no-decoupling spectrum, which does not detect protonated chains, and the full-decoupled spectrum, which detects them quantitatively, is unity. It is useful to scale intensities this way since the delayed-decoupling spectra we are about to compare reflect contributions from only part of the protonated chains.

We now construct a spectrum which has a fraction f of protonated polystyrene as a deuterated–protonated (90/10) mixture and the remaining fraction $(1 - f)$ as pure polystyrene so as to produce an intensity ratio δ_C 145/δ_C 125 of 0.84. We use the relative contributions of these two components to observed delayed decoupling intensities (Table I) and so find $f = 0.404$ by solving the proportion

$$\frac{1.15f}{1.15f + 0.48(1 - f)} = \frac{0.52}{0.84}$$

For this mixture, the weighted average of the relaxation rates for the two kinds of aromatic protons (40.4% in polystyrene-d_8/polystyrene (90/10) and 59.6% in polystyrene) predicts $T_{1\rho}(\mathrm{H}) = 6.8$ ms, as compared to 7.6 ms observed for the polystyrene-d_8/K-resin blend. In addition, the overall composition combines $0.404 + 0.596 = 1$ part of polystyrene with $9 \times 0.404 = 3.636$ parts of polystyrene-d_8 to give 21.6% polystyrene as compared with 27% in the actual K-resin blend. Not only do these two sets of figures not agree particularly well, they cannot *both* be made to agree better by altering the composition of the heterogeneous mixture. In fact, the only way to achieve better agreement is to make the components of the heterogeneous mixture less different. Thus, we are led to the conclusion that the *combined* evidence of our several different measurements is only consistent with a random or near-random mixing model.

Acknowledgment. We thank R. Kruse (Monsanto, Springfield) for preparation of the K-resin blend and T. R. Steger (Monsanto, Springfield) for many helpful discussions and suggestions.

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Small-Angle Neutron Scattering from Sulfonate Ionomers

T. R. Earnest, Jr.,[†] J. S. Higgins, D. L. Handlin, and W. J. MacKnight[*]

Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London, United Kingdom. *Received October 23, 1980*

ABSTRACT: Small-angle neutron scattering experiments (SANS) have been performed on sulfonated polystyrene ionomers. Sulfonate concentrations were studied over the range 0–8.5 mol %. The radius of gyration of the polystyrene ionomers showed a regular increase with increasing sulfonate content. The radius of gyration was insensitive to thermal annealing and remained unchanged at temperatures well above the glass transition temperature.

Introduction

Ionomers are defined as linear polymers with predominantly nonpolar backbones which contain 10 mol % or less of neutralizable side groups. The backbone may or may not be crystalline. Despite extensive studies carried out on ionomers, the important question of the state of aggregation of the salt groups in the bulk remains unanswered. The literature concerning ionomers has become vast and a suitable introduction to the subject may be found in two recent books and a review.[1-3] From the structural studies involving various techniques, including electron microscopy, X-ray scattering, neutron scattering, vibrational spectroscopy, and Mössbauer spectroscopy, several different models have been suggested. We shall here be concerned with only one of these which we believe to be generally applicable. For a discussion of the others, the reader should consult ref 1–3. The model envisages the presence of at least two kinds of ionic aggregates. These will be referred to as clusters and multiplets to conform to the nomenclature of Eisenberg.[2] The clusters have dimensions in the 10–50-Å range, contain 50–100 ion pairs, and possess an internal structure. The multiplets consist of isolated ion pairs or quartets. The model implies a multiphase structure for ionomers. For amorphous ionomers two phases are present: a dispersed phase consisting of the clusters and a continuous phase consisting of the hydrocarbon matrix and the multiplets. Examples of ionomers in this category are poly(butadienecarboxylates) and poly(styrenecarboxylates). Crystalline ionomers contain a third phase consisting of the crystallized portions of the backbone. The best known examples of ionomers in this category are the poly(ethylenecarboxylates).

The most striking feature present in both the X-ray and neutron scattering patterns of ionomers is a peak corresponding to a Bragg spacing from 20 to 60 Å, depending upon the chemical structure of the ionomer and the presence or absence of polar impurities such as water. This peak appears for all salt forms but is absent in the acid form. It persists in the melt up to decomposition tem-

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[†] Present address: E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE 19878.

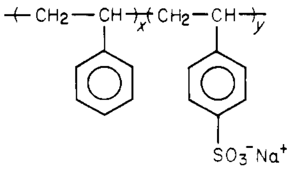
[*] To whom correspondence should be addressed at the Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003.

0024-9297/81/2214-0192$01.00/0

peratures and is moved to larger Bragg spacings by water. Saturation with water causes the X-ray peak to disappear in poly(ethylenecarboxylates) and poly(butadienecarboxylates). A recent deformation study reveals that in a poly(cesium ethylenecarboxylate) ionomer, the X-ray peak is azimuthally dependent on sample elongation.[4] A synthesis of all available information leads to the conclusion that this peak arises from intraparticle scattering caused by a structural feature of the cluster. The exact nature of this structural feature remains unclear. It has been suggested that the cluster consists of a core of 3–13 Å in dimension which is separated from a surrounding shell of multiplets by a distance corresponding to the observed Bragg spacing. The cluster is not necessarily spherical. In fact, the X-ray orientation data have been interpreted to imply that it has a lamellar morphology.[4]

Small-angle neutron scattering (SANS) has been carried out on several types of ionomers.[5-7] The presence of a SANS peak corresponding to the X-ray "ionic" peak has already been alluded to. An analysis based on the integrated intensity of the SANS peak led to a distribution of cluster sizes very similar to that previously obtained from the X-ray scattering results.[8] This was remarkable in that the SANS results were obtained on coordination complex ionomers which had an amorphous poly(styrene or butadiene) backbone with pyridine side groups to which were coordinated Fe^{II} ions. The X-ray results were obtained on poly(ethylenecarboxylate) ionomers, mainly cesium and sodium salts. In other words, although the multiplet structures in the two cases were quite dissimilar, the clusters appeared to be nearly the same. A preliminary study of polystyrene–sodium methacrylate ionomers has reached the tentative conclusion that the radius of gyration of the individual chains is not altered in going from the acid form to the salt form but that evidence for clustering exists.[7]

In this paper we report the results of a SANS study of a series of ionomers. These are poly(sodium sulfonates) (I). The inclusion of a small quantity of deuterated



I

polystyrene chains in the polystyrene ionomers enabled us to determine the radius of gyration as a function of salt group content and to compare radii of gyration among unsubstituted polystyrene, the acid form, and the salt form. Complementary X-ray studies were carried out on the ionomers and the preliminary results of these studies are also reported here.

Experimental Section

Polymer Preparation. Anionically polymerized styrene and perdeuteriostyrene were purchased from Polymer Laboratories, Ltd. The molecular weight of the polystyrene (HPS) was 90 000 with $M_w/M_n = 1.05$. The poly(perdeuteriostyrene) (DPS) molecular weight was 100 000 with $M_w/M_n = 1.06$, as determined by gel permeation chromatography. Solutions containing 5 wt % polymer were prepared in dichloroethane (DCE) of which 0, 2, 2.5, and 3% of the total polymer was DPS. The sulfonation reaction used was similar to that described by Makowski and Lundberg.[9] To obtain a sulfonation level of 5%, 60 μL of acetic anhydride and 25 μL of concentrated sulfuric acid were added to 20 mL of the 5 wt % polymer solutions in DCE. Sulfonation was carried out for 90 min at 323 K after which the reaction was stopped by the addition of methanol. The solution of sulfonated polystyrene was then diluted with 20 mL of additional DCE, centrifuged, filtered, and isolated in the acid form by steam stripping. After the polymer was vacuum dried overnight at 323 K, the sulfonate content was determined by titrating two 0.100-g portions of each batch (DCE/methanol solvent) with 0.1 N NaOH, using phenolphthalein as an indicator. Elemental analysis of the sulfonated polystyrenes indicates that this titration procedure overestimates the sulfur content by 20%.[10] Half of the remaining sulfonated polymer (0.4 g) was then neutralized with the calculated amount of NaOH and again isolated by steam stripping, and the resulting powder was vacuum dried. Polymers were prepared containing nominal 2, 5, and 10 mol % sulfonate groups for each of the DPS concentrations (Table I).

Table I
Characterization Data for Polystyrene Sulfonate Ionomers

material	salt content, % nominal	salt content, % actual	T_g, °C
polystyrene (M_w = 100 000)			103
20S	2.0	1.9	106
50S	5.0	4.2	110
100S	10.0	8.5	120

Films for use in the neutron scattering experiments were compression molded under vacuum with a 16-mm Specac KBr pellet die. For 1.0-mm-thick disks, 0.20 g of polymer powder was placed in the die which was then evacuated. The powder was compressed at room temperature for 3 min at the maximum load of 15 tons. The pressure was released and the temperature raised and held at 423 K for 20 min. The die assembly was then slowly cooled to room temperature and the polymer film removed. The free-acid polymers tended to discolor when molded and were difficult to remove from the metal die. The salts were obtained colorless and clear. All of the polymer films were annealed under vacuum at 406 K for 18–20 h, after which the salts developed a slightly rough surface, giving the films a translucent appearance. In a second set of experiments some of the films were annealed at 433 K for 20 h to determine the effects of thermal treatment on the scattering measurements.

Neutron Scattering. SANS experiments were carried out with the D11 spectrometer at the Institut Laue-Langevin (ILL),[11] Grenoble. The polymer films were held between quartz windows, with the sample area being defined by a 1.0-cm-diameter diaphragm. Detector normalization was made by using the incoherent scattering from a water sample held in a 1-cm quartz cell under identical experimental conditions. The radii of gyration measurements for the sulfonated polystyrene ionomers were conducted by using a sample-to-detector distance of 10 m and wavelengths of 7 and 12 Å. Scattering experiments at 433 K were carried out with a specially designed brass heating cell to hold the polymer in the neutron beam. Temperature was held constant to ±1 K.

X-ray Scattering. Small-angle X-ray scattering experiments were carried out at Queen Elizabeth College (University of London), using a Kratky X-ray camera. Copper radiation (Kα) was used in conjunction with a nickel filter and the sample cavity was evacuated to less than 2 torr. The sample-to-detector distance was 25.3 cm and a stepping-motor-controlled counter was used to scan the small-angle range. The 8.5 mol % sulfonated polystyrene sample was the sodium salt and the same as used in the neutron scattering experiments (1.0-mm film).

Analysis. The SANS intensity at a scattering angle θ is calculated as the average scattering around the multidetector at a radial distance r from the neutron beam center. The angle θ is then defined as r/D, where D is the sample-to-detector distance. The scattering vector Q is calculated by the expression

$$Q = \frac{4\pi}{\lambda} \sin (\theta/2) = \frac{2\pi}{\lambda} r/D \qquad (1)$$

where λ is the incident wavelength. For a monodisperse polymer in dilute solution at concentration c[12]

$$\frac{Kc}{I(Q)} = \frac{1}{M}\left[1 + \frac{Q^2\langle R_g^2\rangle}{3}\right] + 2A_2C \qquad (2)$$

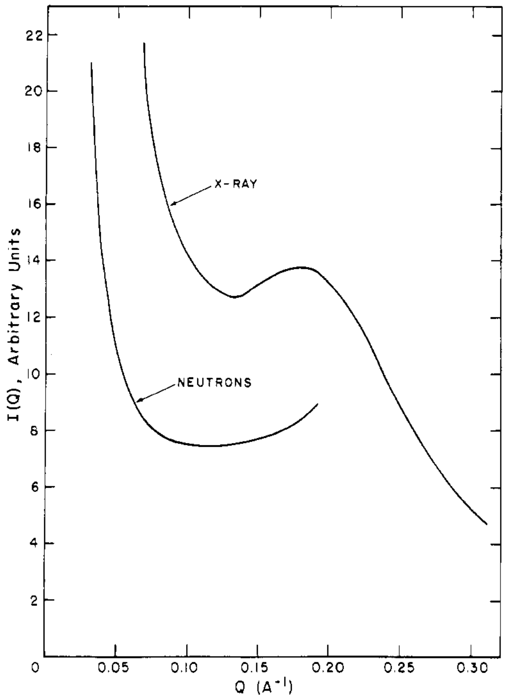


Figure 1. $I(Q)$ vs. Q for an 8.5 mol % poly(sodium styrenesulfonate), SANS and SAXS.

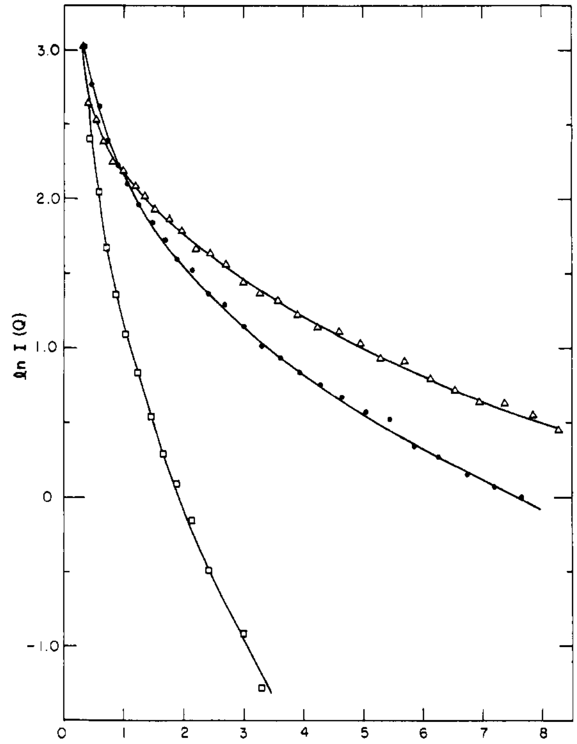


Figure 2. Guinier plots in the low Q range for poly(sodium styrenesulfonates): (□) 1.9; (●) 4.2; (▲) 8.5 mol %.

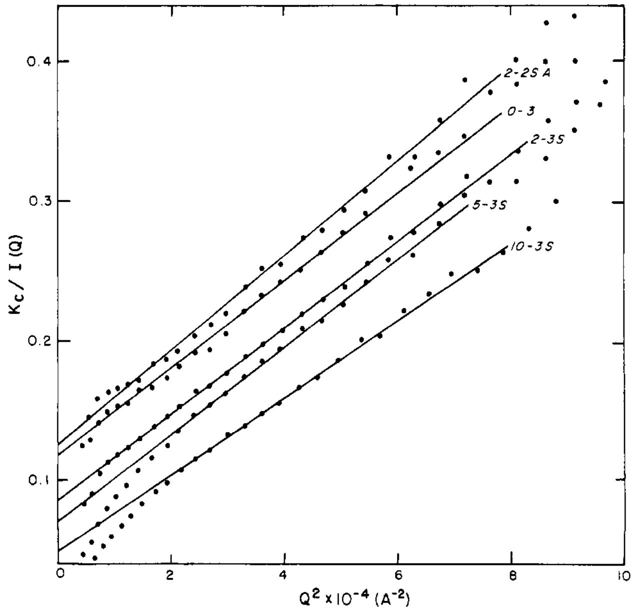


Figure 3. Zimm plots for the various derivatives: (0–3) unmodified polystyrene containing 3% poly(deuteriostyrene); (2–2S A) 1.9 mol % acid containing 2.5% deuterated acid; (2–3S) 1.9 mol % salt containing 3% deuterated salt; (5–3S) 4.2 mol % salt containing 3% deuterated salt; (10–3S) 8.5 mol % salt containing 3% deuterated salt.

where M is the molecular weight, $\langle R_g^2 \rangle$ is the mean-square radius of gyration, and A_2 is the second virial coefficient. The constant K contains a contrast factor and machine parameters. A plot of $c/I(Q)$ vs. Q^2 is linear and the radius of gyration can be determined from the slope and intercept and is independent of normalization and the constant K. The molecular weight M is determined by the intercept and its value is correspondingly less accurate due to its dependence on absolute intensity and the contrast factor in K.

The scattering from widely separated identical particles can be represented by Guinier's law[13]

$$\ln [I(Q)] = -Q^2 R_g^2/3 + \text{constant} \qquad (3)$$

so that from a plot of ln $[I(Q)]$ against Q^2, the radius of gyration of the scattering particles is simply determined by the slope.

Results

Figure 1 compares the neutron and X-ray scattered intensity $I(Q)$ as a function of the wave vector Q for the sodium salt of an 8.5 mol % sulfonated polystyrene. The intensity scale for both curves is arbitrary and chosen only for comparative purposes. Although the Q range of the neutron data is limited, it is apparent from the X-ray curve that a small-angle scattering peak occurs in this polymer near a Q value of 0.18. This corresponds to a Bragg spacing of 35 Å.

Figure 2 shows neutron scattering Guinier plots for the 1.9, 4.2, and 8.5 mol % sulfonated polystyrenes in the very low Q region. Assuming the scattering to be due to particles with a distribution of sizes, these curves would indicate that the maximum size is about 275 Å for each of the ionomer salts, with the proportion of smaller particles increasing with increasing salt content.

Figure 3 contains Zimm plots for the starting polystyrene and the three salt concentrations, each with 3% perdeuterio chains, and the Zimm plot for the 2% sulfonated polystyrene in the acid form containing 2.5 % perdeuterio chains. The background subtracted from each salt was the scattering resulting from HPS sulfonated to the same level. Therefore, the curves in Figure 3 represent the scattering of only the tagged sulfonated DPS chains. The slight downturn at low Q in Figure 3 is a consequence of the scattering in this region shown in Figures 1 and 2. The introduction of deuterated chains slightly changes the overall contrast levels in the sample, causing imperfect background subtraction in this region. The radius of gyration and the molecular weights are calculated by eq 2 and the results are listed in Table II.

The results of heating a sample above its glass transition temperature during a SANS experiment are illustrated in Figure 4. It is clear from this Zimm plot that the intensity of scattering is less for the sample at the elevated tem-

Table II
R_g and Molecular Weight Calculated for Polystyrene Sulfonate Ionomers

	description			
polymer	mol % sulfonate	% DPS	R_g, Å	MW × 10^4
0-25	0	2.5	84 ± 2	1.5
0-3	0	3	87 ± 2	1.5
2-25A	1.9 (acid)	2.5	92 ± 4	1.6
2-2S	1.9 (salt)	2	109 ± 5	2.1
2-25S	1.9 (salt)	25	106 ± 5	2.3
2-3S	1.9 (salt)	3	105 ± 3	2.5
5-2S	4.2 (salt)	2	103 ± 3	2.0
5-25S	4.2 (salt)	2.5	113 ± 6	2.4
5-3S	4.2 (salt)	3	116 ± 4	2.6
10-2S	8.5 (salt)	2	126 ± 10	2.1
10-25S	8.5 (salt)	2.5	110 ± 10	2.2
10-3S	8.5 (salt)	3	132 ± 5	3.7
average	0		86 ± 2	1.5
average	1.9		105 ± 5	2.3
average	4.2		111 ± 5	2.3
average	8.5		123 ± 9	2.7

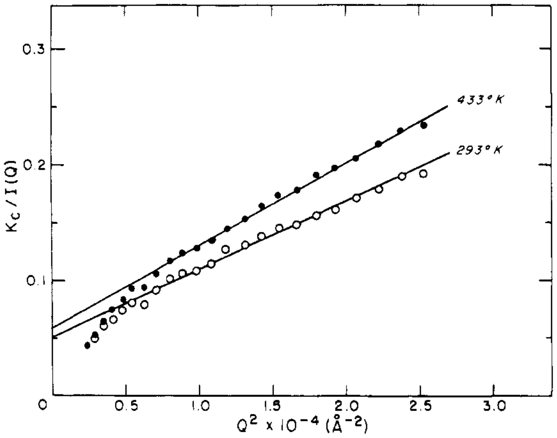


Figure 4. Zimm plots comparing the scattering from (5-3S) 4.2 mol % salt containing 3% deuterated salt at room temperature (○) and 433 K (●).

perature than for the room-temperature scan. The two curves in Figure 4 can be superimposed, within experimental error, by the use of a simple multiplicative factor of between 1.10 and 1.15. The calculated radius of gyration, in addition, does not change for the heated sample.

Figure 5 compares the scattering curves for the 4.2% salt sample that has been annealed at two different temperatures, 406 and 433 K. The Zimm plots in this figure are directly superimposable and show no differences in R_g values as a result of annealing well above the glass transition temperature of 383 K.

The slope and intercept for the unmodified polystyrenes and the 2% acid samples were determined by a linear least-squares fit of the data between $Q^2 = 2 \times 10^{-4}$ and $Q^2 = 6 \times 10^{-4}$. The error given in Table II for the R_g of these materials represents the standard error of the slope. Several straight-line fits to the data of each salt were determined including or excluding data points at low Q^2 related to the zero-order scattering. Each of the fits for a given salt had a standard error of about ±3 Å, the same as for the unmodified polystyrene. However, to include the effect of this low-angle scattering on the determination of R_g, the values listed in Table II for the salts reflect the minimum and maximum values calculated for each salt using different straight-line fits. There is no systematic variation of R_g as a function of DPS content for the salts, indicating that the second virial coefficient is very small or zero. The differences in values determined for each salt concentration are more likely due to slight differences in ion content between sample and background or other random differences in sample preparation.

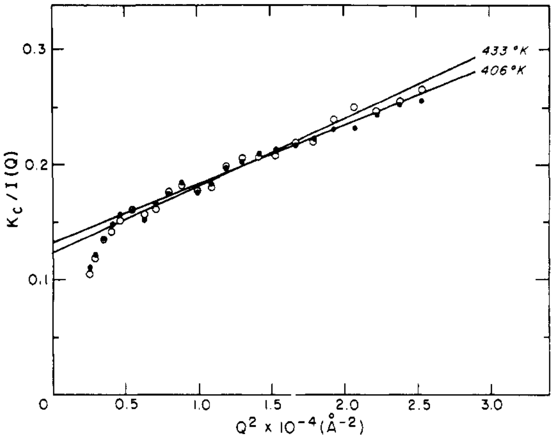


Figure 5. Zimm plots comparing the room-temperature scattering from (5-2S) 4.2 mol % salt containing 2% deuterated chains annealed at 406 K (●) and 433 K (○).

Discussion

In the Introduction it was noted that the only previous study of R_g in ionomers reached the tentative conclusion that R_g was unaffected by the neutralization of the acid form.[7] The results for the sulfonated polystyrene ionomers presented in Table II show that this is not the case for these polymers. The acid form at the single concentration measured (2 mol %), has a slightly greater R_g than the unmodified polystyrene, and all the salts show increases in R_g compared to both the acid and the unmodified polymers and these increases become greater with increasing salt content. It should be noted that R_g determined for unmodified 100 000 molecular weight polystyrene in this work is consistent with the value of 87 Å generally accepted.[14] The molecular weights measured by neutron scattering which are listed in Table II are generally too high. This is unlikely to be the result of segregation of tagged chains since there are no trends in the molecular weight data for any of the derivatives and it has been well established that poly(deuteriostyrene) is molecularly dispersed in polystyrene of the same molecular weight.[14] It is possible that inaccuracies in the molecular weights are caused by errors in the reference measurements or sample concentration together with difficulties in calculating the contrast factor K for the ionomer samples.

In their study of molten and crystalline polyethylene, Schelten et al.[15] showed that when segregation of the tagged molecules occurs, the observed R_g is 2–3 times greater and the apparent molecular weight 5–10 times larger than for the disperse case. The apparent molecular weights listed in Table II are only 30–60% greater than that obtained for the starting polystyrene and because of the experimental uncertainty involved, it is unlikely that there is aggregation of the perdeuterio tagged chains in the polystyrene ionomers studied; moreover, the determination of R_g is independent of the absolute intensity calibration required in order to obtain MW.

A small increase in R_g occurs even for the 1.9 mol % acid copolymer to 92 Å from the 87 Å of unmodified polystyrene. This may be a consequence of interchain hydrogen bonding. It is unlikely to result from changes in chain conformation introduced by the presence of the sulfonate group since the sulfonate group is primarily in the para position on the ring, well removed from the backbone.

The results of this study do not agree with those of the previous study of poly(styrene–methacrylic acid) ionomers,[7] where no change in R_g was observed as a function of salt group concentration. However, the present results are unequivocal. It might be postulated that the sulfonation reaction leads to an increase in molecular weight. However, recent results from gel permeation chromatography (GPC) characterization on polystyrenes sulfonated in the same way as employed here indicate no change or a slight lowering of molecular weight was a function of sulfonation.[17] It is well-known that the glassy state is a nonequilibrium state so the thermal annealing and high-temperature experiments were carried out to eliminate the possibility that the R_g results might be a consequence of this.

The melt viscosities of all the ionomers examined were high, resulting in considerable difficulty in the preparation of void-free films by compression molding. In order to approach equilibrium conditions as closely as possible, films were reannealed after the first scattering measurements at a temperature just below the onset of degradation (433 K) followed by slow cooling to room temperature.

The annealing treatment did not affect R_g, as shown in Figure 5 for the 4.2 mol % salt. We may conclude that the results for R_g reported in this paper reflect equilibrium conditions.

A second set of experiments was conducted with both sample and background 60 °C above T_g. From the Zimm plots in Figure 4 it can be seen that for the 8.5 mol % salt there is a decrease in c/I of 10–15% at 433 K compared to its value at room temperature. The two Zimm plots in Figure 4 give the same values for R_g. The decrease in scattering at high temperatures is a result of volume expansion, which is in the neighborhood of 8–10% at 433 K for polystyrene. The reduction in mass of sample in the beam accounts for the decrease in c/I.

The reason that chain expansion should accompany aggregation is not clear at this time. In his theoretical treatment of cluster formation of ionomers, Eisenberg[18] made the a priori assumption that half the chain would expand and the other half contract as a result of aggregation, leaving the mean-square chain dimensions the same. It is easy to show that if the end-to-end distance of a chain changes as a consequence of aggregation and the motion of the chain ends are uncorrelated, then there must be an increase in the mean-square chain dimensions. The argument proceeds as follows: by definition

$$\langle r^2 \rangle = \langle \vec{r} \cdot \vec{r} \rangle \qquad (4)$$

where $\vec{r}$ is the vector end-to-end distance of the chain or subchain before aggregation.

After aggregation the new end-to-end distance is $\vec{r} + \vec{h}$, where $\vec{h}$ can have any direction with respect to $\vec{r}$.

Now

$$\langle r^2 \rangle_{\text{agg}} = \langle (\vec{r} + \vec{h}) \cdot (\vec{r} + \vec{h}) \rangle = \langle r^2 + h^2 \rangle + 2\langle \vec{r} \cdot \vec{h} \rangle \qquad (5)$$

Because of the assumption that $\vec{r}$ and $\vec{h}$ are uncorrelated, eq 5 reduces to

$$\langle r^2 \rangle_{\text{agg}} = \langle r^2 + h^2 \rangle \qquad (6)$$

More experimental and theoretical work must be done before the expansion phenomenon is completely understood.

Conclusions

1. Ionic clusters occur in sulfonated polystyrene ionomers.
2. Clustering in these ionomers is accompanied by considerable chain expansion.

Acknowledgment. We wish to acknowledge the assistance of R. Duplessix as our local contact at the Institut Max V. Laue-Paul Longevin. We thank Dr. David Worcester of Queen Elizabeth College (University of London) for the use of the small-angle X-ray scattering apparatus and Dr. S. L. Clough for experimental assistance. T.R.E. and W.J.M. thank Professor Sir Geoffrey Allen of Imperial College for facilities provided during sabbatical leave from the University of Massachusetts, Amherst. Partial support for this work was provided by the Science Research Council. Partial support for this research under NSF Grant DMR 78-17927 is gratefully acknowledged.

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