from the apparent linear behavior, signifying a notable phase diffusion or a microstructure change and a breakdown of the assumption; i.e., the volume fraction of the ionic phases remained constant.

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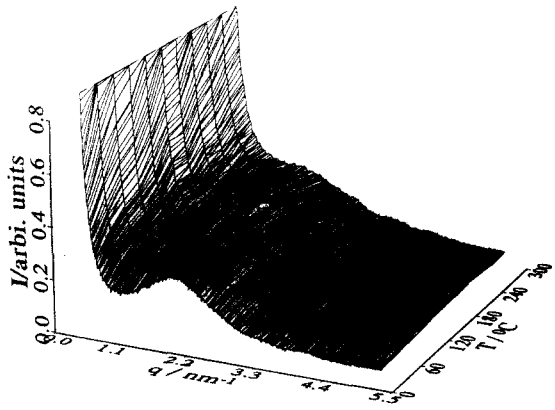

Figure 1. Three-dimensional plot of SAXS profiles of 7.4 mol % ZnSPS. The sample was heated up continuously and was, before being measured, held at each temperature for 15 min when the temperature was lower than 250 °C and for 5 min when the temperature was higher than 250 °C for thermal equilibration. All curves were accumulated for 200 s and presented without smoothing. The temperatures for each curve are, from the bottom, 25, 60, 90, 130, 168, 194, 212, 239, 259, 281, and 300 °C.

Table I. Structure Parameters at Varying Temperatures

temp, °C	I_{fl},[a] ×10^{-3}	E, nm	L_{3d}, nm	$L_{q_{max}}$, nm
25	1.08	0.21	3.8	2.9
259	12.6	0.38	3.3	2.6
281	8.25	0.35	3.3	2.6
300	7.80	0.39	3.3	2.6

[a] The values are in arbitrary units.

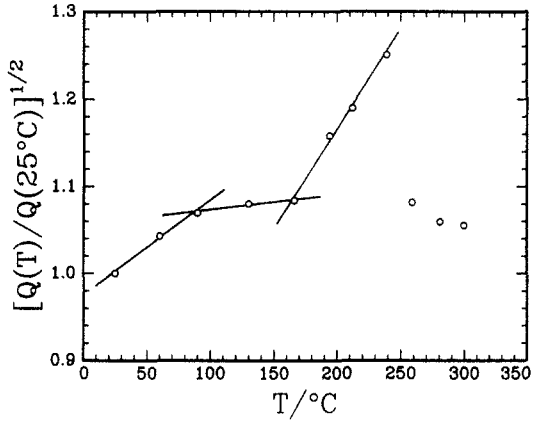

Figure 2. Square root of the normalized invariant for 7.4 mol % ZnSPS as a function of temperature. Two glass transition temperatures were identified at ~100 and ~170 °C where the slopes were changed.

Figure 3 shows the three-dimensional correlation functions, defined by

$$\gamma_3(r) = \frac{1}{Q}\int_0^\infty q^2 I(q)\,\frac{\sin(qr)}{qr}\,dq$$

with $r = |r_1 - r_2|$ being the relative distance for every pair of points and $I(q)$ the relative scattered intensity, for ZnSPS at room and elevated temperatures. The correlation functions showed a minimum and a maximum. As the temperature was raised from room temperature to over 259 °C, the correlation function tended to change toward an exponential curve of a single-phase system, with the inital slope being less sharp and the minimum moving from a negative region to a positive region. This behavior suggests a more smeared phase boundary and a reduced phase contrast in terms of the electron density. The interdomain distances estimated from the position of the first maximum in the correlation functions are denoted in

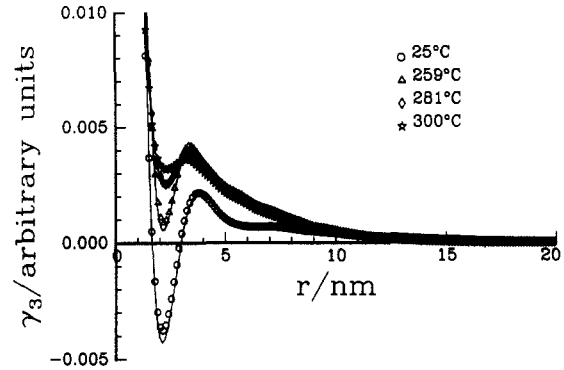

Figure 3. Normalized correlation functions of electron density fluctuations deduced from Figure 1. The solid lines are only for guiding the eyes.

Table I as L_{3d} which are about 25–30% larger than $L_{q_{max}}$ values.

In Table I, the diffuse boundary thickness E and the thermal density fluctuation intensity I_{fl} were estimated using the modified Porod law[12]

$$I(q)\,q^4 = K_p H^2(q) + I_{fl} q^4$$

where K_p is a Porod constant, $H^2(q) = \exp(-\sigma^2 q^2)$ is a Gaussian smoothing function, and σ is related to the diffuse boundary thickness E by the relation $E \approx (12)^{1/2}\sigma$. E was increased 2-fold as the temperature was raised from 25 to 259 °C and I_{fl} at elevated temperatures was roughly an order of magnitude larger than that at room temperature. A very qualitative explanation of the above temperature effects on the ionomer morphology might be that the polymer chains, with increasing temperature, underwent more intense internal rotations which in turn gave rise to enhanced elastic forces that consequently might pull some ion pairs out of the multiplets at looser connection sites; i.e., at high temperature one might expect a decrease in the super-strong separation between the ionic multiplets and the polymer backbone. At temperatures below ~250 °C, the elastic forces might be too weak to overcome the electrostatic interactions and consequently the ionic domains simply underwent a thermal expansion. Only a partial split and limited thermal diffusion of the multiplets occurred at over ~250 °C. If the thermal expansion dominated the temperature-induced structures below ~250 °C, a physical aging of the sample within this temperature range should not manifest a significant effect on the ionic domain structures. This was checked by measuring SAXS of aging samples below and above ~250 °C. For aging below ~250 °C, no appreciable difference was seen. For aging at 280 and 300 °C, the magnitude of the peak was reduced while the peak position remained unchanged.

Figure 4 shows the excess SAXS curves obtained from the Bonse–Hart camera at room temperature for ZnSPS at different annealing temperatures: ○, 25 °C; +, 250 °C; △, 280 °C. It should be noted that since these excess SAXS profiles were essentially the "difference profiles" between the metal-neutralized ionomer and the acid form of the ionomer, the scattering arising from the voids or impurities, if any, could possibly be canceled out. For slit-smeared data collected using a collimation system of an infinite-slit-length geometry, the Debye–Bueche model which assumes a random electron density distribution can be represented by $I(q) = A/(1 + \xi^2 q^2)^{3/2}$ with A and ξ being a constant and an inhomogeneity length, respectively.[16] It has been shown[16] that the Bonse–Hart camera employing a synchrotron X-ray source obeys nearly an infinite-slit-

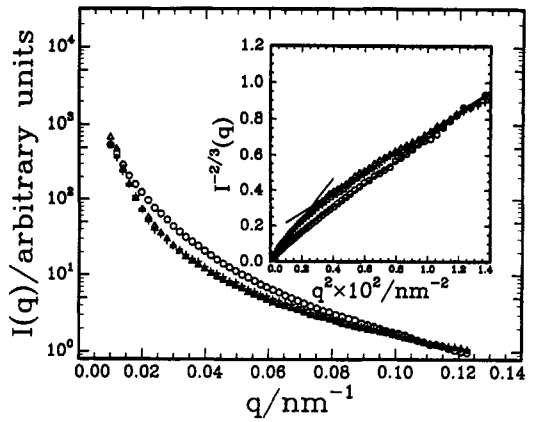

Figure 4. Bonse–Hart SAXS profiles at 25 °C for 7.4 mol % ZnSPS annealed at different temperatures: ○, 25 °C; +, 250 °C for 5 min; △, 280 °C for 5 min. The inset is the corresponding Debye–Bueche plot for smeared SAXS data. The inhomogeneity length was estimated to be 93, 100, and 102 nm for the samples annealed at 25, 250, and 280 °C, respectively.

length geometry at low q values. The Debye–Bueche plot, $I^{-2/3}$ vs q^2, for the smeared data was shown in the inset of Figure 4. From the *initial* slope corresponding to a q range from 0.01 to 0.04 nm^{-1}, the long-range inhomogeneity length, which might represent overlapped restricted regions of the ion-rich phase in the Eisenberg model, was estimated to be 93, 100, and 102 nm for the annealed samples at 25, 250, and 280 °C, respectively. The value for the inhomogeneity length at room temperature is comparable to that reported by other authors.[17] With increasing temperature from 25 to 280 °C, the inhomogeneity length was increased by only ~10%. The origin of the small-angle upturn remains uncertain. Qualitatively, its value depends on sample history and preparation because equilibrium morphology would be difficult to establish since decomposition could take place at elevated temperatures (>250 °C).

The time evolution of the SAXS profiles for ZnSPS was recorded after temperature jumps from 80 to 280 °C and from 280 to 180 °C, respectively, by means of a dual-chambered temperature jumper. The sample was first placed in a sideways chamber at constant temperature and then moved quickly into a middle chamber at measurement temperatures. The SAXS measurement was then immediately started as a function of time. Both the phase diffusion at 280 °C (jumped from lower temperature) and the phase development at 180 °C (jumped from higher temperature) appeared to be very fast, i.e., took ~1 min to reach an equilibrium of our experimental time domain. This fast response could be explained only by a local diffusion mechanism.

Conclusion

Temperature-induced change of SAXS profiles for 7.4 mol % ZnSPS below ~250 °C could be due primarily to the difference in the thermal expansion coefficient of the ion-rich phase and the polystyrene matrix. Two glass transition temperatures at ~100 and ~170 °C were observed in a plot of the square root of the normalized invariant versus temperature. The former corresponds to the glass transition temperature of polystyrene, and the latter, which is qualitatively comparable to those reported by other authors from viscoelastic measurements, is attributed to the ionic domains. The inhomogeneity length associated with the ionic domain size was increased from ~90 to ~100 nm when the temperature was raised from 25 to over ~250 °C. The evidence of the second transition temperature and of the larger inhomogeneity length seems to support the Eisenberg model. The ionic phase could diffuse locally above ~250 °C. The kinetics of the local phase diffusion and the local phase development were extremely fast within a time scale of ~1 min. The change in the ionic domain structures with temperatures below ~250 °C was almost completely reversible, possibly due to the dominant mechanism of thermal expansions, but was incompletely reversible above ~250 °C.

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