Ion Clustering and Viscoelastic Relaxation in Styrene-Based Ionomers. IV. X-Ray and Dynamic Mechanical Studies

A. Eisenberg* and M. Navratil

McGill University, Montreal, Canada. *Received February 5, 1973*

ABSTRACT: Dynamic mechanical and low-angle X-ray results for styrene-based ionomers are presented for the composition region of 0–9.7 mol % of the ionic comonomer. It is shown that above 6% of the cesium salt, a low-angle X-ray peak appears. If a modified Bragg equation is applicable to the data, intercluster distances of *ca.* 70 Å are indicated. Dynamic mechanical data also show a discontinuity at *ca.* 6% salt. All the data are consistent with previously proposed onset of clustering at 6% of the ionic comonomer.

It was shown in previous publications of this series that strong rheological evidence exists which substantiates the hypothesis that in styrene ionomers ion clustering occurs above 6 mol % of ions, while below that concentration simple ion multiplets are found in these materials. It was also shown[1,2] that below 6 mol % these ion multiplets act as temporary cross-links, slowing down the primary diffusional relaxation mechanism. Moreover time–temperature superposition was found to be applicable in this concentration region. The failure of time–temperature superposition above the critical ion concentration suggested that there are two relaxation mechanisms operative. Indeed, it was found[3] that not one but two master curves, each with its own set of shift factors, are required for a complete description of the viscoelastic relaxation in styrene-based ionomers above 6 mol % of ions.

The effects of the nature of the counterion, of partial neutralization, and of plasticizers were investigated in a previous publication.[4] It was established that the ion concentration appears to be of primary importance, while the nature of the counterion is not. The presence of -COOH groups was found to shorten the lifetime of ion clusters and to decrease the effectiveness of the ion multiplets as cross-links. Furthermore, a narrowing of the distribution of relaxation times was observed in materials plasticized by dimethyl sulfoxide while an expected effect (*i.e.*, broadening[5]) was observed for organophilic plasticizers such as alkyl phthalates.

In this paper an attempt is made to adduce additional evidence for ion clustering in styrene-based ionomers using X-ray scattering techniques. In addition, dynamic mechanical investigations were performed which should reflect energy dissipation phenomena related to the various structures proposed.

The results can be briefly summarized as follows. (a) Cesium neutralized samples containing more than 5 mol % of salt exhibited amorphous spacings of *ca.* 70 Å, which can be explained as reflecting the presence of ionic clusters, while lithium neutralized polymer did not show such spacings. (b) In all the samples studied, two amorphous halos were seen corresponding to spacings of 5.8 and 11.3 Å, which are the same as those found in polystyrene. (c) For cesium neutralized samples below 5 mol % and for all the lithium neutralized samples an additional halo was found corresponding to 23 ± 1 Å. (d) A peak was found on the tan δ *vs.* temperature and loss modulus *vs.* temperature curves above T_g in all the samples of sodium neutralized polymers containing between 1 and 6 mol % of salt. This peak might correspond to relaxations involving the ionic aggregates. (e) Marked differences in shapes of loss modulus curves and tan δ curves were observed for samples below and above 6 mol % of ions.

Numerous investigations of morphology and viscoelectric properties of ionomers have been reported during the past decade. Owing to a recent appearance of two reviews[6,7] dealing with properties of ion-containing polymers and to the fact that most of the relevant papers were already discussed in the previous publications,[2,4] no extensive discussion of the literature will be attempted here. Only those studies which have a direct bearing on the present work will be mentioned briefly.

Wilson, Longworth, and Vaughan[8] reported a Bragg spacings of 20–27 Å in dry cesium-ionized copolymer of ethylene–methacrylic acid which is absent in the un-ionized copolymer.

Delf and MacKnight[9] reported the same spacing (20 Å) in all their ionized samples (4.1 mol % of ionizable groups) but in addition to it they found a characteristic spacing 83 Å in the 60% ionized sample. These results provide strong evidence for ionic clusters in these polymers; however, it should be pointed out that results of other studies[10-12] failed to show evidence of clustering.

Phillips[13] studied the copolymer of polyethylene with 7.4 mol % of phosphonic acid fully neutralized by cesium hydroxide. Ionic domains of the size 50–80 Å were observed by electron microscopy. Marx *et al.*[14] studied the morphology of ionized and un-ionized butadiene–methacrylic acid copolymers by electron microscopy. Two types of spherical domains have been observed; the larger ones with a diameter of *ca.* 26 Å and the smaller ones of *ca.* 13 Å in size.

An extensive study of ion aggregation in ethylene and butadiene-based ionomers by Marx, Caulfield, and Cooper[15] resulted in a proposal of the so-called "aggregate" model. In this model, the ions are assumed to exist in the form of ion multiplets (2–7 ion pairs) in an otherwise homogeneous polymer. The degree of ion aggregation can be influenced by the presence of water.

Evidence for microphase separation in copolymer of butadiene with 13% of metal methacrylate (Ni^{2+}, Cu^{2+}, Zn^{2+}) was found by Pineri *et al.*[16] These authors also studied copper and manganese salts of carboxy-terminat-

---

(1) A. Eisenberg and M. Navratil, *J. Polym. Sci., Part B*, **10**, 537 (1972).
(2) A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).
(3) A. Eisenberg, M. King, and M. Navratil, *Macromolecules*, **6**, 734 (1973).
(4) M. Navratil and A. Eisenberg, *Macromolecules*, **7**, 84 (1974).
(5) L. L. Chapoy and A. V. Tobolsky, *Chem. Scr.*, **2**, 44 (1972).
(6) A. Eisenberg, *Advan. Polym. Sci.*, **5**, 59 (1967).
(7) E. P. Otocka, *J. Macromol. Sci. Rev. Macromol. Chem.*, **5**, 275 (1971).
(8) F. C. Wilson, R. Longworth, and D. J. Vaughan, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **9**, 505 (1968).
(9) B. V. Delf and W. J. MacKnight, *Macromolecules*, **2**, 309 (1969).
(10) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 401 (1968).
(11) R.-J. Roe, *J. Phys. Chem.*, **76**, 1311 (1972).
(12) E. P. Otocka and D. D. Davis, *Macromolecules*, **2**, 437 (1969).
(13) P. J. Phillips, *J. Polym. Sci., Part B*, **10**, 433 (1972).
(14) C. L. Marx, J. A. Koutsky, and S. L. Cooper, *J. Polym. Sci., Part B*, **9**, 167 (1971).
(15) C. L. Marx, D. J. Caulfield, and S. L. Cooper, to be published.
(16) M. Pineri, IV^e Congres International de Rheologie, Lyon, 1972, Abstracts, III, p 239.

ed butadiene of molecular weight *ca.* 5000 and found a periodicity 70 Å by low-angle X-ray scattering. An epr spectrum of the copper salt at 0° was the same as that of copper acetate. Thus it was proposed that the ionic aggregates have essentially the copper acetate structure.

The interpretation of small-angle X-ray peaks in materials of this type is by no means simple. While some workers have taken these peaks to be indications of distances between scattering centers, others suggest that the shape of the curve can be more correctly correlated with the size of the scattering center. In this work, the former possibility will be used, although it is recognized that alternate interpretations exist.

I. Experimental Section

Methods of sample preparation (polymerization, neutralization, sample characterization) were given together with the explanation of sample labeling in our previous publications.[2,4]

The torsional pendulum which was utilized for these investigations has been described elsewhere.[17] In this study all the experiments were performed under positive nitrogen pressure with a temperature control of ±1°. Heating rates of *ca.* 1-1.5°/min were employed. Samples prepared by compression molding were utilized. The results were obtained in the form of a damped sinusoidal trace from which the logarithmic decrement and period of vibration were calculated. A simple computer program was utilized to calculate values of the storage shear modulus (G'), loss shear modulus (G'') and loss tangent ($\tan \delta$). The formulas employed were those given by Markovitz[18] which include the correction for the torsional constant of the wire.

For the X-ray experiments *ca.* 1-mm thick samples were prepared by compression molding (cooling rate *ca.* 1°/min). A Kiessig vacuum camera was employed with nickel-filtered Cu Kα(1.54 Å) radiation (40 kV, 20 mA). In the arrangement used here, limit of resolution was *ca.* 150 Å. The exposure times were of the order of 100 hr. All the experiments were done at room temperature. In accordance with similar studies done on ethylene-based ionomers,[8,9] the Bragg equation was used to calculate Bragg spacings (d_B). It was shown before, however,[19] that for scattering in amorphous materials average spacings (d) can be calculated more precisely as $d = 1.22d_B$. The results are expressed as amorphous spacing "d."

II. Results

a. X-Ray. Figure 1 shows the results of calculations based on X-ray scattering data for the lithium- and cesium-neutralized samples and for polystyrene assuming that the scattering angles can be correlated with distances between scattering centers. The curves shown for ion concentrations below 6 mol % were calculated for theoretical intermultiplet distances between ion pairs, quadruplets, or octuplets. Because one of the possible interpretations of the spacings found in these samples is that these reflect distances between ionic domains (multiplets or clusters) these curves are helpful for estimating the average multiplet size present in the sample, provided that such an interpretation is correct.

The curve drawn above 6 mol % is the theoretical curve for intercluster distances (and cluster sizes marked at different points) calculated as a function of ion concentration from a previously published theory[20] using the equation

$$n = \frac{\rho N_{\mathrm{Av}}}{M_{\mathrm{c}}} \left[\frac{4l^2}{3kT_{\mathrm{c}}} \frac{\overline{h^2}}{h_0{}^2} \frac{M_{\mathrm{c}}}{M_0} \frac{k'}{K} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + 2\left(\frac{n_0 M_{\mathrm{c}}}{\rho N_{\mathrm{Av}}}\right)^{2/3}\right]^{3/2} \quad (1)$$

The adjustable parameter k' was set equal to 0.046 to get the best fit through the experimental points. An explanation of the symbols is given in the appendix.

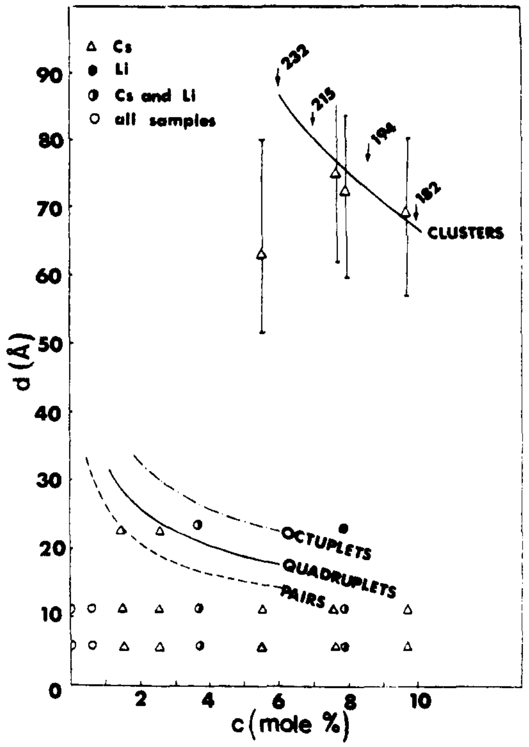

Figure 1. X-Ray scattering maxima for Cs- and Li-neutralized polymers. Curves correspond to calculated intermultiplet or intercluster distances as marked. Numbers on the curve indicating intercluster distances refer to the number of ion pairs in the cluster.

The intensity of the halo corresponding to the 23-Å distance increases with increasing ion concentration for the lithium neutralized samples, as can be seen from Figure 2. However, such a halo cannot be seen in cesium neutralized polymers above 6 mol %. Instead of it, a new low-angle halo appears corresponding to *ca.* 70 Å. This is also shown in Figure 2. The original polystyrene pattern (5.8 and 11.3 Å) becomes very weak in Cs-ionized polymers (also shown in Figure 2). The sample containing 5.5 mol % of Cs represents an intermediate case. While its pattern strongly resembles those found above 6 mol %, the ionic domains seem to be somewhat smaller than one would expect. It should be recalled that time-temperature superposition was found applicable for this sample[2] but this might not be true for very long time periods since only 10,000-sec runs were used. Deviations from time-temperature superposition might be observable in this case only if very long time runs are superposed.

It should be mentioned that X-ray studies of un-ionized copolymers with concentrations of methacrylic acid below 10 mol % reveal the same pattern as that observed in polystyrenes. Sodium neutralized samples show the same pattern as those neutralized by lithium.

b. Dynamic Mechanical Measurements. The data presented in this part were obtained at frequencies which varied between *ca.* 1 Hz for the glassy region and *ca.* 0.03 Hz for the low modulus region. For the sake of clarity, experimental points are omitted on most of the curves; however, some of these are plotted to illustrate typical scatter of the data. Figure 3 shows the storage shear modulus plotted against temperature. In the glassy region these values are close to those found by stress relaxation, recalling that $3G = E$. An inflection point whose position increases with increasing ion concentration can be seen. Figure 4 shows the loss shear modulus against temperature. In addition to the peak found at T_g another maxi-

(17) B. Cayrol, Ph.D. Thesis, McGill University, Montreal, 1972.

(18) H. Markovitz, *J. Appl. Phys.*, 34, 21 (1963).

(19) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," John Wiley, New York, N. Y., 1954.

(20) A. Eisenberg, *Macromolecules*, 3, 147 (1970).

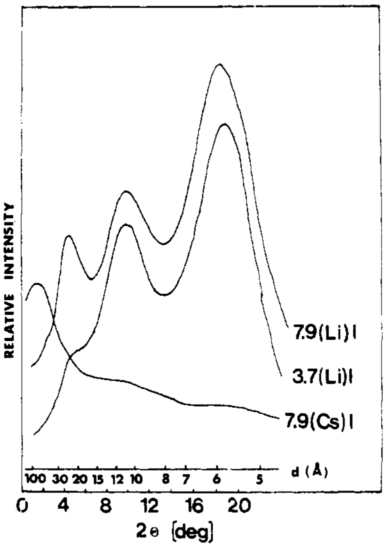

Figure 2. Relative intensities of X-ray patterns for the Cs- and Li-neutralized samples as labeled on right.

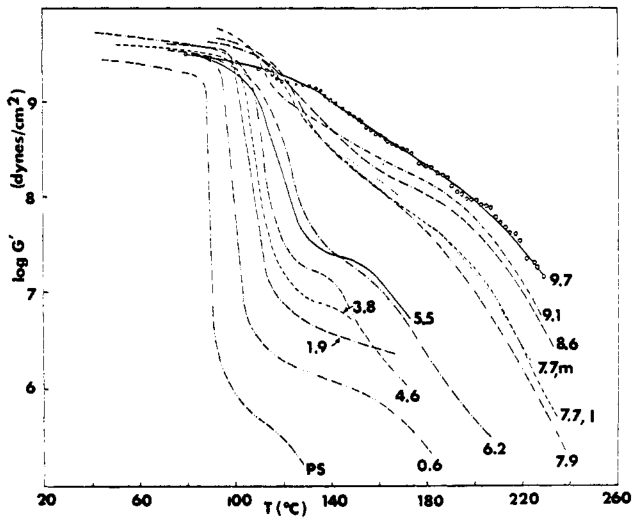

Figure 3. Storage shear modulus *vs.* temperature. All samples are neutralized by sodium. Samples 0.6, 1.9, 3.8, 4.6, 6.2, 8.6, and 9.7 are of high molecular weight. Samples 5.5, 7.7l, and 7.9 are of low molecular weight. Samples 7.7m, and 9.1 are of medium molecular weight. Numbers on the curves refer to concentration of sodium in mol %.

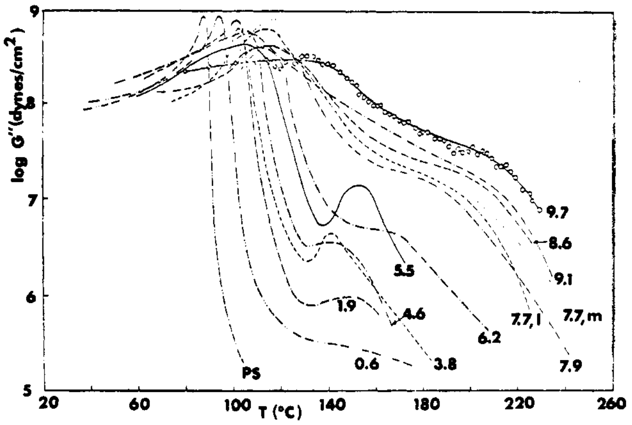

Figure 4. Loss shear modulus *vs.* temperature. All samples are neutralized by sodium. Samples 0.6, 1.9, 3.8, 4.6, 6.2, 8.6, and 9.7 are of high molecular weight. Samples 5.5, 7.7l, and 7.9 are of low molecular weight. Samples 7.7m, and 9.1 are of medium molecular weight. Numbers on the curves refer to concentration of sodium in mol %.

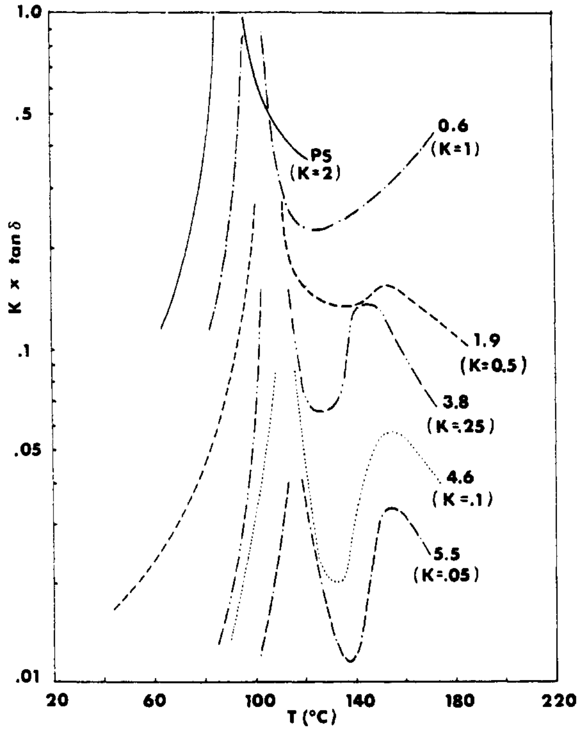

Figure 5. Loss tangent *vs.* temperature. Numbers on the curves refer to ion concentration (mol %). The sample containing 5.5 mol % of sodium is of low molecular weight, while all the other samples are of high molecular weight.

mum above T_g can be seen for samples containing between 1 and 6 mol % of salt; however, samples of higher ion concentration do not show such a maximum. Instead of it, an inflection point appears on the curves. Loss tangent data are shown in Figure 5 for samples below the critical ion concentration. Again two peaks are observed for concentrations above 1 mol %. The glass transition temperature increases with increasing ion concentration, as expected, but the upper peak occurs at approximately the same temperature, *ca.* 150°, and remains relatively unaffected by the ion concentration. The intensity of this peak appears to be increasing with increasing ion concentration. Sample 0.6(Na)h shows a continuous increase of tan δ as the flow region is approached. [It is recalled that in agreement with previous nomenclature, the label 0.6(Na)h means completely neutralized polymer containing 0.6 mol % of sodium methylacrylate of high molecular weight ($M_n > 400{,}000$).] The same continuous increase of tan δ above *ca.* 150° is observed for samples above the critical ion concentration as can be seen from Figure 6. It can be seen that the T_g peak moves to higher temperatures and broadens with increasing ion concentration; no additional peaks are observed above room temperature.

Figure 7 shows the positions of the peaks on the tan δ *vs.* temperature curves plotted against the ion concentration. The T_g peaks are included. For samples above 6 mol %, for which no second peak can be found, the temperature at which tan δ is equal to 0.5 was chosen arbitrarily to illustrate the shift in corresponding behavior to high temperatures for samples of higher ion concentration.

III. Discussion

a. X-Ray. The concept of ionic multiplets and clusters, discussed in great detail in the previous publication[2] can well explain most of the results shown here. X-Ray scat-

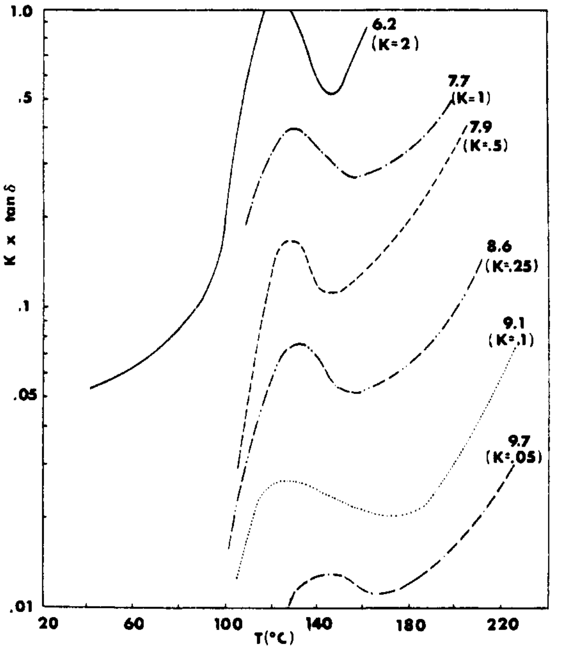

Figure 6. Loss tangent *vs.* temperature for samples above the critical ion concentration. Numbers on the curves refer to the ion concentration in mol %.

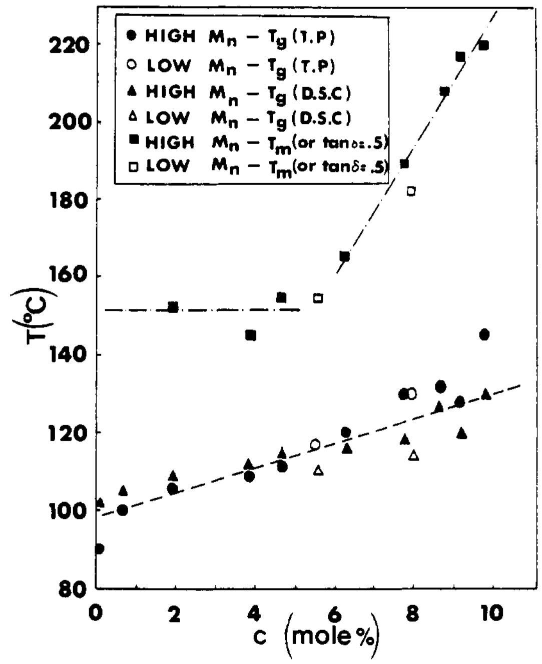

Figure 7. Temperature corresponding to the maxima found on the tan δ *vs.* temperature curves (T_m) or to tan δ = 0.5 for samples with more than 6 mol % of salt. T's determined by differential scanning calorimeter (DSC) are also shown.

tering of isotactic polystyrene has been subject of several investigations[21-24] and the published values of 11.5 and 5.85 Å are identical with those reported here. While Katz[23] interpreted the amorphous peaks 11.5 and 5.85 Å as corresponding to the interchain and intrachain distances, respectively, more detail study of the glassy polystyrenes of various tacticities[24] showed that both inter- and intramolecular scattering contributes to the polystyrene radial distribution function at distances beyond 3.7 Å with the steric interaction of the phenyl ring playing an important role in the chain conformation and molecular packing.

The existence of X-ray low-angle peaks found for cesium salts seems to indicate that the ionized samples above 6 mol % contain structural features which are fairly regular and which are not present in the unionized material or material containing less than 6 mol % of ions. Guinier's[25] spherical shape function or other approaches[26] should be employed to calculate the "feature" size but the nature of the present data does not allow such a calculation. We merely wish to document that there is a substantial difference in the structure of the neutralized and unneutralized polymers and also in the structure of the material below and above the critical ion concentration. Low-angle peaks can reflect either distances between scattering centers or the size of scattering centers, depending on their regularity. Without much more extensive work it seems difficult to conclude which of these two possibilities exists here. If one assumes that the low-angle peak reflects the intercluster distances, values of *ca.* 70 Å are obtained which correspond to cluster sizes of *ca.* 200 ion pairs.

As was mentioned earlier, a spacing of 83 Å was found in ionized copolymers of polyethylene.[9] A similar spacing was found in metal salts of carboxyl-terminated butadiene of mol wt *ca.* 5000.[16] The geometry-dependent factor in eq 1, which was set equal to 0.046 in the styrene ionomers to make the curve fit the experimental data, gives the magnitude of the electrostatic energy released per ion pair upon cluster formation. This value is well within the range of values which can be calculated from various hypothetical cluster structures (see part IV, A, B, and C of ref 20).

Lithium salts show an amorphous spacing of 23 Å throughout the whole region of concentrations studied; in cesium salts this spacing is seen only below 5 mol %. It is tempting to ascribe this distance to separations between ionic multiplets, although this interpretation is admittedly highly speculative. The constancy of the spacing is puzzling, because to interpret it one has to assume that the average size of the ion aggregates is changing with increasing ion concentration. Thus one can see from Figure 1 that a distance of 23 Å in the sample containing 1.5 mol % of cesium agrees well with theoretical average distance between separated ion pairs, while for a sample with 2.5 mol % of ions, 23 Å correspond to the distance between quadruplets, and so on. It is surprising to see that this spacing can be seen in the lithium salts even in the region above 6 mol %, in which clustering can be observed for the cesium slats. The 23-Å distance probably reflects the average distance between ion aggregates (multiplets) which remain outside of the ionic clusters. While this spacing is not basically unreasonable, it remains to be seen why it is so uniform. As was mentioned in the introduction, a Bragg spacing of 20–27 Å was found in cesium-ionized copolymers of ethylene–methacrylic acid; this spacing is absent in the un-ionized copolymer.[8] Owing to the fact that size of the ionic aggregates appears to be increasing with increasing ion concentration, it seems reasonable that the intensity of this scattering increases with increasing ion concentration too, as can be seen from Figure 2. In comparing the ionized and un-ionized samples it becomes apparent that the un-ionized materials exhibit only those peaks which were formed in pure polystyrene

---

(21) S. Krimm and A. V. Tobolsky, *J. Polym. Sci.*, **6**, 667 (1951).
(22) S. Krimm and A. V. Tobolsky, *Textile Res. J.*, **21**, 805 (1951).
(23) J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936).
(24) S. M. Wecker, T. Davidson, and J. B. Cohen, *J. Mater. Sci.*, **7**, 1249 (1972).
(25) A. Guinier, *Annal. Phys.*, **12**, 161 (1939).
(26) K. L. Yudowitch, *J. Appl. Phys.*, **20**, 147 (1949).

and no others. This suggests that the carboxylic acid groups are dispersed throughout the sample, probably as dimers, but that no other type of aggregation is encountered. The fact that no peak corresponding to 23 Å was observed in these materials suggests that the structures of the ionized and the un-ionized materials are quite different.

It should be recalled that viscoelastic studies, which were discussed previously,[4] suggest that the structure of these ionomers is not greatly affected by the nature of the counterion; studying the same materials by X-rays, however, one can see different patterns depending on the atomic number (electron density) of the counterion. Thus one can explain the fact that although the same structures are assumed to be present in lithium and cesium salts (7.9%), as reflected in the similarity of mechanical properties for various counterions, these materials show drastically different X-ray patterns (Figure 2) because of the differences in the scattering power of the various counterions. If the cluster model is correct, the ionic clusters contain also a substantial fraction of polystyrene chains (see ref 2). Thus, the average electron density of the clusters in the case of the lithium salt is not sufficiently higher than that of pure polystyrene in the intercluster regions. Therefore, low-angle scattering, which would be caused by the presence of the clusters, cannot be observed. However, tightly packed ionic multiplets outside of the clusters can be seen (possibly because of the oxygens), and these show an average spacing of *ca.* 23 Å. Introduction of heavy cesium ions causes a substantial increase of electron density inside the clusters which then become the primary scattering centers, and the system behaves like a two phase structure; one of high and the second of low electron density.

b. Dynamic Mechanical Measurements. Storage modulus values obtained in the styrene salts are consistent with the modulus *vs.* temperature curves found by stress relaxation shown in Figure 11 of ref 2. These were discussed previously.[2] Loss modulus data show a small peak in energy dissipation at *ca.* 150° for samples between 1.9 and 5.5 mol %. This can be attributed to "softening" of ionic multiplets, but these have to persist even at higher temperatures since they appear to slow down the primary relaxation mechanism at all temperatures (as was shown in Figure 9 of ref 2). Samples above 6 mol % do not show such a peak, apparently because ionic clusters do soften with increasing temperature, the transition is very broad, and the clusters change their structure continuously rather than over a narrow temperature range. These effects become even more apparent on tan δ *vs.* temperature curves. A high temperature peak, which is present for samples between 1 and 6 mol %, is not seen at higher concentrations, but tan δ remains very high and increases with increasing temperature.

The activation energy related to the process at 150° is probably very high because the peak appearing at this temperature did not shift its position appreciably with changing frequency. In other words, a frequency-dependent shift was not separable from the experimental error, which is *ca.* ±3°. This might indicate that this transition is comparable to the glass transition which is known to have a high activation energy (100–200 kcal/mol).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Appendix: List of Symbols for eq 1

e = electron charge
$\overline{h^2}$ = mean-square end-to-end distance of polymer chain
h_0^2 = mean-square end-to-end distance of freely jointed chain
K = dielectric constant of polymer
k = Boltzmann's constant
k' = dimensionless geometry-dependent factor giving the magnitude of the electrostatic energy released per ion pair in cluster formation
l = length of repeat unit
$\bar{M}_c$ = average molecular weight of chain between ionic groups
M_0 = molecular weight of repeat unit
N_{Av} = Avogadro's number
n = average number of ion pairs in cluster
n_0 = average number of ion pairs in multiplet
r = distance between centers of charge in ion pair
T_c = cluster decomposition temperature or cluster formation temperature
$1/(4\pi\epsilon_0) = 1\ (\text{dyn cm}^2)/\text{statcoulomb}^2$
ρ = density of polymer