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Observation of Cluster Formation in an Ionomer

Ionomers exhibit unique mechanical and rheological properties as a consequence of strong associations between the ionic species. Although the spatial arrangement of the ionic groups in ionomers is still an unresolved question, it is now generally agreed that in most ionomers microphase-separated ion-rich aggregates, termed clusters,[1] are the dominant morphological feature. The primary evidence for ionic clusters comes from small-angle X-ray (SAXS) and neutron scattering (SANS) experiments where a maximum corresponding to a distance of 2–4.5 nm is observed for most ionomers.[2,3]

We have been studying the effects of thermal history and low molecular weight diluents on the structure–property relationships of ionomers, particularly lightly sulfonated atactic polystyrene (SPS). In several recent publications[4-6] we showed by electron spin resonance spectroscopy and SAXS experiments that polar solvents, such as alcohols or water, can preferentially solvate the ionic interactions in SPS ionomers in solution or in the solid state. This result suggested that solvent history might be used for controlling the structure and properties of ionomers. In fact, when films of an SPS ionomer were cast from different solvents, very different morphologies occurred, as is demonstrated by the SAXS data for a Mn(II) salt of 7.6 mol % SPS shown in Figure 1. Similar results were obtained for other metal salts of SPS.

The most striking observation in Figure 1 is the absence of the SAXS maximum for the sample cast from a mixture of 90% tetrahydrofuran (THF) and 10% water. This result suggests the absence of ionic clusters in this sample. We should point out, however, that an alternative interpretation might be that the characteristic size for the cluster morphology is sufficiently large that the scattering maximum is positioned too close to the beam stop for adequate resolution. Such a conclusion might be based on the fact that a high degree of zero angle scattering was observed for this sample (as it was for most ionomer samples studied by us as well as other laboratories) and that the addition of water to a compression-molded SPS ionomer tends to shift the SAXS peak to lower scattering angle.[7,8] It should be emphasized, however, that no water could be detected in the sample used to generate the data in Figure 1 by either gravimetric techniques or infrared spectroscopy. Although this does not exclude the possibility of trace amounts of water, we have found that detectable water concentrations of several percent cannot account for the disappearance of the SAXS maximum in this SPS ionomer.

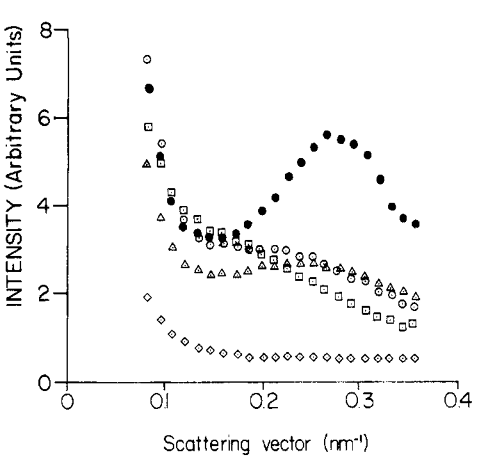

Figure 1. Scattered X-ray intensity versus scattering vector for 7.6 mol % MnSPS samples prepared by (●) compression molding: (○) casting from THF solution; (□) casting from DMF solution; (△) casting from 90% toluene/10% methanol; and (◇) casting from 90% THF/10% water. (Reprinted with permission from ref 5.)

In this paper, we report recent results of an experiment in which an ionomer with a microstructure characterized by the absence of a SAXS maximum (herein interpreted as being void of ionic clusters) is heated to elevated temperatures. By use of the high flux afforded by a synchrotron radiation source the formation of the cluster morphology in this material was observed during heating at a controlled rate. To our knowledge, this represents the first time that the development and growth of microphase separation in an ionomer has been reported.

Experimental Section. SPS containing 7.6 mol % sulfonic acid groups was prepared by the homogeneous sulfonation of polystyrene (M_n = 100 000 and M_w = 260 000) in dichloroethane solution with acetyl sulfate.[9] This was neutralized with an equivalent amount of manganese acetate. A 25-μm film was prepared by casting a 10% solution of the ionomer in a mixed solvent of 90% THF and 10% deionized water onto glass. The solvent was evaporated in air and the film was dried under vacuum for 5 days at 60 °C.

The X-ray scattering experiments were performed at Beam Line I-4 of the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA. The ionomer film was placed in an aluminum sample cell that was fashioned from a conventional DSC pan. The pan contained thin Kapton windows in the top and the bottom so as to maximize the transmission of X-rays. The sample assembly was placed in a Mettler FP82 Hot Stage that controlled the heating of the sample at a rate of 10 °C/min between 40 and 240 °C. SAXS curves were collected every 26 s and reflect the scattering integrated over a temperature interval of ca. 4 °C.

The sample-to-detector distance was 35 cm. The wavelength of the incident radiation was 0.143 nm and the detector covered a range of scattering angles, 2θ, from 0.6° to 3.3°. This corresponded to long periods of 13–2.5 nm. Beam monitors placed before and after the sample cell allowed for correction for specimen adsorption effects and normalization of the reported intensities by the sample thickness and incident beam intensity. Additional information on the experimental setup can be found elsewhere.[10]

Results and Discussion. The corrected SAXS data collected during the heating cycle at controlled heating rate are given in Figure 2. A scattering maximum is not de-

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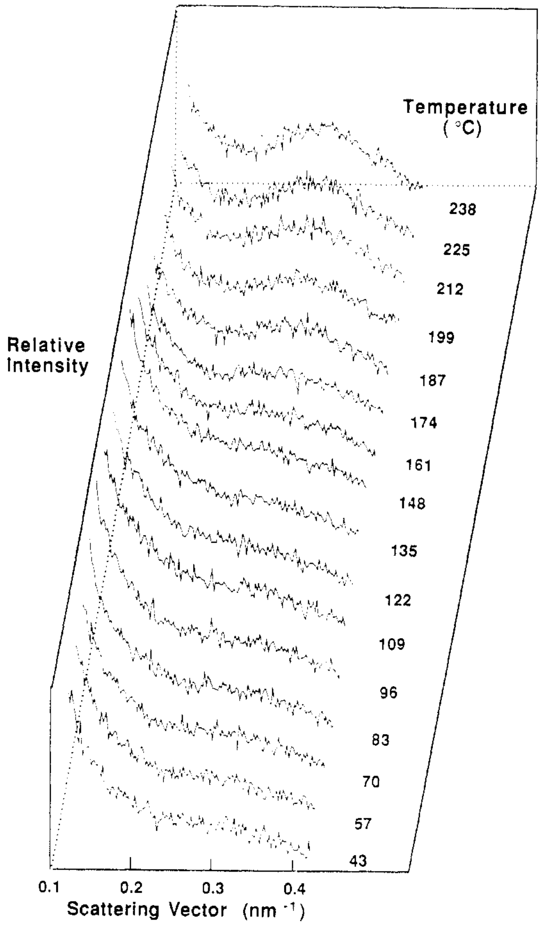

Figure 2. SAXS intensity versus scattering vector for 7.6 mol % MnSPS film cast from THF/water as a function of temperature. Heating rate was 10°/min.

tectable in the unheated film, though substantial zero angle scattering is evident. This intense zero angle scattering has been observed in many ionomer samples with no agreement as to its origin. From the changes in the zero angle scattering observed in these experiments as a function of temperature it is evident that this scattering must be associated with the presence of ions. As discussed above, the as-cast ionomer film possessed a microphase structure significantly different from that usually observed for similar SPS ionomers.[11-13] We feel that these data are indicative of the absence of microphase-separated ion-rich clusters in the as-cast ionomer.

As the ionomer film was heated, a broad SAXS peak centered at a scattering vector ($s = 2 \sin \theta/\lambda$) of about 0.27 nm^{-1} developed at 165 °C and increased in intensity with increasing temperature. This corresponds to a characteristic spacing of ca. 3.7 nm, which is consistent with that measured for compression-molded SPS ionomers.[11-13] It appears that the usual microstructure observed for these ionomers forms upon heating the cast film. The ions that are present in the as-cast ionomer as contact ion pairs or small multiple ion pairs (i.e., multiplets, in the terminology of Eisenberg[1]) aggregate when the ionomer is heated. That the ions initially exist as associated ion pairs and not isolated ion pairs was confirmed by the electron spin resonance spectrum of the cast film shown in Figure 3. The broad single-line spectrum in which the hyperfine structure is unresolved is characteristic of associated Mn(II) ions.[14] No differences were observed between spectra measured at 25 and 150 °C, which indicates that the local environments of the cations are similar both below and above T_g.

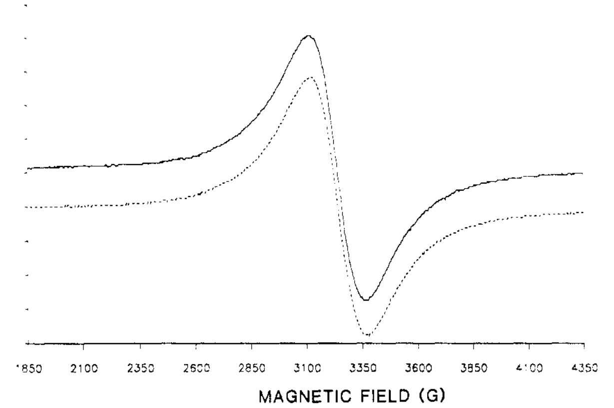

Figure 3. ESR spectra of 7.6 mol % MnSPS cast from THF/H_2O: (- - -) 25 °C and (—) 150 °C.

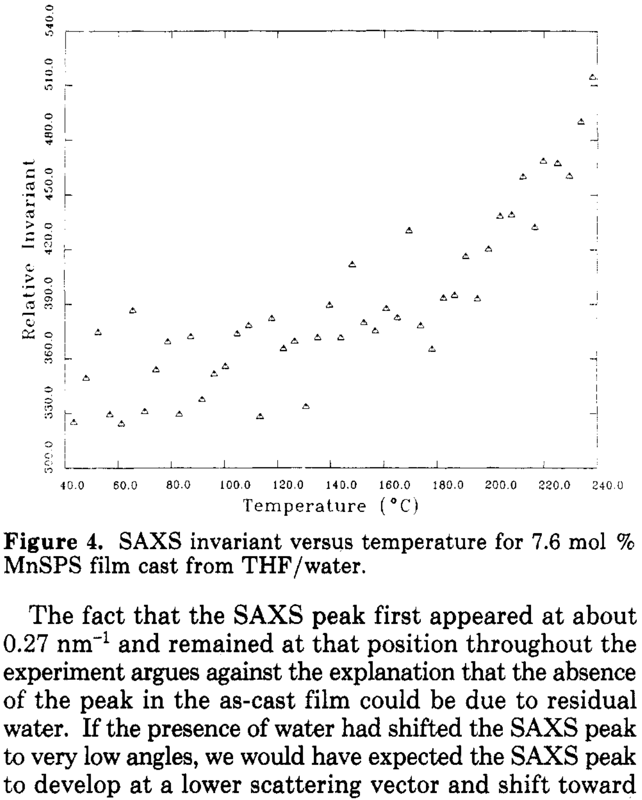

Figure 4. SAXS invariant versus temperature for 7.6 mol % MnSPS film cast from THF/water.

The fact that the SAXS peak first appeared at about 0.27 nm^{-1} and remained at that position throughout the experiment argues against the explanation that the absence of the peak in the as-cast film could be due to residual water. If the presence of water had shifted the SAXS peak to very low angles, we would have expected the SAXS peak to develop at a lower scattering vector and shift toward 0.27 nm^{-1} as water diffused from the sample during heating. The growth of the SAXS peak at a constant scattering angle is similar to the behavior we have observed for disorder–order transitions in microphase-separated block copolymers.[15]

Another interesting observation associated with the data in Figure 2 concerns the zero angle scattering. As the SAXS peak developed, there was a corresponding decrease in the intensity of the zero angle scattering. This suggests that the latter phenomenon is also associated with the spatial arrangement of the ions. These two features in the SAXS curves, the peak and the zero angle scattering, suggest the existence of two distinct environments for the ions (e.g., clusters and multiplets), though at this point we do not have sufficient information for such assignments.

The SAXS invariant is plotted against temperature in Figure 4. Due to the limited angular range of the experimental detector configuration, it was not possible to correct the scattering intensity for background contributions arising from thermal density fluctuations.[16] For this reason, the reported invariants are not absolute values, but they are self-consistent. A small increase in the invariant for temperatures above T_g (~100 °C) is probably associ-

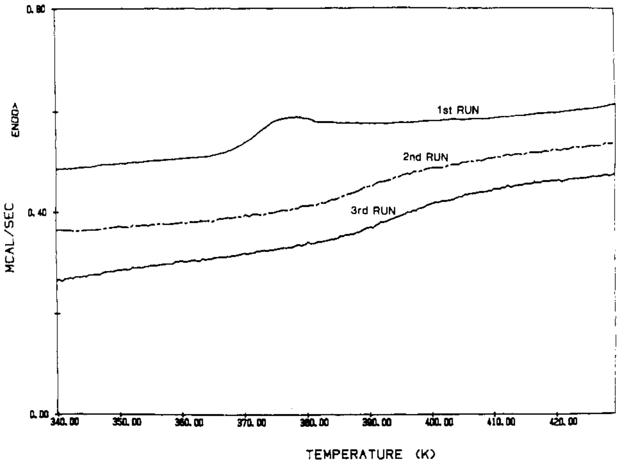

Figure 5. DSC thermograms of 7.6 mol % MnSPS film cast from THF/water.

ated with the expected increase in thermal density fluctuations with temperature.

A distinct transition in the scattering invariant occurs at ca. 180 °C. The invariant increases, coincident with the emergence of a scattering maximum, suggesting the development of ion-rich microdomains or clusters. Although the noise level of the invariant data is rather high, the observed transition is nonetheless important, since it is clearly indicative of the development of microphase separation at the transition temperature, rather than a redistribution or reorganization of existing microphases.

The present experiments were carried out under dynamic conditions and may not represent equilibrium data. Although we have not studied the effects of thermal cycling thoroughly, the formation of clusters observed does not appear to be reversible upon cooling. The influence of thermal history on the small-angle X-ray scattering from SPS ionomers was discussed previously for the case of the sodium and zinc salts.[13] Future experiments will consider temperature jumps to above Tg in order to assess the kinetics and, perhaps elucidate the mechanism of microphase separation.

The effect of the changing morphology on T_g is shown by the DSC thermograms in Figure 5. The as-cast film had a T_g of about 97 °C, which increased to 116 and 123 °C on the second and third DSC heating scans, respectively. This result was somewhat surprising in that one might have expected that by analogy to other phase-separated polymers, the T_g would decrease upon phase separation. On the other hand, the mobility of the matrix chains, which is responsible for Tg, is inherently coupled to that of the microdomains. Unlike block copolymers where the chains have a single coupling between phases, or idealized immiscible blends where there is no connectivity between phases, an ionomer chain may be anchored to more than one domain.

It is important to remember that the cross-link in ionomers is not permanent. Unlike covalent networks, in an ionomer the network chains are not fixed to a specific junction point. That is, the cross-link density depends on a dynamic equilibrium that is affected by temperature and stress. The ionic groups may migrate between junction points by a dissociative–associative mechanism referred to as "ion-hopping". Whereas the kinetics of ion-hopping has a dramatic influence on the macroscopic stiffness of the polymer, as evidenced by a decrease of modulus with increasing temperature, the effect on T_g is not known. Intuitively, one might argue that intercluster migration of ions is inherently more difficult or less favored than migration of an ionic group from one multiplet to another. The presumption here is that the cluster is more "rigid" than a multiplet. Therefore, although the absolute number of cross-link sites does not change upon cluster formation, the cluster is a more effective cross-link.

An alternative explanation, that the lower T_g observed on the first scan may be due to residual water, was proposed by one of the reviewers of the paper. Risen[17] has reported that extremely small amounts of water can be responsible for a dramatic decline in the T_g of SPS ionomers. In response to this proposal, we determined the T_g of an ionomer specimen that had been soaked overnight in water and found a change of only a few degrees with respect to a dry sample. Although we were unable to detect water in the latter specimen, we cannot rule out the possibility that water was present in the concentrations discussed by Risen. It should be noted, however, that water in the concentrations being discussed here cannot be responsible for the absence of the peak in the SAXS. This is obviously a result that requires further study.

Conclusions. These results represent our initial attempts at studying the kinetics of phase separation in ionomers as well as establishing structure–property relationships in these systems. These types of experiments hold out promise for answering a number of outstanding questions in this field, namely the structure of these materials, the origin of the zero angle scattering, and the origin of the increase in T_g for ionomers.

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Study of the Thermochromic Phase Transition of Polydiacetylene by Solid-State ^{13}C NMR

Poly(diacetylenes) (PDA) have been studied extensively by many researchers,[1,2] because they have unusual optical properties. They are also unique among synthetic organic polymers in that they can be obtained as single crystals by solid-state polymerization of suitably substituted diacetylenes. PDA has a backbone consisting of conjugated double and triple bonds as shown in Figure 1a. This is the so-called acetylenic structure. The substituents R are in the trans position with regard to the double bond. The optical properties are closely related to the electronic state of the conjugated backbone. The carbon atoms of the backbone are in a plane within the lattice and chains are extended along the *c* axis of the crystal. Another structure called the butatrienic structure (see Figure 1b) has also been proposed for the PDA backbone; however, its existence has not been firmly established.[2]

Some PDA show the thermochromic solid-state transition accompanying the changes in optical absorption and color, which is ascribed to a change in the electronic state of the backbone. Some models have been proposed for the thermochromic transition,[1,2] however, the mechanism is still not experimentally established.

The side-chain organization should strongly influence the electronic properties of the backbone through the strain it places on the backbone. The thermally induced change in molecular conformation of the side chain and its influence on the electron density distribution of the backbone will be studied in this paper.

Solid-state ^{13}C nuclear magnetic resonance (NMR) is a powerful tool for studying the conformation and the dynamics of motion in macromolecules. The chemical shift position reflects the shielding of the magnetic field due to the electronic environment of carbons; therefore, it should be sensitive to the electronic structure of the backbone, such as the conjugation length or the delocalization of electrons. There are several ^{13}C NMR studies of PDA in solutions[3-5] and in the solid state;[6] however, to our knowledge, there has been no study of the thermochromic phase transition of PDA in the solid state by NMR. Compared to other methods, such as optical,[7,8] IR,[9,10] and Raman[7,8] spectroscopic measurement, ^{13}C NMR should give much more direct information on the conformation of the backbone. Since the quality of some PDA crystals is less than optimal for a precise X-ray crystal structure determination, solid-state ^{13}C NMR provides an alternative approach for obtaining detailed structural information about the backbone. Furthermore, the motional state of both the side chain and the backbone can be studied by NMR.

Here we report the preliminary results of a ^{13}C NMR study of the thermochromic phase transition of poly(ETCD) whose substituent R is $(CH_2)_4OCONHCH_2CH_3$. Poly(ETCD) is one of the typical polydiacetylenes with a thermochromic phase transition.

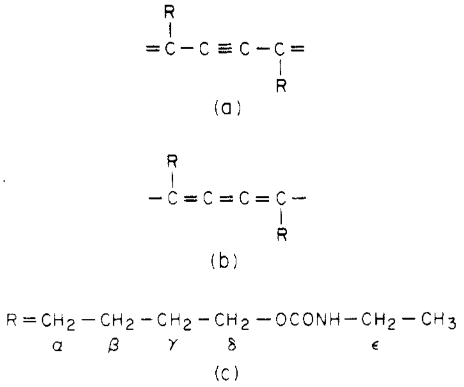

Figure 1. (a) Acetylenic structure, (b) butatrienic structure, and (c) the substituent R of poly(ETCD).

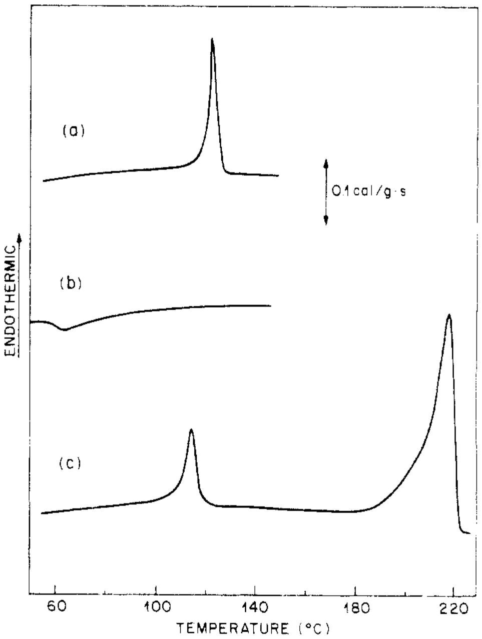

Figure 2. DSC scans at 10 °C/min for (a) the first heating process, (b) the following cooling process, and (c) the second heating process to above the melting point.

Poly(ETCD) was obtained by the solid-state polymerization of ETCD (5,7-dodecadiyne-1,12-diol bis(ethylurethane)). The synthesis of ETCD was performed by the procedure reported in the literature.[11] The polymerization was accomplished by irradiation with 50 Mrd of ^{60}Co γ-rays at room temperature. Unreacted monomer was removed by extraction with acetone.

^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135 °C by use of heated flow. Temperature was controlled within ±1 °C. Poly(ETCD) in powder form was packed in an aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] caps. A 45-KHz rf field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimum cross polarization (CP) time was found to be 2 ms at room temperature and we used this value at all temperatures. The spectra were referenced to the resonance of POM (89.1 ppm from TMS) added to the rotor.

The thermochromic transition was also studied by dif-

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