

polymer papers

The influence of thermal history on the small-angle X-ray scattering of sulphonated polystyrene ionomers

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The influence of thermal history on the small-angle X-ray scattering of the sodium and zinc salts of lightly sulphonated polystyrene (SPS) ionomers is described. Increasing temperature above T_g promotes phase mixing in ZnSPS and increased phase separation in NaSPS. The effect of annealing at elevated temperatures on the microstructure of ZnSPS is reversible, but dependent on the cooling rate. Changes in the microstructure of NaSPS on annealing are irreversible.

(Keywords: ionomers; small-angle X-ray scattering; sulphonated polystyrene; thermal effects; microstructure)

INTRODUCTION

Ionomers are predominantly hydrocarbon polymers that contain less than about 10 mol% of acid-salt side groups. They are of considerable technological and scientific interest due to the unique properties that arise from electrostatic or dipole interactions of the ionic species. Several recent reviews¹⁻³ and monographs⁴⁻⁶ discuss the properties and applications of ionomers.

It is generally agreed that in most ionomers micro-phase-separated aggregates rich in the ionic species form due to the strong attractive interactions that occur between the ionic monomer units. The major evidence for these structures, termed ionic clusters by Eisenberg⁵, is a maximum in the intensity of the small-angle X-ray scattering (SAXS). This normally occurs for values of the scattering vector, q , of 1.5 to 2.5 nm⁻¹, where $q = 4\pi \sin \theta / \lambda$ (λ is the X-ray wavelength and 2θ is the scattering angle). These values of q correspond to Bragg spacings of 2.5–4.0 nm. Although the occurrence of a SAXS peak in various ionomers is well documented, the origin of this peak is not known with certainty and has been the subject of numerous experimental and theoretical studies. Much of the uncertainty arises from the fact that interpretation of the SAXS data is model dependent, and no single model adequately accounts for all features of the available SAXS results. In general, the different proposed models can be divided into two categories: those that attribute the scattering to *inter*-particle interference and those that attribute it to *intra*-particle interference. In a recent paper, Yarusso and Cooper⁷ discussed the various ionomer models and compared the predicted SAXS with experimental results.

One particular ionomer that has been characterized by small-angle scattering experiments in several laboratories is lightly sulphonated polystyrene (SPS)⁷⁻¹⁴. These investigators found a SAXS peak at about $q = 1.8 \text{ nm}^{-1}$ for the metal salt ionomers. The only major difference between these studies was the fact that Yarusso and

Cooper^{7,12} reported a scattering peak for the SPS-sulphonic acid derivatives, while Peiffer *et al.*⁸ and Weiss *et al.*^{10,11,13} observed no peak.

In a previous paper¹⁰, we reported some preliminary studies of the effect of temperature history on the SAXS from the Na⁺ and Zn²⁺ salts of SPS ionomers, NaSPS and ZnSPS. We found that when the ionomers were exposed to elevated temperatures, the SAXS peak intensity decreased for the ZnSPS and increased for the NaSPS. The q -value for the SAXS maximum of the ZnSPS did not change with thermal ageing, while the peak shifted to lower q for the NaSPS. We concluded that partial decomposition of the ionic clusters occurs at high temperature for the ZnSPS and growth of the clusters occurs in the NaSPS. An attempt to explain these results on the basis of closest-packing inorganic crystal models was presented in another paper¹¹.

In this paper, we present in more detail studies of the effect of temperature on the SAXS of SPS-ionomers. Three kinds of experiments are discussed: (1) experiments where samples were aged at various temperatures below T_g and SAXS measurements were made at room temperature as a function of ageing time, (2) those in which the samples were heated to elevated temperature above T_g and then cooled to room temperature for the SAXS measurements, and (3) those in which the SAXS experiments were conducted at elevated temperatures. Only data for NaSPS and ZnSPS are given here; in future papers we will describe experiments for other counterions, including ammonium and alkyl-substituted ammonium salts.

EXPERIMENTAL

Sulphonated polystyrene was prepared from a commercial polystyrene, STYRON 666 (Dow Chemical Company), in 1,2-dichloroethane at 50°C using acetyl sulphate as the sulphonating reagent¹⁵. NaSPS and ZnSPS were prepared by titrating the resulting polystyrene sulphonic acid with a small excess of sodium

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hydroxide or zinc acetate, respectively. The ionomers were compression moulded into films at 215°C.

Disc-shaped samples were cut from the moulded films and placed in a vacuum oven at 65°C for three weeks prior to the SAXS analysis. SAXS measurements were made at the National Center for Small-Angle Scattering Research at Oak Ridge National Laboratory using the 10 m SAXS camera. The instrument utilizes a rotating anode CuK α ($\lambda = 1.542$ nm) X-ray source, crystal monochromatization of the incident beam, pinhole collimation, and a two dimensional, position sensitive, proportional counter, located in these experiments at either 110 cm or 156.25 cm from the sample. SAXS scans were made over the range of $q = 0.1$ – 4.4 nm $^{-1}$ for the shorter geometry and from $q = 0.05$ – 2.7 nm $^{-1}$ for the longer geometry. A calibrated Lupolin polyethylene standard was used to determine absolute intensities¹⁶.

SAXS experiments were conducted on samples with various thermal histories. At one week intervals over a period of 2 months, samples of the free acid derivative and the sodium and zinc salts of an SPS containing 5.53 mol% sulphonate¹⁷, hereafter referred to as 5.53 HSPS, 5.53 NaSPS, and 5.53 ZnSPS, were heated to 250°C under nitrogen or helium for 30 min in a Perkin Elmer differential scanning calorimeter, Model 2. The samples were then cooled at about 100°C/min to room temperature and stored in a desiccator over calcium sulphate until the SAXS experiment. In addition to the samples aged at room temperature, 5.53 NaSPS and 5.53 ZnSPS were aged in a vacuum oven at 65°C or 95°C. (T_g for these samples was about 123°C). Other samples were heated to various temperatures between 175°C and 250°C for 30 min and quenched to room temperature the day before the SAXS experiments. On the day of the SAXS measurements, samples of the 5.53 NaSPS and 5.53 ZnSPS were heated to 300°C for 5 min and quenched to room temperature.

SAXS measurements were also made at various temperatures between 25°C and 265°C. Temperature control of the sample was accomplished with a specially constructed aluminium sample holder that was wrapped with nichrome wire. Temperature was varied using a voltage regulator and was controlled to within $\pm 1.5^\circ\text{C}$. SAXS measurements were made at 20°C increments and each measurement took approximately 30 min. After the measurements at 265°C the sample was allowed to cool quiescently over several hours and another SAXS measurement was made at room temperature.

When possible, Porod plots ($q^4 I$ vs. q^4 , where I is the scattering intensity) were used to determine a background correction factor and to derive the Porod constant, which was used to extrapolate the data to higher q -values. The scattering invariant, Q , which is directly related to the mean square electron density fluctuation, was calculated by integrating the SAXS intensity over q ,¹⁸

$$Q = \int_0^\infty q^2 I(q) dq \quad (1)$$

RESULTS AND DISCUSSION

Effect of counterion and concentration

SAXS data for two SPS–sulphonic acids are given in Figure 1. In contrast to the relatively intense SAXS peak observed at about $q = 1.5$ nm $^{-1}$ by Yarusso and Cooper¹²

for an SPS–acid containing 5.6 mol% acid, no peak is evident in Figure 1 for the 5.5 HSPS sample. For the 11.5 HSPS there is considerable scattering below $q = 3.0$ nm $^{-1}$, and a shoulder is observed that may be due to a peak centered around about $q = 1.4$ nm $^{-1}$.

The difference between the SAXS analysis of the sulphonic acid derivatives reported here and by Yarusso and Cooper may be due to differences in sample preparation. Yarusso and Cooper isolated their samples from mixed solvent solutions of toluene and dimethyl sulphoxide (DMSO). We have observed, however, that high boiling, polar solvents such as DMSO (b.pt. = 180°C) are extremely difficult to remove from these ionomers. The SAXS peak observed by Yarusso and Cooper for the acid derivatives may arise from the presence of residual solvent.

A question raised by these data and the study by Yarusso and Cooper is whether microphase separation occurs in the sulphonic acid derivatives of SPS. The driving force for cluster formation would presumably be hydrogen bonding between sulphonic acid groups. Based on their observation of a SAXS peak, Yarusso and Cooper concluded that microphase separation occurs in the free acid derivatives. The data presented here for 5.5 HSPS show no SAXS peak, but this result does not necessarily preclude a second phase. Absence of the peak may be due to lack of contrast, i.e., an insufficient electron density difference between phases. The contrast may have been unintentionally improved in Yarusso and Cooper's experiment by the presence of residual solvent. The data in Figure 1 for the higher sulphonation level suggest that there is a second phase and it appears to be more than coincidence that the peak occurs at the same scattering angle as reported by Yarusso and Cooper.

Dynamic mechanical data, Figure 2, indicate that microphase separation occurs in an SPS–acid containing 5.8 mol% sulphonic acid groups. Above T_g , a rubbery

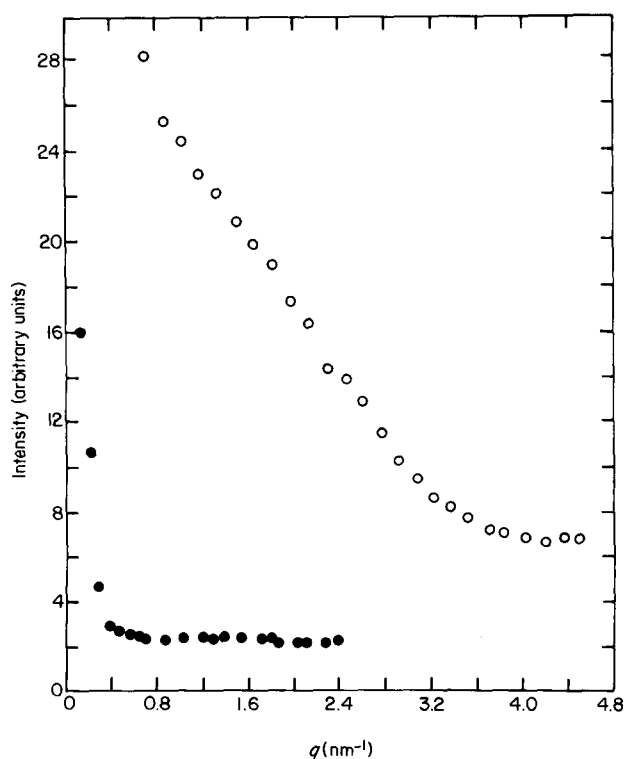


Figure 1 Scattered X-ray intensity for SPS–acid derivatives. (●) 5.5 mol% sulphonic acid, (○) 11.5 mol% sulphonic acid

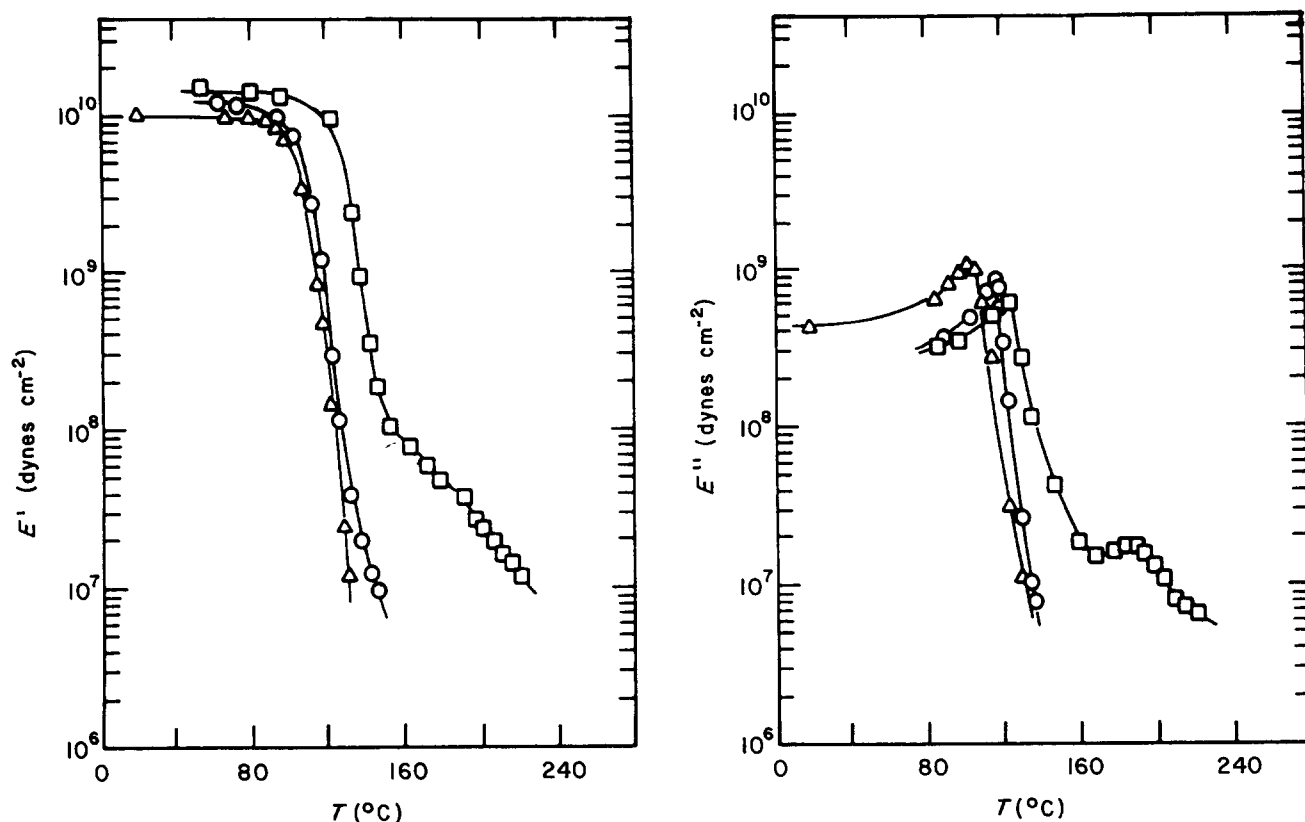


Figure 2 Dynamic mechanical data for SPS-acid derivatives: (a) dynamic modulus; (b) loss modulus. (Δ) polystyrene, (\circ) 1.8 mol% sulphonic acid, (\square) 5.8 mol% sulphonic acid

plateau is observed in the E' data for the HSPS samples, *Figure 2a*. This indicates the presence of a network in these materials, which is most likely due to intermolecular hydrogen bonding. The crosslinks are not permanent as evidenced by the decrease in E' at temperatures in excess of 200°C . The loss moduli data given in *Figure 2b* indicate a multiphase system for the 5.8 HSPS sample. For polystyrene and the lower sulphonated HSPS, only one relaxation is observed, the glass transition of the matrix. For the 5.8 HSPS, however, a high temperature loss maximum is observed. A similar peak was observed in NaSPS^{19,20} and ZnSPS²⁰, and this was attributed to the glass transition of the microphase separated ionic clusters¹⁹. Similar high temperature dynamic mechanical relaxations have been observed in other ionomers⁵ and have been attributed to a second, ionic-rich phase.

SAXS of NaSPS and ZnSPS was measured as a function of sulphonation, and the results are shown in *Figures 3* and *4*. For the metal salts the intensity of the ionic peak increases and the peak maximum moves to a higher q -value as the sulphonation level increases. The maximum peak intensities and position of the peaks are summarized in *Table 1*. For both salts, the ionic peak becomes sharper as the sulphonate concentration increases, which is consistent with the observation of Peiffer *et al.*⁶. With increasing sulphonation the number of scattering sites increases and the size distribution of the scattering sites becomes narrower.

The increase of q with increasing sulphonate concentration indicates that the characteristic scattering distance, represented by a Bragg spacing, d ($d = 2\pi/q$), in *Table 1*, decreases. As mentioned earlier the physical interpretation of d is model-dependent and there is not universal agreement as to the origin of this ionomer peak.

It is generally accepted, however, that the ionic peak reflects an electron density difference between an ion-rich region of clustered sulphonate groups and an ion-poor polymer matrix.

Physical ageing experiments

Because of the kinetic nature of the glass transition, amorphous polymers do not readily achieve thermodynamic equilibrium when cooled below the glass transition temperature²¹. As a consequence, glasses undergo slow relaxation processes in order to establish equilibrium. An important point here is that even below the glass transition temperature, T_g , molecular mobility is finite.

The approach to equilibrium in glassy polymers, termed *physical ageing* affects the thermodynamic and physical properties of the material. This phenomenon has received very little consideration in the study of ionomers. In this case, one would expect the aggregation of the ionic species to be sensitive to temperature above T_g , and it is not clear how the thermal history above T_g affects the microstructure of an ionomer in the glassy state. (This subject will be considered later in this paper.) The fact that the molecules have finite mobility below T_g suggests that changes in the microstructure may occur with time.

Changes in the microstructure may explain several effects of thermal history noted in the literature for glassy ionomers. Eisenberg and Trepman²² observed changes in the thermal coefficient of expansion in styrene-sodium methacrylate ionomers containing greater than 6 mol% sodium methacrylate as a result of varying the thermal history. They attributed this to differences in the state of ionic aggregation. Weiss²³ observed a sub- T_g endotherm in ZnSPS ionomers that depended on the sulphonate

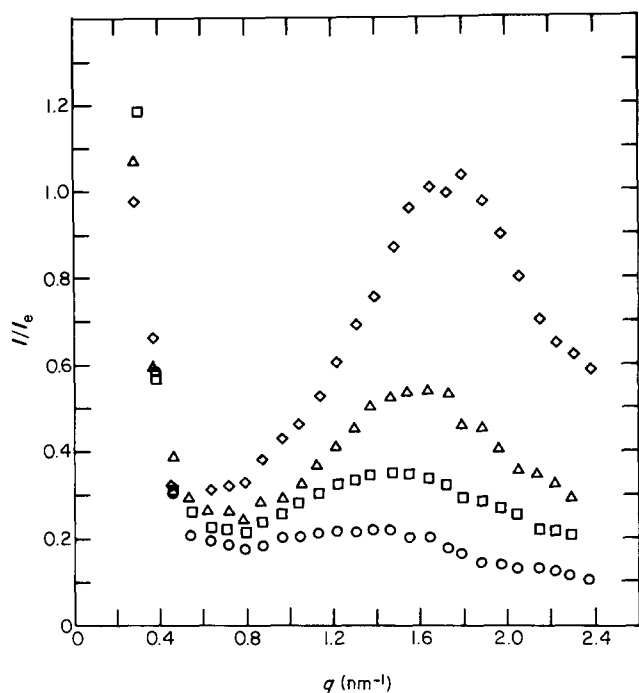


Figure 3 Scattered X-ray intensity of NaSPS ionomers as a function of sulphate concentration: (○) 1.38 mol%, (□) 2.25%, (△) 3.24%, (◇) 5.53%

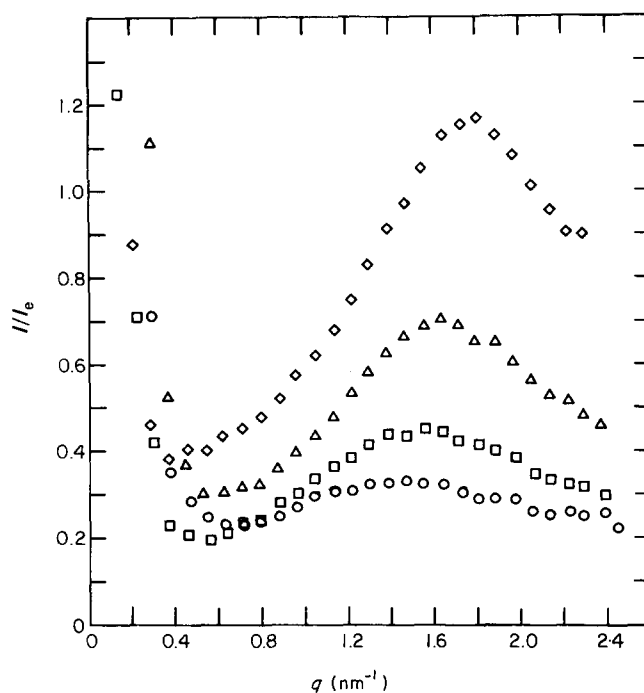


Figure 4 Scattered X-ray intensity of ZnSPS ionomers as a function of sulphate concentration: (○) 1.38 mol%, (□) 2.25%, (△) 3.24%, (◇) 5.53%

Table 1 SAXS data for SPS ionomers

Sulphonate Concentration (mol fraction) ¹⁷	NaSPS			ZnSPS		
	q (nm ⁻¹)	d (nm)	$(I/I_e)_{\max}$	q (nm ⁻¹)	d (nm)	$(I/I_e)_{\max}$
0.0138	1.38	4.56	0.22	1.47	4.28	0.33
0.0225	1.46	4.29	0.35	1.55	4.06	0.45
0.0324	1.59	3.95	0.54	1.63	3.85	0.71
0.0553	1.80	3.50	1.04	1.76	3.58	1.16

concentration and time. This excess enthalpy appeared to be similar to that observed in stressed glasses, and Weiss suggested that the origin of this event might be related to the process of ionic cluster formation, which should, if it takes place in a glass, give rise to internal stresses.

In the present study, samples vitrified from the melt were studied in order to assess any structural changes or density fluctuations that may occur upon physical ageing at various temperatures below T_g . SAXS measurements were made on samples of 5.53 NaSPS and 5.53 ZnSPS that were aged for 0 to 8 weeks at 21°C, 65°C, and 95°C.

SAXS data for the ionomers aged at 21°C for 0 to 5 weeks are shown in Figures 5 and 6 for the NaSPS and ZnSPS samples, respectively. Superposition of the SAXS data is good, which indicates that no significant change in the structure responsible for the scattering occurred within this time period. The peak position ($q \sim 1.7$ nm⁻¹) corresponded to a Bragg spacing of about 3.7 nm. The sample to detector distance used to generate the SAXS data in Figures 5 and 6 did not allow observation of the entire ionic peak. Because the high q side of the peak was distorted and incomplete, it was not possible to construct sufficiently accurate Porod plots in order to obtain the background correction needed for calculating the scattering invariant or the distance distribution function.

In another set of experiments, the samples were aged at 65°C and 95°C. No changes in the scattering curves were

observed over a period of 9 weeks at 65°C or 4 weeks at 95°C. The Bragg spacing calculated from these data was about 3.5 nm ($q \sim 1.8$ nm⁻¹). A shorter sample to detector distance was used in the studies, which allowed for the calculation of the scattering invariant. No significant trends were observed in the invariants of the two samples, which indicates that no changes in the mean squared electron density fluctuation occurred with time. This result means that no changes in the cluster microstructure occurred with time below T_g , and that the sub- T_g endotherm observed in d.s.c. experiments by Weiss²³ is not due to cluster formation.

Effect of thermal history

In this experiment compression moulded films of 3.24 ZnSPS, 5.53 NaSPS, and 5.53 ZnSPS were heated in a d.s.c. to different temperatures above T_g , held for 30 min (samples were held at 300°C for only 5 min), and then rapidly cooled to room temperature. The SAXS measurements were made at room temperature within one day of the thermal history. The scattering curves normalized by the thickness of the specimens are given in Figures 7–9.

The effect of temperature history on the scattering is different for the two counterions studied. In the case of the 3.24 ZnSPS sample, thermally ageing the ionomer at 300°C resulted in a substantial decrease of the scattering intensity. The general shape of the scattering curve and the SAXS peak position did not change. This result

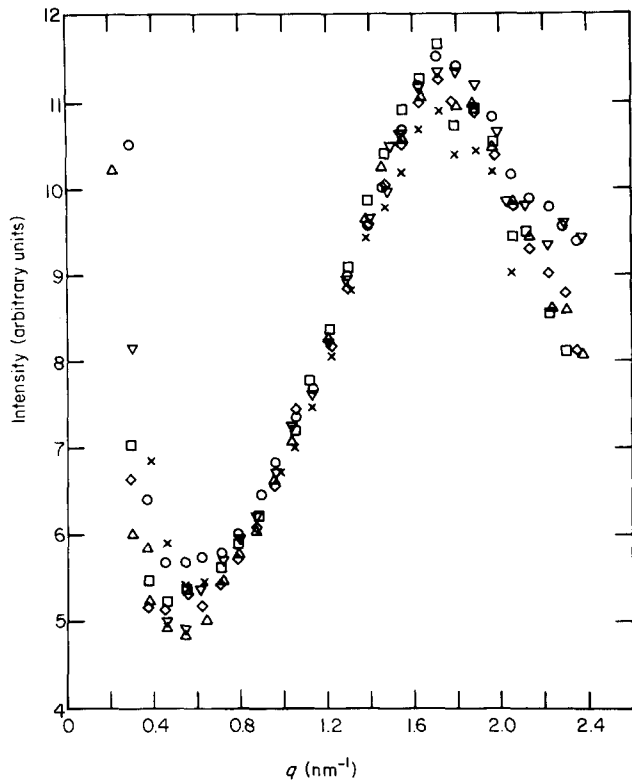


Figure 5 Scattered X-ray intensity for 5.53 NaSPS aged at 21°C for 1 day (▽), 7 days (◇), 14 days (○), 21 days (□), 28 days (△), and 35 days (×)

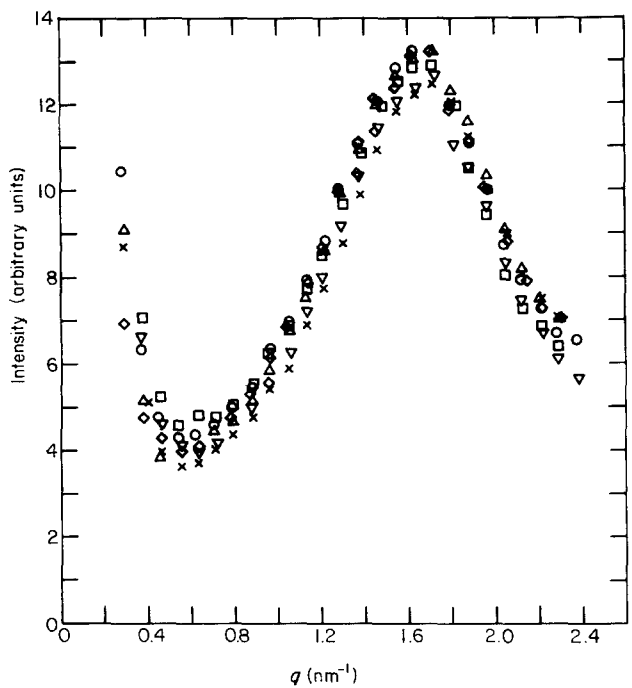


Figure 6 Scattered X-ray intensity for 5.53 ZnSPS aged 21°C for 1 day (○), 7 days (□), 14 days (△), 21 days (×), 28 days (▽), 35 days (◇)

indicates that the concentration of the ionic clusters has decreased in this sample, which is consistent with the observation that melt flow of the material occurs under its own weight at elevated temperature. In order for an ionomer to flow, dissociation or relaxation of the ionic aggregates must occur. If the ionomer is rapidly cooled from elevated temperature to below T_g , insufficient time is available for the cluster microstructure to completely reform.

SAXS data for 5.5 ZnSPS as a function of thermal history is shown in Figure 8. Again, although the general shape and position of the scattering curves do not change, the intensities are dependent upon the thermal history. The highest SAXS intensity was observed for the sample that was compression moulded at 215°C and slowly cooled to room temperature, but which was not further

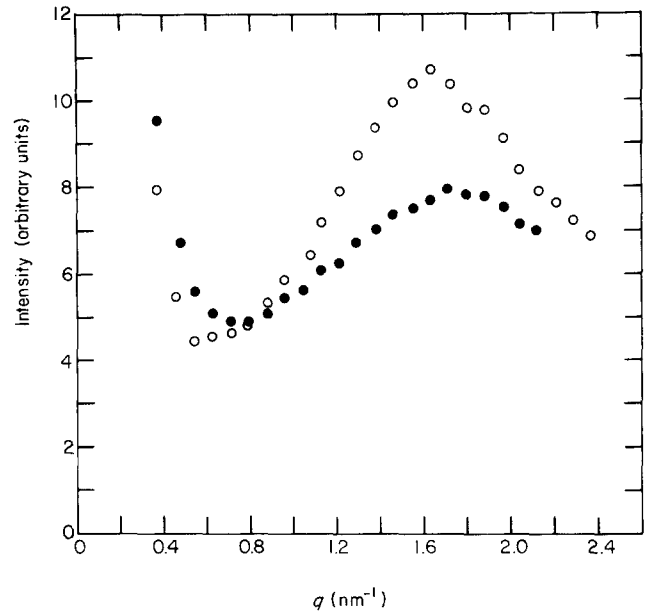


Figure 7 Scattered X-ray intensity for 3.24 ZnSPS. (○) aged at 21°C; (●) 300°C. Measurements were made at room temperature

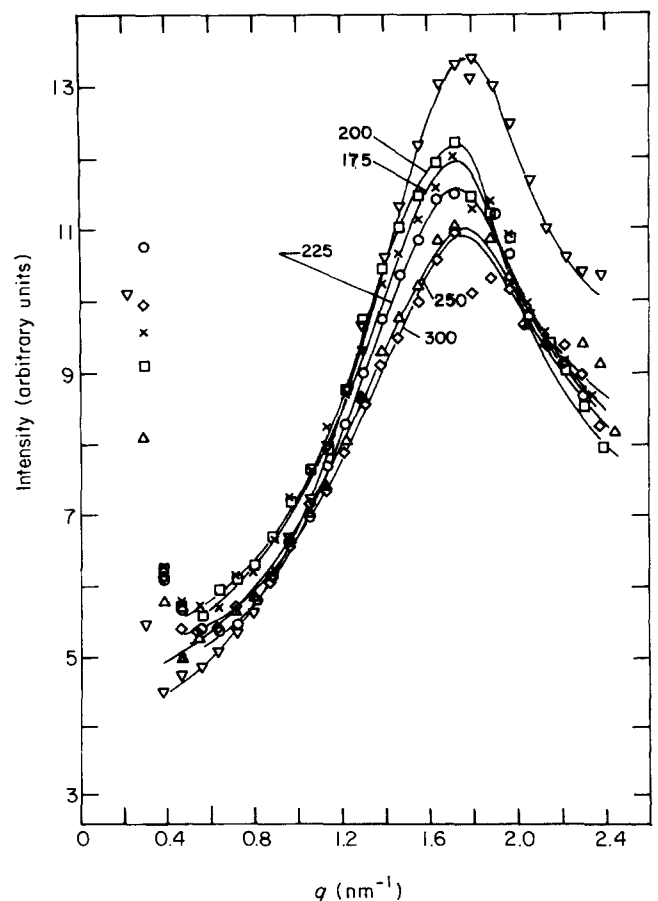


Figure 8 Scattered X-ray intensity for 5.53 ZnSPS: (▽) aged at 21°C, (×) 175°C, (□) 200°C, (○) 225°C, (△) 250°C, and (◇) 300°C. Measurements were made at room temperature

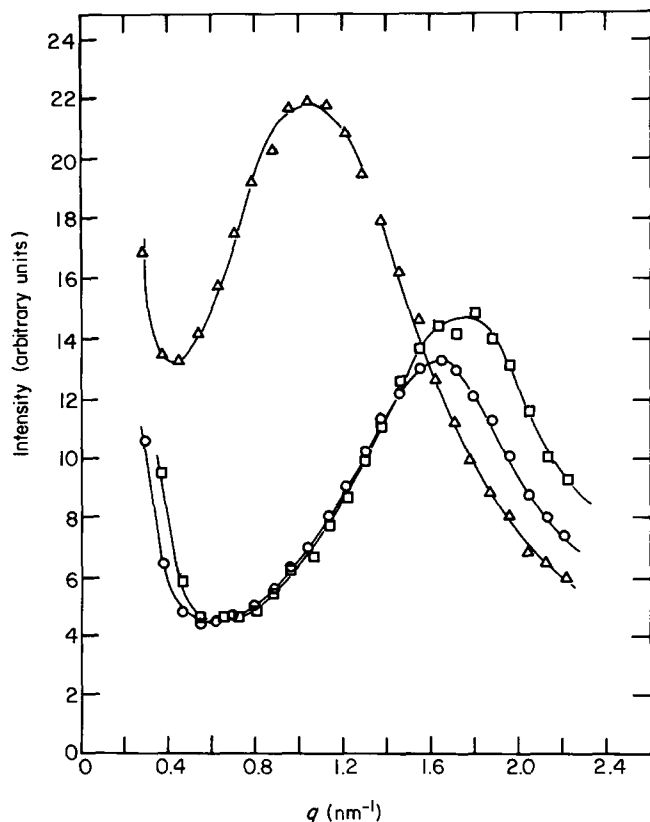


Figure 9 Scattered X-ray intensity for 5.53 NaSPS: (□) aged at 21°C, (○) 250°C, (△) 300°C. Measurements were made at room temperature

annealed at elevated temperatures. With the exception of the sample annealed at 175°C the SAXS intensity decreases monotonically with increasing annealing temperature. Although small differences between the SAXS curves may be experimental uncertainty, the overall changes between the sample with no thermal history and those annealed at the highest temperatures are significant, *cf.* Figures 3 and 4 which demonstrate the reproducibility of the SAXS measurements. Again, these data show that the structure giving rise to the scattering is partially disappearing upon heating the ZnSPS sample to elevated temperatures followed by quenching to below T_g .

The effect of thermal history on the SAXS for 5.53 NaSPS is shown in Figure 9. The maximum in the scattering peak moves to smaller q , which corresponds to a larger characteristic distance, as the annealing temperature is increased. When moulded at 215°C with no subsequent thermal annealing, this ionomer had a characteristic distance, d , of 3.59 nm ($q = 1.75 \text{ nm}^{-1}$), but when the ionomer was annealed for 5 min at 300°C, d nearly doubled to 6.04 nm ($q = 1.04 \text{ nm}^{-1}$). In addition, the intensity of the scattering increased dramatically when the ionomer was annealed at 300°C. It appears that not only are the clusters in the sodium salt-ionomer more persistent than in the zinc salt, but that the structure actually anneals, much like a crystal. Unlike the zinc salt, the NaSPS did not flow under its own weight, even at 300°C. This observation is consistent with the SAXS result that no breakup of the cluster structure occurred at elevated temperature.

SAXS measurements at elevated temperatures

In order to directly determine the changes that occur in the ionomer microstructure at elevated temperatures,

SAXS measurements were made at various temperatures between 21°C and 266°C. The corrected intensity data for the Zn^{2+} and Na^+ salts of a 5.53 mole percent SPS are given in Figures 10 and 11, respectively. The data points are shown only for the measurements at 21°C; for clarity, lines have been drawn through the data points for the other temperatures.

For 5.53 ZnSPS, Figure 10, the intensity of the ionic peak first increased as the temperature was raised below T_g , but then decreased with increasing temperature above T_g . The peak also broadened with increasing temperature. The peak maximum moved to lower q as the temperature increased below T_g (from 1.82 nm^{-1} to 1.66 nm^{-1}), but above T_g the position of the peak remained constant. The SAXS curve for the ZnSPS was reversible with tempera-

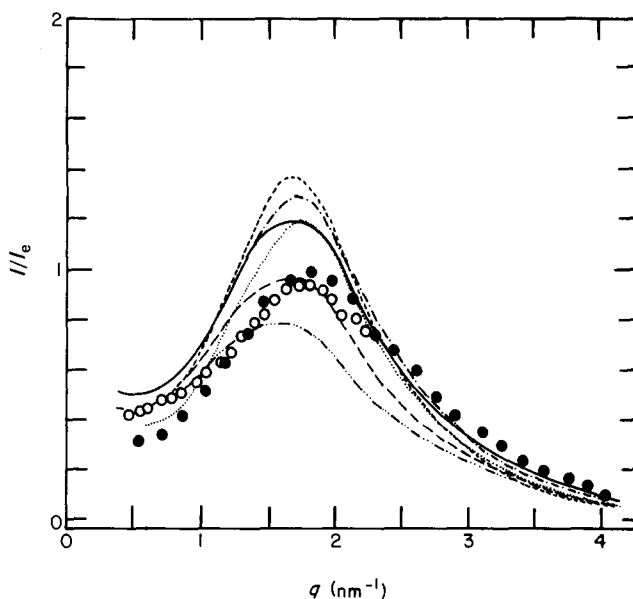


Figure 10 Scattered X-ray intensity for 5.53 ZnSPS at various temperatures: (○) 21°C, (⋯) 63°C, (---) 106°C, (—) 144°C, (—) 183°C, (—) 228°C, (—) 266°C, (●) 21°C after being cooled from 266°C

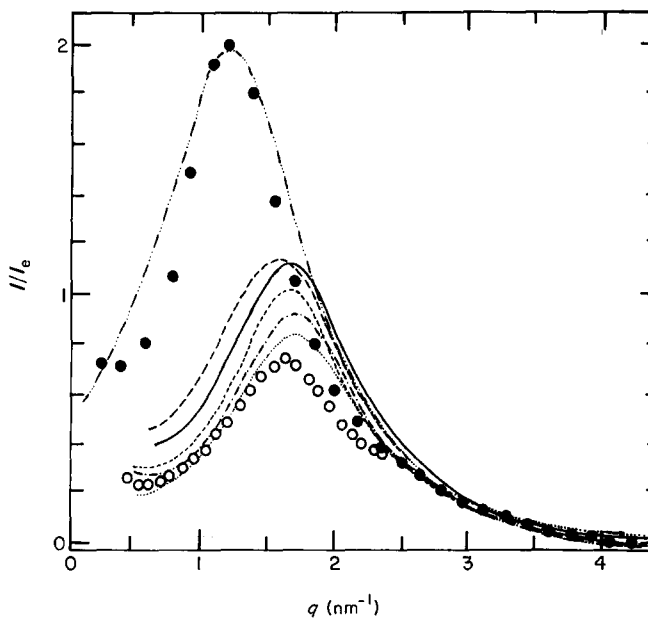


Figure 11 Scattered X-ray intensity for 5.53 NaSPS at various temperatures: ○, 21°C, (⋯) 63°C, (---) 106°C, (---) 140°C, (—) 186°C, (—) 230°C, (—) 263°C, (●) 21°C after being cooled from 263°C

ture; when the sample was cooled to 21°C from 266°C the original room temperature SAXS curve was obtained.

It is important to note that in this experiment the cooling rate from 263°C to 21°C was extremely slow; the process took several hours. This is in contrast to the experiment discussed earlier where samples were heated to elevated temperatures and then cooled at 100°C/min to room temperature. SAXS data from the latter experiment, *cf.* Figure 8, revealed that the structure of the ionomer at the higher temperature is frozen in by the rapid vitrification process. As a consequence, a declining SAXS intensity was observed with increasing annealing temperature. On the other hand, when the sample was slowly cooled, sufficient time was allowed for the microstructure to equilibrate before T_g was reached. In this case, the microstructure was reversible.

The influence of temperature on the SAXS of 5.53 NaSPS was different, Figure 11. The peak intensity increased and the maximum moved to lower q (from 1.82 nm^{-1} to 1.19 nm^{-1}) as the temperature was raised from 21°C to 263°C. No apparent broadening of the peak was observed. Unlike the ZnSPS, the SAXS curve for NaSPS was not thermally reversible. The intensity and peak position for the sample cooled to room temperature from 263°C reflected the high temperature treatment and did not return to the values originally obtained at 21°C prior to heating. Similarly, no effect of cooling rate was observed for the NaSPS.

The scattering invariant, Q , as defined in equation (1) measures the mean square fluctuation of electron density, and this quantity is sensitive to changes in the ionomer microstructure. If one assumes a two-phase system of electron densities ρ_1 and ρ_2 for each phase and a sharp boundary between the phases then the mean square fluctuation of electron density, $\langle(\rho - \bar{\rho})^2\rangle$ is²⁴,

$$\langle(\rho - \bar{\rho})^2\rangle = \phi_1\phi_2(\rho_2 - \rho_1)^2 \quad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of the phases.

The calculated scattering invariants for the 5.53 NaSPS and 5.53 ZnSPS samples are plotted *versus* temperature in Figure 12. For NaSPS, Q increases monotonically with temperature. This corresponds to either an increase in the mean square electron density difference between the two phases or an increase in the volume fraction of clusters. Such a result might be expected if the local concentration of the ionic species in a dispersed phase, i.e. the ionic cluster, increased at the expense of isolated ion-pairs, multiplets, in the surrounding matrix.

The invariant results for ZnSPS are not as clear. The overall trend, however, appears to be a decline in Q with increasing temperature, which would correspond to an increased mixing of the two phases or a more diffuse phase boundary. This would correspond to an increase in multiplets in the matrix that would decrease the mean square density fluctuation.

For a two phase material one can estimate the magnitude of the inhomogeneity by calculating a correlation length, l_c ,²⁴

$$l_c = 4V/S \quad (3)$$

where S/V , the ratio of the phase interface and the phase volume, is given by,

$$\frac{S}{V} = \frac{2\pi^2 \lim[q^4 I(q)]}{Q} \quad (4)$$

The calculated values of S/V and l_c for the 5.53 SPS ionomers are given in Table 2. For the NaSPS, S/V decreases and l_c increases with increasing temperature, which is consistent with the idea that the clusters are being annealed, i.e. growing.

The trend in the S/V and l_c data is more complicated for the Zn^{2+} salt. Below 106°C, S/V decreases and l_c increases, which suggests that the clusters are growing. Above 106°C, however, S/V increases and l_c decreases, which suggests a decline in the cluster size. It is noteworthy that the change in behaviour occurs near T_g , which is about 120°C for this material. One possible explanation for this result is that when the ionomer was cooled from the melt to below T_g a non-equilibrium microstructure was frozen in as a result of the low mobility of the polymer chains below T_g . When the polymer is heated below T_g the local mobility of the chains increases allowing ion-pairs trapped in the matrix to diffuse into the clusters. Above T_g , large scale motions of the chains may occur.

It was postulated by Eisenberg³ that formation of the ionic clusters involves a competition between dipole-dipole interactions that promote clustering and rubber elasticity effects that oppose clustering. The elasticity effects are temperature dependent, while the dipole-dipole interactions are relatively insensitive to temperature. Therefore, as the temperature increases, increased mobility of the chains gives rise to higher elastic forces that may promote breakup of the clusters. This explanation appears to be consistent with the behaviour of ZnSPS, but not NaSPS. The difference between the two salts may be due to differences in the packing of the ionic species in the cluster. Since attraction between dipoles scales as the reciprocal third power of the separation, a tighter packing of the sodium sulphonates *versus* zinc sulphonates as proposed in a recent model by Lefelar and Weiss¹¹ may account for the better temperature resistance of the clusters in NaSPS. In this case, the increased mobility of the polymer at the higher temperature should allow a high percentage of the ionic groups to participate in the cluster, thus increasing Q and l_c .

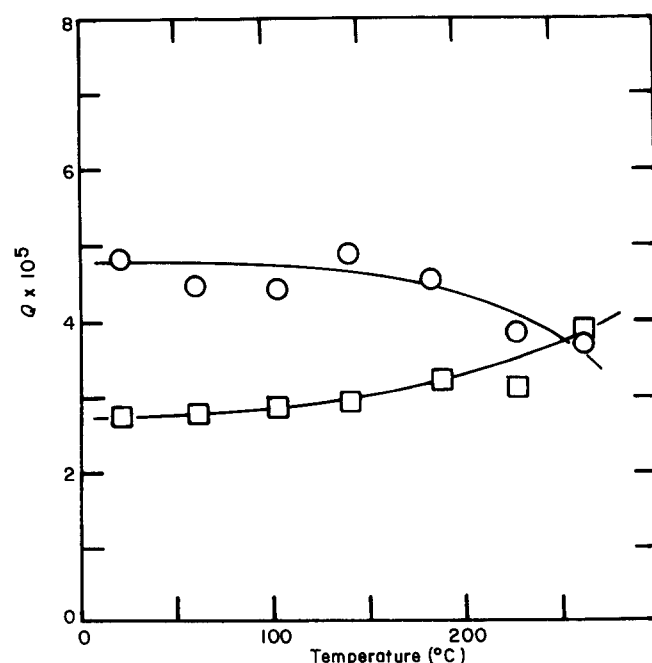


Figure 12 Scattering invariant *versus* temperature for 5.53 NaSPS (\square) and 5.53 ZnSPS (\circ)

Table 2 SAXS parameters as a function of temperature for the Na⁺ and Zn²⁺ salts of 5.53 mole percent SPS

Temp (°C) Na ⁺ /Zn ²⁺	Na ⁺ salt			Zn ²⁺ salt		
	$Q \times 10^5$	S/V	l_c	$Q \times 10^5$	S/V	l_c
21/21	2.74	0.71	5.6	4.81	0.80	5.0
61/60	2.77	0.72	5.6	4.48	0.75	5.3
104/106	2.82	0.67	6.0	4.48	0.70	5.7
140/144	2.95	0.66	6.1	4.89	0.75	5.3
186/183	3.20	0.62	6.4	4.59	0.78	5.1
228/228	3.11	0.58	6.9	3.85	0.77	5.2
263/266	3.93	0.54	7.4	3.77	0.85	4.7
21 ^a	3.05	0.54	7.4	4.90	0.87	4.6

^a Measured after being heated to about 260°C

CONCLUSIONS

The influence of thermal history on the structure of SPS has been shown to be different for two salts, sodium and zinc. Increasing temperature promotes phase mixing in ZnSPS and increased phase separation in NaSPS. This conclusion is consistent with the observation that for a comparable degree of sulphonation, the viscosity of NaSPS is considerably greater than that of ZnSPS.

The effect of annealing on the microstructure at elevated temperatures is reversible, and dependent on cooling rate, for ZnSPS, but irreversible for NaSPS. Scattering data obtained at room temperature for slowly cooled ZnSPS samples are identical regardless of the previous thermal history. The SAXS data for NaSPS, however, depends on the maximum annealing temperature of the sample.

In light of the dramatic differences in the behaviour of the two metal salts considered here, additional studies with other cations is warranted. In addition, a study of the effect of solvent on the SAXS of SPS ionomers is now underway.

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