sion ratio should also show up in Figures 4 and 5 by making the experimental points fall more and more below the theoretical line with increasing extension ratio during irradiation, more so for Young's modulus measured directly than for the modulus from swelling since the latter corresponds to expansion in all three directions. There is unfortunately too much scatter in the data of Figures 4 and 5 to substantiate this prediction.

Further work is in progress, including birefringence measurements to study anisotropy in the state of ease, stress relaxation during irradiation to measure whether chain scission plays a role, and studies of the effects of polymer molecular weight, irradiation temperature and dose rates, which should throw light on the question regarding possible entanglement slippage before entrapment between chemical cross-links.

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Ion Clustering and Viscoelastic Relaxation in Styrene-Based Ionomers. III. Effect of Counterions, Carboxylic Groups, and Plasticizers

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ABSTRACT: The effect of the nature of the counterion on the viscoelastic relaxation and glass transition behavior is evaluated for styrene ionomers. It is shown that neither the ion size nor valence play a major role in influencing the viscoelasticity of ion-containing polymers. The effect of the un-ionized carboxylic groups is also investigated and results indicate that the introduction of such groups accelerates the rate of viscoelastic relaxation. Finally, the effect of hydrophilic and organophilic plasticizers on the width of stress relaxation master curves is evaluated. The results of these studies are consistent with the previously proposed hypothesis that below *ca.* 6 mol % of the salt the ions exist in a form of simple multiplets, while above that concentration more extensive ion clustering is encountered.

Despite the effort devoted to the investigation of ion-containing polymers during the past decade, several major questions concerning the state of aggregation of the ions and their influence on the viscoelastic properties remain unanswered.

In previous publications of this series[1,2] it was shown that ion concentration has an important effect on viscoelasticity and morphology of styrene–sodium methacrylate (NaMA) copolymers. The results presented were in agreement with the hypothesis that below *ca.* 6 mol % of the salt, the ions exist in a form of simple multiplets which act as temporary cross-links, and which slow down the primary diffusional relaxation mechanism; above that concentration, more extensive ion clustering is encountered. In this publication, results of some additional studies of styrene-based ionomers are presented. These address themselves to the following questions. (a) Since the ion multiplets act as cross-links of finite lifetime, how is the stability of these multiplets affected by the nature of the counterion? (b) Is the critical ion concentration above which the time–temperature superposition breaks down, also a function of the nature of the counterion? If so, what is the correlation? (c) How does the presence of un-ionized carboxylic groups affect the structure and stability of the ion multiplets and/or the ionic clusters? (d) How would various types of plasticizers (*i.e.*, hydrophilic or hydrophobic) influence the mechanical properties other than by a change in T_g? These questions can be briefly answered as follows. (a) The fact that ions are present in polymeric materials appears to be of primary importance, while the nature of the counterion is not. However the ion size seems to have some effect on the stability of the ion multiplets in the region of low ion concentration. The large Cs^+ ions yield cross-links of somewhat lower stability than smaller Na^+ ions. (b) No change of the critical ion concentration with the nature of the counterion has been observed. (c) The presence of –COOH groups in partially neutralized polymers appears to suppress ion clustering and to decrease the effectiveness of the ionic multiplets as cross-links. Completely neutralized polymers, which are not subject to time–temperature superposition, remain nonsuperposable in their partially neutralized state even at intermediate degrees of neutralization (40%). If two copolymers contain the same amount of ions but one of them contains additional –COOH groups, then stress relaxation is faster in the partially neutralized copolymer, indicating a supporting role of –COOH groups in ion hopping or in weakening of the electrostatic interaction within the ion aggregates. (d) A narrowing of the stress relaxation spectrum was observed in materials plasticized by dimethyl sulfoxide (Me_2SO). Organophilic plasticizers such as dioctyl phthalate (DOP) exhibit the same effect as they have on pure polystyrene.[3]

Owing to the recent appearance of two reviews dealing with the properties of ion-containing polymers[4,5] and to the fact that most of the papers relevant for this investigation were discussed in our previous publication[2] no discussion of the literature is attempted here; however, four papers which have a direct bearing on the present work are mentioned briefly. Fitzgerald and Nielsen[6] did a pre-

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(1) A. Eisenberg and M. Navratil, *J. Polym. Sci., Part B,* **10**, 7, 537 (1972).

(2) A. Eisenberg and M. Navratil, *Macromolecules,* **6**, 604 (1973).

(3) L. L. Chapoy and A. V. Tobolsky, *Chem. Scr.,* **2**, 44 (1972).

(4) A. Eisenberg, *Advan. Polym. Sci.,* **5**, 59 (1967).

(5) E. P. Otocka, *J. Macromol. Sci. Rev. Macromol. Chem.,* **5**, 275 (1971).

(6) W. E. Fitzgerald and L. E. Nielsen, *Proc. Roy. Soc., Ser. A,* **282**, 137 (1964).

liminary investigation of the stress relaxation behavior of mono- and divalent salts of styrene–methacrylic acid copolymers. In addition to the increase of T_g they observed a decrease in rate of relaxation in polymer salts going from the acid to Na^+ to Ba^{2+}; however, no further conclusions can be drawn since the temperatures at which the relaxation moduli are being compared are neither the same for both salts nor are they the T_g's of the corresponding salts.

Erdi and Morawetz[7] studied the copolymer of styrene–methacrylic acid neutralized by various metal ions and plasticized by 25% of dioctyl phthalate. They found that the irrecoverable flow decreases in order -COOH > COOLi > -$COOBa_{0.5}$ when compared at the temperatures corresponding to the same compliance. This was interpreted as an indication of occurrence of temporary cross-links due to the ion multiplets.

Ward and Toblosky[8] studied the stress relaxation behavior of sodium and calcium salts (*ca.* 2–4 mol %) of copolymers based on α-olefines and carboxylic acid and obtained "reasonably good superposition" if both vertical and horizontal shifts were applied to original modulus *vs.* time data. However, the shift factors did not obey a WLF-type equation and the vertical shift may have been necessitated by a change in the degree of crystallinity. Certain differences between the behavior of sodium and calcium salts are apparent but their evaluation is difficult.

A dynamic melt rheology study by Sakamoto *et al.* also showed a breakdown in time–temperature superposition[9] in sodium and calcium neutralized ethylene–methacrylic acid copolymers (4.1 mol %), while time–temperature superposition was obeyed in the acidic copolymer; the authors concluded that failure is due to the temperature-dependent structure of the ionic clusters. The storage shear modulus has been found to decrease in order -$COOCa_{0.5}$ > -COONa > -COOH when compared at the same temperature.

I. Experimental Section

The procedures employed in polymerization, neutralization, sample molding, molecular weight determination, calorimetry, and stress relaxation were the same as those described previously;[2] however, during stress relaxation runs on plasticized samples, a small container of plasticizer was placed in the sample chamber to maintain a high relative humidity. To obtain the Cs^+, Li^+, and Ba^{2+} salts of the polymers, cesium ethoxide, lithium ethoxide, and barium methoxide were utilized for neutralization. No precipitation occurred during the neutralization. To obtain partially neutralized samples, calculated amounts of sodium ethoxide solution were utilized. Otherwise, the procedure was the same. A stress relaxometer whose temperature control was within ±0.01° was utilized for experiments below room temperature. This instrument is very similar to that described previously.[10] Prior to the beginning of the experiments the sample cell was always evacuated and refilled with dry nitrogen at ambient pressure to provide an anhydrous environment.

A known amount of the dry polymer was placed into a mold of known weight and then dissolved by adding a mixture of benzene and methanol (90:10) with slightly more plasticizer than necessary to obtain the desired degree of plasticization. Me_2SO (Baker Chemicals Co.) and DOP (Baker Chemicals Co.) were used as received. Solvent was evaporated first at ambient temperature in air, then under vacuum, and finally under vacuum at elevated temperature until the weight corresponded to the desired degree of plasticization. It is assumed that because the boiling points of Me_2SO (185°), and DOP (>340°) were much higher than those of benzene and methanol, the plasticized samples contained only negligible amounts of benzene and methanol.

Table I
Sample Designation[a] and Glass Transition Temperatures

Varying Counterion		Partially Neutralized		Plasticized	
Sample Label	T_g (°C)	Sample Label	T_g (°C)	Sample Label	T_g (°C)
3.7(Na)l	107	4.6(Na)h	114	9.7(Na)h-(23Me_2SO)	18
3.7(Cs)l	107	4.6(0.80Na)h	114	9.7(Na)h	130
3.7(Li)l	114	4.6(0.60Na)h	113		
3.7(Ba)l	107	4.6(0.40Na)h	112		
3.8(Na)h	112	8.6(0.44Na)h	119		
3.8(Cs)h	108	6.2(0.61Na)h	116		
4.6(Ba)h	115	6.2(Na)h	116		
6.2(Ba)h	118				

[a] The following scheme of symbols was used:

4.2(0.50Cs)h(23Me_2SO) ← sample designation
→type of plasticizer (dimethyl sulfoxide)
→weight per cent of plasticizer
→high molecular weight (*ca.* 400,000), "l" refers to low molecular weight (50–70,000)
→type of counterion
→degree of neutralization (if number is omitted then polymer is 100% neutralized)
→concentration of MAA in original copolymer in mole per cent

If the material obtained by this procedure was bubble free, samples of proper size were cut and used. In some cases, however, the material had to be remolded to obtain homogeneous, bubble-free samples. No changes in degree of plasticization were expected during compression molding because the temperatures were much lower than those used in the previous evaporation procedure. No loss of plasticizer was observed during stress relaxation experiments; furthermore, no differences in stress relaxation behavior of cast or molded samples were observed. No deviations from linear viscoelasticity were observed in the region of deformations employed.

The mixed sample was prepared by dissolving appropriate amounts of PS and sample 8.6 (Na)h in a 90:10 mixture of benzene and methanol and subsequently freeze-drying. The later procedures such as drying and compression molding were the same as those employed for all the other materials.

Table I lists all the samples used in this study along with their glass transition temperatures. The detailed preparation of the samples was given in the previous paper.

Table I also contains an explanation of a sample nomenclature.

II. Results

A. Glass Transition Temperatures (T_g). Table I shows the T_g's of the copolymers investigated. It is evident that for the polymers of low methacrylate content studied here, neither the nature of the counterion nor the degree of neutralization has a pronounced effect. The changes in the T_g's are very small and not much can be concluded except for general trends. A normal decrease in T_g with plasticization is, however, observed.

B. Stress Relaxation. 1. Counterion Effect. Figure 1 shows the stress relaxation master curves for the cesium and sodium neutralized polymers of high and low molecular weight which contain 3.7 or 3.8 mol % salt. At these concentrations, time–temperature superposition was found to be applicable. The shape of the curves is similar but the rate of stress relaxation is faster for the Cs salts; the molecular weight effect is identical for both materials. The shift factors follow an equation of the WLF type with the constants c_1 and c_2 listed in Table II. The WLF pa-

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(7) N. Z. Erdi and H. Morawetz, *J. Colloid Sci.*, **19,** 708 (1964).
(8) T. C. Ward and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11,** 2403 (1967).
(9) K. Sakamoto, W. J. MacKnight, and R. Porter, *J. Polym. Sci., Part A-2,* **8,** 277 (1970).
(10) A. Eisenberg annnd T. Sasada, *J. Polym. Sci., Part C,* **16,** 3473 (1968).

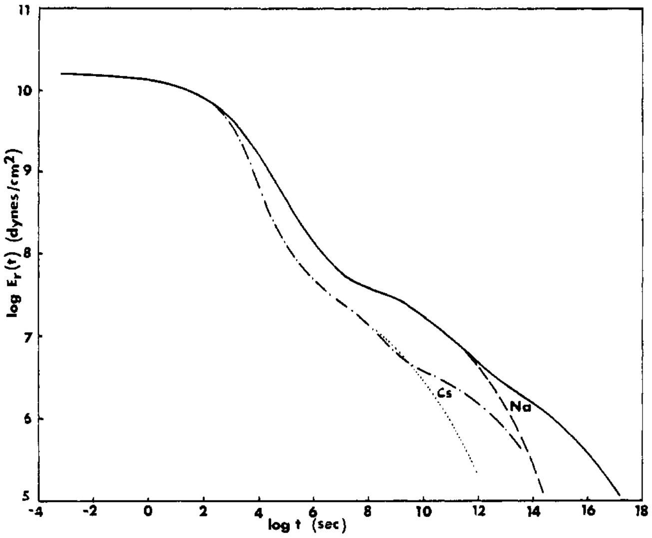

Figure 1. Stress relaxation master curves for samples 3.7(Na)l (- - -), 3.7(Cs)l (....), 3.8(Cs)h (- • -), 3.8(Na)h (——).

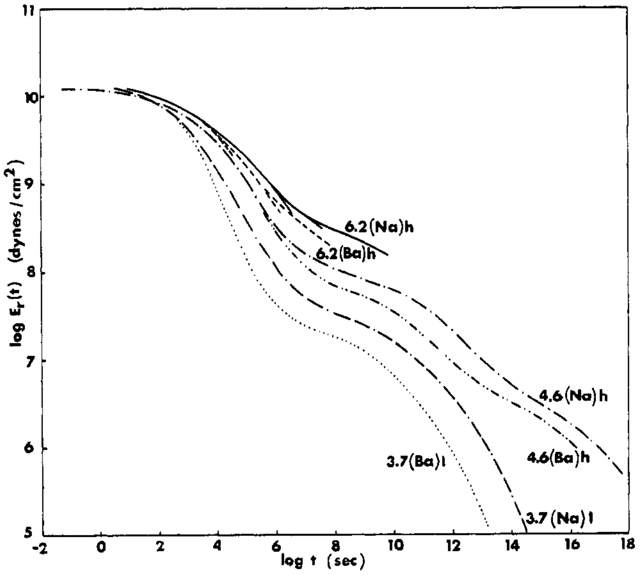

Figure 2. Stress relaxation master curves for Na- and Ba-neutralized polymers.

rameters, which were found to be independent of the molecular weight, are lower for the Cs-neutralized polymers than they are for the Na salts.

An investigation of the Ba salts yielded surprising results. Figure 2 shows the stress relaxation master curves (or the pseudo-master curves) for the Ba and the Na salts of polymers with three different ion concentrations. Several features are noteworthy.

The rate of stress relaxation is higher in the Ba salts than it is in the Na-neutralized polymers, as can be seen in all the cases that were studied. Therefore a narrowing of the distribution of the relaxation times is to be expected.

The critical ion concentration above which the time–temperature superposition fails does not appear to be influenced by the nature of the counterion.

Comparing Figure 1 and 2 one can see that the transition region of the Ba salts appears to be very similar to that for the Cs salts but the pseudo-rubbery region is more pronounced in the Ba salts than it is in the Cs and the Na salts.

The shift factors for the Ba salts also follow the WLF equation. The constants c_1 and c_2 listed in Table II are lower than those for the Na salts of same ion concentration but are identical with those for the Cs salts.

Table II
WLF Constants c_1 and c_2 of the Samples Investigated

Varying Counterion			Partially Neutralized		
Sample Label	c_1	c_2	Sample Label	c_1	c_2
3.7(Na)l	23	73	4.6(Na)h	23	73
3.7(Cs)l	18	60	4.6(0.80Na)h	22	81
3.7(Ba)l	18	60	4.6(0.60Na)h	22	81
3.8(Na)h	23	73	4.6(0.40Na)h	22	81
3.8(Cs)h	18	60	8.6(0.44Na)h	32	110
4.6(Ba)h	20	69	6.2(0.61Na)h	21	73
6.2(Ba)h	28	119	6.2(Na)h	47	227

As was shown in the previous publication[2] the height of the upper inflection point on the stress relaxation master curves (or the pseudo-master curves) can be expressed as a linear function of the concentration of Na. An attempt to correlate this height with the nature of the counterion was inconclusive. While the curves shown in Figures 1 and 2 exhibit upper inflection points for the Ba and Cs salts at a lower modulus than those for the same concentration of the Na salt, additional stress relaxation experiments, performed on samples 7.9(Li)l and 7.7(Ba)m yielded the upper inflection points (found on the pseudo-master curves) at about the same value of the modulus as that found for the Na-neutralized polymer. In the previous publication[2] it was shown that for low molecular weight polymer above the critical ion concentration time–temperature superposition was reestablished above the certain temperature. For the 7.9(Na)l sample this temperature was 180°, suggesting that the total contribution of the clusters is negligible above that temperature. This is due most probably to a decrease in the cluster lifetimes. An attempt was made to see to what extent the above phenomenon was also encountered in polymers containing cations other than sodium. Only lithium was investigated and it was found that above 150° time–temperature superposition is indeed reestablished. No reason can be given at this time why the reestablishment occurs at a temperature 30° lower than in the sodium case.

2. Partially Neutralized Polymers. Figure 3 shows a family of stress relaxation master curves for the polymer containing 4.6% of methacrylic acid (MAA) neutralized to varying extents, together with that for PS. The position of the upper inflection point itself disappears for a degree of neutralization lower than *ca.* 50%. Time–temperature superposition is obeyed, with the shift factors following an equation of the WLF type. The c_1 and c_2 constants, listed in Table II, are not greatly affected by the degree of neutralization within the region studied. As can be concluded from an inspection of Figure 3, the distribution of the relaxation times would be expected to narrow with a decreasing degree of neutralization.

In conjunction with the previous investigation, it was decided that partially neutralized samples should be studied in which the concentration of the ions is kept unchanged while the content of the -COOH groups is varied. This should give an idea about the effect of carboxylic groups on the rate of decomposition or lifetimes of the ionic multiplets and/or the clusters. The results of this study are shown in Figures 4–6. Figure 4 shows the stress relaxation master curves (or the pseudomaster curves) for four different samples, each containing 3.8 mol % of NaMA and a different amount of -COOH groups, together with that for polystyrene. Several features are noteworthy.

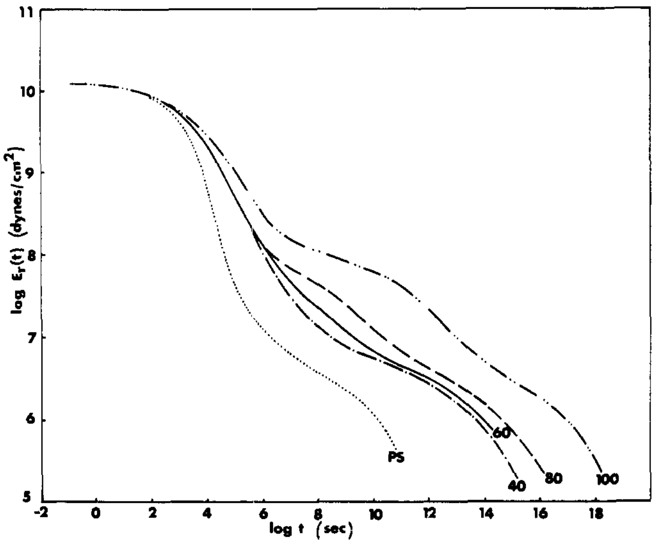

Figure 3. Stress relaxation master curves for the partially neutralized polymer 4.6(H)h. The number on each curve refers to the degree of neutralization. The master curve for polystyrene (PS) is also shown.

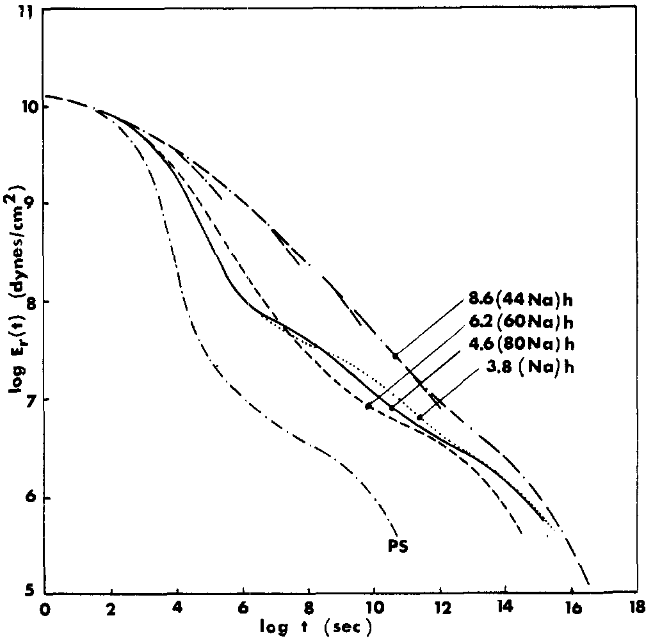

Figure 4. Stress relaxation master curves of polymers of identical ion content but of differing -COOH content.

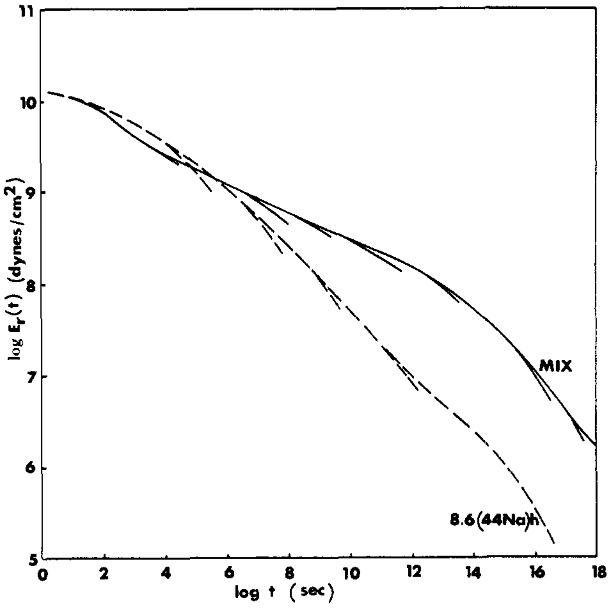

Figure 5. Stress relaxation pseudo-master curves of polymer 8.6(0.44Na)h and of a mixture of 56 mol % of PS and 44 mol % of polymer 8.6(Na)h (MIX).

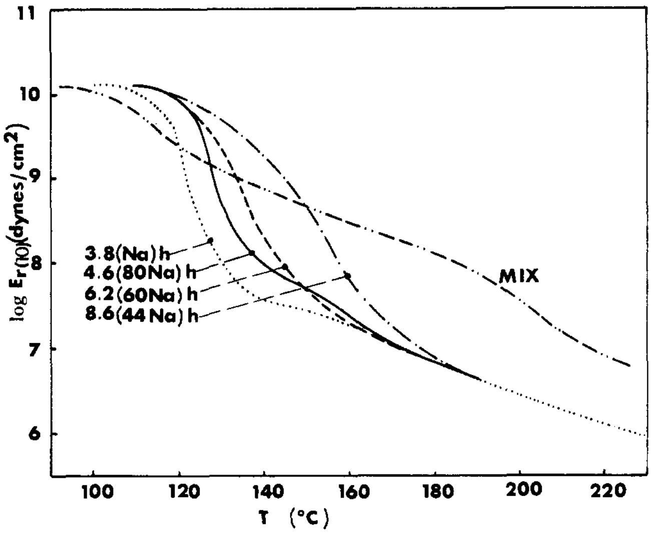

Figure 6. Modulus *vs.* temperature data for five different samples whose labels are on the curves.

While no breakdown of time-temperature superposition was observed in the 6.2(0.60 Na)h sample, which is probably due to the fact that only short time runs (2-10,000 sec) were employed for the construction of the master curve, a typical pseudo-master curve was obtained for the 8.6(0.44Na)h sample suggesting the presence of ionic clusters. The results indicate that if time-temperature superposition is not applicable for the completely neutralized polymer, it tends to remain inapplicable also for its partially neutralized form at a sufficiently high degree of neutralization. In the region of modulus lower than *ca.* 6 × 10^7 dyn cm^{-2}, in which the movements of long-chain segments (>75 monomer units, see Table III of ref 2) come into consideration, it seems that the -COOH groups accelerate the stress relaxation to a certain extent. This is seen in the fact that master curves for materials containing progressively higher -COOH contents are brought progressively closer to that for polystyrene. An additional complication is introduced in the case of sample 8.6(0.44Na)h in which the total concentration of ionized and unionized -COOH groups is high enough to induce the formation of ionic clusters and thus to introduce another relaxation mechanism. The shift factors, which are of the WLF form (with c_1 and c_2 listed in Table II), are not greatly affected by the presence of -COOH groups, with the exception of the pseudo-shift factors utilized for the 8.6(0.44Na)h sample; these are somewhat higher than those for the polymers labelled 6.2(0.61Na)h, 4.6(0.80Na)h, and 3.8(Na)h.

The question arises whether the observed effect is really due to the -COOH groups. It might conceivably be argued that the partial neutralization might not yield a homogeneous product, but rather a mixture of completely neutralized chains and those which are not neutralized at all. The effect observed might thus reflect nothing else but a type of phase separation due to the varying mixture of unneutralized and neutralized chains, with the -COOH groups playing only a minor role or no role at all. If this

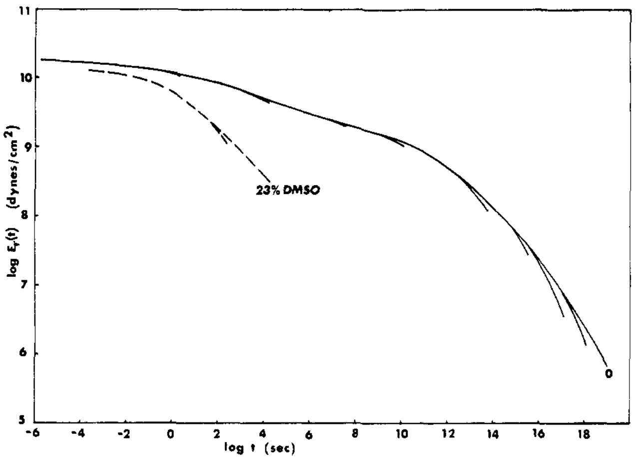

Figure 7. Stress relaxation master curves for plasticized and unplasticized sample 9.7(Na)h.

would be the case, then one would expect that the stress relaxation behavior of a mixture of a fully neutralized polymer with PS will be similar or even the same as that of its partially neutralized version, provided that same overall ion concentration was achieved. The results of such an experiment are shown in Figure 5 (and Figure 6) in which the pronounced difference in behavior of the 8.6(0.44Na)h sample and a mixture consisting of 56 mol % of PS and 44 mol % of polymer 8.6(Na)h can easily be seen. It is clear that while for both these polymers time–temperature superposition is not applicable, the shapes of the curves are quite different.

The 10-sec moduli for samples of the same ion concentration and varying concentration of -COOH groups obtained from the stress relaxation experiments are plotted as a function of the temperature in Figure 6. It is worth noting that at high temperatures (>180°) all the curves with the exception of that for the mixed sample appear to coalesce into one, again confirming the short cluster lifetimes above 180°, and suggesting that the -COOH groups have no effect whatever above that temperature. However, the distribution of -COONa groups along the polymer chain appears to be playing an important role in viscoelastic properties. The modulus *vs.* temperature curve for the mixed sample is quite different from those for partially neutralized materials and also from sample 3.8(Na)h all of which can be considered to have the same distributions of -COONa groups along the chain but different from those of the mixed sample.

3. Plasticized Polymers. To investigate the effect of the plasticizer upon the state of ion aggregation as it is reflected in its relaxation behavior, two markedly different types of plasticizers were used; one hydrophilic and the other hydrophobic.

Plasticization of styrene ionomers by dioctyl phthalate or diethyl phthalate resulted in the same effect as that observed by Chapoy and Tobolsky[3] in polystyrenes plasticized with the same solvent, namely, in broadening of the stress relaxation master curves. By contrast if Me_2SO was used as a plasticizer, a narrowing of the stress relaxation curves was observed. Unfortunately, the low modulus region ($<10^8$ dyn cm^{-2} could not be studied because the temperatures required resulted in a loss of plasticizer. Also, an attempt to prepare a more highly plasticized sample failed because of the apparent limited solubility of Me_2SO in these polymers. The accessible part of the pseudo-master curve for the 9.7(Na)h(23Me_2SO) sample is shown in Figure 7 together with that for the unplasticized 9.7(Na)h sample. Time–temperature superposition is inapplicable for any of these polymers. It is not clear whether the narrowing of the curve would have also been observed if pure polystyrenes were plasticized with Me_2SO. The solubility of Me_2SO in polystyrene is so low that no sample of meaningful Me_2SO content could be prepared.

III. Discussion

It will be shown that the results presented in this paper are consistent with the previously proposed structural model for the styrene-based ionomers. This model was discussed in great detail in the discussion part of ref 2 and is based on the existence of multiplets below 6 mol % of ions and of clusters above that.

The discussion is divided into three parts, dealing with the counterion effect, partially neutralized polymers, and the effect of plasticization.

A. Counterion Effect. In the region of low ion concentration the ions are assumed to exist in the form of simple multiplets. The ease with which these multiplets dissociate should clearly be a function of the interion distance in such a multiplet. The larger the interion distance, the lower the energy required to remove an ion pair. Thus it is not surprising that the big Cs^+ ions were found to form less stable cross-links than the Na^+ ions, as manifested in less well-developed rubber-like plateaus seen on the stress relaxation master curves in Figure 1. The divalent Ba^{2+} ions represent a slightly different case. The results shown in Figure 2 indicate that the inflection point corresponding to the rubbery modulus for the Ba^{2+} salt occurs at a lower value than in the Na^+ salt, in spite of the fact that the same number of carboxyl groups is involved in both cases. Therefore unless the front factor for these two polymers is drastically different (which seems unlikely), one must conclude that the crosslink density in the Ba^{2+} salt is lower than in the Na^+ salt. By contrast the pseudo-rubbery region is more pronounced in the Ba^{2+} salts than it is in the Na^+ and the Cs^+ salts (Figures 1 and 2), which in turn suggests that the lifetimes of the multiplets containing Ba^{2+} are longer than those of Na^+.

It seems intuitively correct that the critical ion concentration above which time–temperature superposition fails should not be influenced by the nature of the counterion. The existence of ionic clusters seems to be much more a function of the presence of the ionic species and their concentration than on the detailed size or charge of the ions involved. There may very well be small differences in the critical ion concentration but these are within the experimental error of this investigation. There appears to be no reason why the structure of the ionic clusters should be greatly influenced by the nature of the counterion if the long range electrostatic interactions which cause cluster formation remain unchanged.

B. Effect of Carboxylic Groups. By inspecting Figure 3 it becomes apparent that the ions cease to act as cross-links if the degree of neutralization is below *ca.* 50% in polymer containing 4.6 mol % of carboxylic groups. One can see that the position of the upper inflection point decreases with decreasing ion concentration (decreasing degree of neutralization); however, the decrease is faster than one would calculate with the simple assumption that -COOH groups do not participate in cross-links, while all the -COONa groups do. As can be seen from Figure 4, the 80% neutralized polymer appears to contain only *ca.* 50% of the original number of cross-links present in the 100% neutralized polymer. This value was obtained from the following consideration. The upper inflection point on the stress relaxation master curve for the 4.6(Na)h sample appears at log $E_{r(t)}$ = 8.0 dyn cm^{-2}, while for the

4.6(0.80Na)h sample log $E_{\mathrm{r}(i)} = 7.7$ dyn cm^{-2}. The simplest theory of ideal rubber elasticity[11,12] shows that for two different samples the ratio of rubbery moduli is equal to the inverse of the ratio of their cross-link densities. In this case

$$E_{\mathrm{r}(i)}[4.6(\mathrm{Na})\mathrm{h}]/E_{\mathrm{r}(i)}[4.6(0.80\mathrm{Na})\mathrm{h}] = 2$$

Thus it was concluded that the number of ionic cross-links in the 4.6(0.80Na)h sample is equal to half that in the 4.6(Na)h polymer. An identical drop in the pseudorubbery modulus for the 60% ionized sample indicates that only *ca.* 25% of the original number of cross-links is present. In addition to a drop in the apparent number of cross-links the average lifetime of those remaining seems to be reduced significantly as manifested by the more poorly developed inflection points (plateaus) for lower degrees of neutralization. This reduction in the lifetime is probably caused by some type of exchange reactions, *i.e.*

$$-\mathrm{COOH} + -\mathrm{COO^-Na^+} = -\mathrm{COO^-Na^+} + -\mathrm{COOH}$$

This would enable the -OOO$^-$Na$^+$ groups which are attached to chains, to be transformed into the acidic version, which would make them more freely moveable because of the much weaker attraction. It should be recalled that for the completely neutralized system the interchange reaction is also possible and this is, most likely, the relaxation mechanism in these materials. Such a possibility was already mentioned earlier.[13]

It was shown in the previous paper[2] that in the region of high ion concentration (more than 6 mol %) the ion pairs are likely to exist in some type of ionic clusters. On the basis of these present results (Figures 4 and 5) it has to be concluded that by replacing some of the ions by unionized carboxylic groups, the presence of the ionic clusters is not affected, as manifested by the continued inapplicability of time-temperature superposition. The fact that the upper inflection point is absent on the stress relaxation pseudo-master curve and modulus *vs.* temperature curve for sample 8.6(0.44Na)h indicates a decreased stability of the clusters which are no longer acting as "hard" ionic filler.

As in the case of multiplets, the carboxylic groups participate also in formation of the ionic clusters in partially neutralized polymers. If one would assume that they are mainly outside of these clusters, then it would be expected that all stress relaxation master curves would exhibit two inflection points for all the degrees of neutralization. The upper inflection point (the ionic one) would shift to higher modulus with increasing degree of neutralization due to the increasing fraction of total volume occupied by clusters. It is shown in Figure 4 that this is not the case. The ionic inflection point disappears for a degree of neutralization lower than *ca.* 50%.

C. Plasticized Polymers. Chapoy and Tobolsky[3] proposed and verified experimentally that a broadening of the stress relaxation spectrum in polystyrene plasticized by organophilic solvent is caused by the fact that, due to the presence of diluent, intermolecular forces among PS molecules are greatly reduced. This means that while unplasticized PS can be regarded as a three-dimensional damped Debye solid, plasticizer causes the system to degenerate to a one-dimensional lattice, and behavior more in accord with the Rouse–Bueche[14,15] theory can be observed (m approaches -0.5). The same effect was observed in the styrene ionomers plasticized by alkyl phthalates in all regions of ion concentration. On the other hand, the effect of dimethyl sulfoxide, which has a much higher dielectric constant ($K = 45$)[16] than DOP or DEP ($K \leq 8.5$) (K of dimethyl phthalate is 8.5[17]), lies predominantly in plasticizing of the ionic clusters. These still exist but the rate of ion pair migration in and out of the cluster is higher. This is reflected in the increased rate of relaxation as seen in Figure 7.

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

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