corresponding to eq 2 for this polymer (c = 0.07 g/ml gives 2.8 × 10^4 for the product cM). This result is in contrast with that for low M-high c systems for which no sign of the plateau region was seen even at the highest concentration for the sample **7a** (cM = 3.6 × 10^4). Thus the shape of the relaxation spectrum seems to change very gradually with varying c in the case of high M-low c systems. The viscosity, given in Table I, varies gradually with varying M and the power dependences as shown in eq 1 do not apply for these systems. Accordingly the critical molecular weight, even if defined in some way, will not have such a definite significance as in the case of low M-high c systems.

The steady-state compliance J_e^0 for high M-low c systems as given in Table I is plotted against c in Figure 6 to improve the figure shown in the previous paper.[4] Thick solid lines represent the results given before.[4] The present results seem to confirm the existence of minima in the relation of log J_e^0 and log c for two samples, **1b′** and **4a.** It is seen that J_e^0 for these samples below the concentration corresponding to the minima are approximately equal to the predicted values of the Rouse theory shown by thin solid lines.[14] For higher M, no minimum is observed and the slope decreases gradually as c decreases. J_e^0 for the sample of the highest M, **14a,** of the present study is lower than that reported before (solid line at the top). It was revealed from the gel permeation chromatogram that the sample **14a** used before had a wide distribution of molecular weight probably due to thermal degradation at the last stage of the study.

Acknowledgment. One of the authors (Y. E.) is grateful for the financial aid of the postdoctoral fellowship of Japan Society for the Promotion of Science.

Ion Clustering and Viscoelastic Relaxation in Styrene-Based Ionomers. II. Effect of Ion Concentration

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ABSTRACT: A study of the viscoelastic properties of styrene ionomers containing up to 10 mol % of sodium methacrylate was undertaken. It was found that in the region of low ion concentration (up to 6 mol % of salt) time–temperature superposition is obeyed and equations of the WLF type are applicable. For the material for which time–temperature superposition is valid, the glass transition temperature (T_g) increases approximately linearly with concentration of ions, with $dT_g/dC \approx 2°/\text{mol } \%$ up to 6 mol % salt. For the samples above that value, the increase in T_g is faster. With increasing ion concentration there is an increase in both WLF parameters C_1 and C_2 and also a broadening of the distribution of relaxation times. In all samples of high molecular weight and an ion concentration above 1% two inflection points are visible on the stress relaxation master curve. The upper inflection point increases with increasing ion concentration. Water uptake experiments for samples which are subject to time–temperature superposition reveal that only one water molecule is absorbed per ion pair at equilibrium. With increasing ion concentration the primary (*i.e.,* diffusional) relaxation mechanism is observed to slow down. This slowing down is a function of both the ion concentration and the length of the polymer chain which has to cooperate to reach a specific modulus. Above 6 mol % of salt time–temperature superposition is no longer applicable. Water uptake experiments for these samples do not seem to lead to equilibrium values; the rate of water uptake increases with increasing ion concentration and after 6 months the number of water molecules per ion pair ranges from 3 to 6 per sodium ion. Failure of time–temperature superposition above 6 mol % of ionic groups, results of water uptake, and the glass transition studies are consistent with the hypothesis that clustering occurs above 6 mol % of our system. The failure of time–temperature superposition in these materials seems to result from the introduction of an additional relaxational mechanism due to the presence of microphase separation. For polymers of low molecular weight containing more than 6% of ions, time–temperature superposition is found to be applicable again above *ca.* 180°. Clustering is confirmed by preliminary X-ray studies.

The unusual physical properties of ion-containing polymers have been the subject of considerable attention during the past decade as evidenced by two recent review articles.[1,2] Two main problems complicating the interpretation of viscoelastic results have emerged. The first of these is the fact in the ion-containing polymers, time–temperature superposition has, by and large, been found inapplicable.[3-5] The second concerns the supermolecular structure of these polymers. While some workers found experimental[6-10] and theoretical[11] evidence for microphase separation, results of other studies fail to show these phenomena.[12-14] If microphase separation occurs and the lifetime of the aggregates thus formed is finite, time–temperature superposition would not be expected to hold since it is most probable that the clusters contribute to the relaxation behavior and since the activation energies of the two resulting processes are probably not the same. Thus it is of interest to investigate both microphase separation and

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time-temperature superposition in noncrystallizable polymers.

In our previous communication[15] we have reported some preliminary results concerning the applicability of time-temperature superposition in styrene-sodium methacrylate copolymers. We have found that below a critical ion concentration (6 mol %) time-temperature superposition is obeyed, with the ions acting merely to slow down the primary mechanism. The shift factors are of the WLF[16] form, the constants being higher than in the case of simple polystyrene. Above that concentration, however, time-temperature superposition becomes invalid. Superposition still can be affected by using only short segments of the original stress relaxation curves, *i.e.*, those which extend over the same two decades of time. However, the shape of the pseudo-master curve thus obtained varies depending on the time interval selected.

In this paper we shall describe a study in which the effect of ions on the viscoelastic relaxation behavior is investigated over wide ranges of concentration, and we shall discuss the implications of the results on the structure of the ionic aggregates in the material. Specifically, we shall attempt to answer the following questions. (1) How do the viscoelastic properties vary with ion concentration in the regions above and below the critical ion concentration? (2) How do the WLF constants and distribution of relaxation times vary in the region of applicability of time-temperature superposition?[17,18] (3) What is the reason for failure of time-temperature superposition? Is this failure due to a multiplicity of mechanisms or is it due to a change of the structure of the ionic aggregates with temperature, or both? (4) Do ions act as cross-links, and if so, is the behavior explainable in terms of theory of rubber elasticity?[19-20]

Owing to the recent appearance of a review dealing with the properties of ion-containing polymers[2] 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 before proceeding with a detailed description of our work.

Ward and Tobolsky[3] studied the stress relaxation behavior of sodium and calcium salts (*ca.* 2-4 mol %) of copolymers based on α-olefins and carboxylic acid and obtained "reasonably good superposition" if both vertical and horizontal shifts were applied on original modulus *vs.* time data. However, the shift factors did not obey a WLF type of equation, and the vertical shift may have been necessitated by a change in the degree of crystallinity.

Several copolymer systems based on materials which are noncrystalline in a homopolymer state were also investigated. One of these is the copolymer of butadiene with lithium acrylate studied by Otocka and Eirich.[21,22] For the purpose of this paper their most important finding lies in fact that a lithium content up to 11 mol % does not influence the shape of the master curve above the rubber-like plateau. Also the latter remains practically unchanged and the only effect observed is in the flow region. Time-temperature superposition was found applicable and the shift factors followed the WLF equation.

Fitzgerald and Neilsen[23] did a preliminary investigation of the stress relaxation behavior of mono- and divalent salts of styrene-methacrylic acid copolymers. In addition to the increase in T_g they observed an increase in the relaxation modulus in polymer salts going from the acid to Na^+ to Ba^{2+} to Al^{3+}. Their master curves look similar in shape, except for a vertical and horizontal displacement from one another, however, their experiments do not allow to draw any conclusion about applicability of time-temperature superposition.

S. Tamura *et al.*[24] investigated the stress relaxation behavior of styrene-methacrylic acid copolymer and salts of this material of low degree of ionization. No deviation from time-temperature superposition was observed and only one inflection point at $\log E = 6.5$ was found.

I. Experimental Section

A. Sample Preparation. 1. Polymer Synthesis. a. Chemicals. Styrene and methacrylic acid (Fisher Scientific Co.) were distilled at room temperature and stored at −15° prior to use. The distillations were performed no more than 24 hr prior to polymerization. Benzoyl peroxide initiator, reagent grade benzene, methanol and sodium hydroxide (Fisher Scientific Co.) were used as received.

b. Polymerization. Appropriate amounts of styrene, methacrylic acid and benzoyl peroxide were measured into 150-cm^3 ampoules. The composition of the monomer mixture was calculated for the specific copolymer composition on the basis of r_1 or r_2 values reported in the literature.[25] The amount of initiator necessary to get the required rate of polymerization was assumed to be the same as that for pure polystyrene and therefore polymerization kinetics for polystyrene were applied.[26] The mixture was placed in glass ampoules and degassed by several freeze-thaw cycles under vacuum ($<10^{-4}$ mm). The ampoules were then sealed off and immersed in an 80° bath. The time of polymerization varied between 1 and 33 hr and was chosen so as to achieve a conversion between 10 and 15%. The ampoules were removed, the contents were diluted with two volumes of benzene, and the mixture was precipitated into eight volumes of rapidly stirred cold methanol. The polymers were isolated and dried under high vacuum at 100° for 24 hr. The details of the polymerization runs and of the resulting polymers are given in Table I.

c. Neutralization. Solutions of 3-5% of the polymers in benzene (in case of acid contents higher than 7 mol % a mixture of benzene and methanol 90:10 v/v was employed) were titrated under nitrogen by a standard solution of NaOH in methanol (*ca.* 1 *N*) with phenophtalein as an indicator, a procedure similar to that used by Erdi and Morawetz.[27] At the end point, pink solutions were obtained which were then freeze-dried. To show that no retarded neutralization reaction takes place, a sample just reaching the end point was stirred at 50° for 48 hr under nitrogen; it was shown that the pink color persists. Blank titrations of benzene were performed showing that the volume of NaOH solution necessary to titrate 70 ml of benzene is of the order of one drop. Identical results were obtained if the copolymer was titrated by sodium hydroxide in methanol or by sodium ethoxide in ethanol.

2. Sample Molding. Just prior to molding, the polymers were dried at temperatures 20° above their T_g's in vacuum for 12 hr. Between 0.5 and 0.9 g of polymer was weighed into a mold; then a pressure of 20,000 psi was applied while the temperature was allowed to increase. When the pressure dropped to 12,000 psi due to the softening of the sample, the pressure was further lowered to 200 psi and the temperature was allowed to increase another 20-30°. The mold was then removed from the press and, after partial cooling, the sample was released from the mold at a temperature still above its T_g. The rest of the cooling proceeded in a desicca-

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Table I
Polymerization Conditions and Data on Resulting Polymers

	Polymer Samples				Polymerization Conditions			
Sample Designation[a]	Concn of $-COO-$ (mol %)	$M_{n,d}$ (Dioxane)	$M_{n,t}$ (Toluene or Cyclohexanone*)	$M_{n,t}/M_{n,d}$	Concn of MAA in Monomer Mix (mol %)	Bz_2O_2 (wt %)	Temp (°C)	Time (hr)
0.6(Na)h	0.6				0.22	0	80	32
1.9(Na)h	1.9	470,000	700,000	1.49	0.55	0	80	32
2.5(Na)h	2.5				0.85	0	80	32
3.8(Na)h	3.8	400,000	660,000	1.65	1.25	0	80	32
4.6(Na)h	4.6				1.50	0	80	32
6.2(Na)h	6.2				2.00	0	80	32
9.7(Na)h	9.7		500,000*		3.30	0.008	80	13.5
1.5(Na)l	1.5				0.55	0.44	80	2
3.7(Na)l	3.7	50,000	75,000	1.50	1.25	0.44	80	2
5.5(Na)l	5.5				2.00	0.44	80	2
7.9(Na)l	7.9	70,000	75,000*	1.07	3.30	0.44	80	2
7.7(Na)m	7.7	140,000	250,000*	1.78	3.30	0.032	80	5.5
9.1(Na)m	9.1		320,000*		3.30	0.016	80	10.0

[a] The samples are labeled by a number giving the concentration of methacrylic acid (MAA) comonomer in mole per cent followed by letters (H) or (Na) in parentheses indicating acidic or sodium neutralized polymer, respectively, followed by a letter l or m or h indicating low (50,000–70,000), medium (150,000–200,000), or high (*ca.* 400,000) molecular weights, respectively.

tor. This procedure was adopted because samples tended to crack if allowed to cool completely in the mold.

B. Calorimetry. The T_g's of the polymers were determined on a Perkin-Elmer differential scanning calorimeter (Model DSC-1); heating and cooling rates of 10°/min were employed.

C. Infrared Spectroscopy. Infrared spectra of the thin films, prepared by compression molding, were taken on a Perkin-Elmer spectrometer Model 257.

D. Molecular Weight Determination. Number-average molecular weights, $\bar{M}_n$, were determined on a Hewlett-Packard 502 high-speed membrane osometer in solutions of cyclohexanone, toluene, or 1,4-dioxane for the acidic (nonneutralized) samples at 30°. The $\bar{M}_n$'s were averaged from two or three determinations.

E. Stress Relaxation. The experiments were performed on a vacuum stress relaxometer described elsewhere,[28] which was calibrated for forces varying from 1 to 500 g. Special attention was paid to precise temperature control. Five iron-constantan thermocouples monitored the temperature at various places in the vicinity of the sample chamber. Usually, the temperature inside the sample cell was recorded continuously during the experiment and was found to vary less than ±0.02° in the range of 70–250°. Prior to the beginning of the experiments, the sample cell was evacuated and refilled with dry nitrogen at ambient pressure. Deformations between 0.3 and 15% were employed. Rectangular samples (length 7–30 mm, width 6.4 mm, thickness 1–3 mm) were used for bending and stretching and cylindrical ones (diameter 8 mm, length 5–10 mm) for compression. Dimensions below 10 mm were measured by micrometer with a precision 0.01 mm, above 10 mm by a vernier caliper with a precision of 0.05 mm. In the experimental arrangement bending is realiable in the region between 10^{11} and 4×10^7 dyn cm^{-2}, stretching between 10^9 and 3×10^5 dyn cm^{-2} and compression between 10^7 and 2×10^4 dyn cm^{-2}. Data obtained by means of stretching, bending, or compression were found reproducible and superimposable within the limits in which time-temperature superposition is applicable (see below). No deviations from linear viscoelasticity were observed in the region of deformations employed.

It was observed that for low molecular weight polymers only very small deformations could be employed in the region of modulus above 10^9 dyn cm^{-2} because samples tended to be very brittle.

F. Water Uptake. Samples which were of the same type as those used in stress relaxation experiments were kept under water at room temperature. Periodically they were removed, the surface was wiped off. The samples were left in air for about 10 min, weighed and dropped again into water. From the weight difference between the dry and "swollen" sample the number of water molecules per sodium ion was calculated and followed as a function of time for the polymers of different ion content.

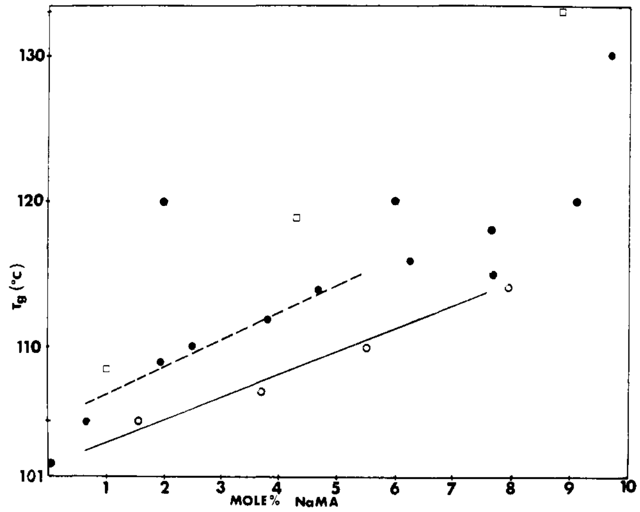

Figure 1. Glass transition temperature (T_g) *vs.* concentration of sodium methacrylate (NaMA): (○) Low molecular weight, (●) high molecular weight, (◉) medium molecular weight, (□) Otocka and Eirich (ref 21), (★) Fitzgerald and Nielsen (ref 23).

II. Results

A. Molecular Weights ($\bar{M}_n$). As can be seen from Table I, three different concentrations of initiator were employed which yielded polymers with three distinctly different molecular weights labeled h, m, or l. Molecular weights of several representative samples synthesized for this study were determined osmometrically in both hydrogen-bonding and non-hydrogen-bondings solvents, and these are also listed in Table I. It was found that molecular weights determined in non-hydrogen-bonding solvents such as toluene or cyclohexanone were higher than those measured in 1,4-dioxane by a factor of 1.5–1.8 (with exception of sample 7.7(Na)l where both determinations gave virtually the same result). This is in a good agreement with results obtained by Erdi and Morawetz[24] who found the molecular association factor of the same copolymer in benzene to be approximately 1.5–2, depending on the ion concentration.

B. Infrared Spectra. From the infrared spectra taken, the concentration of carboxylic groups present in the neutralized polymers can be computed.[18] Both the 1740 and

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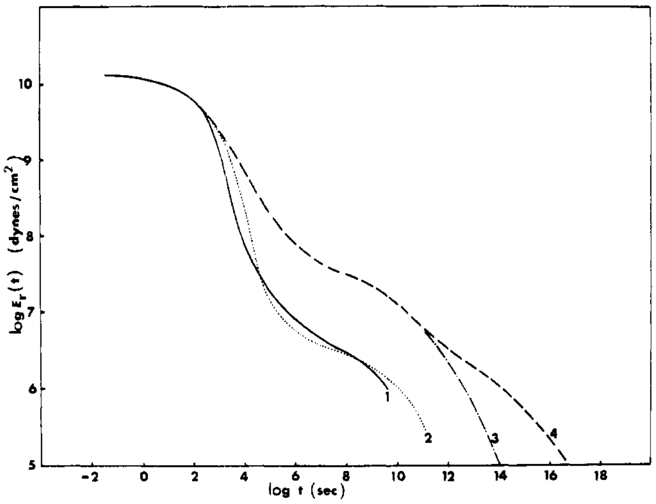


Figure 2. Stress relaxation master curves for four different samples: curve 1, PS; 2, 3.8(H)h; 3, 3.7(Na)l; 4, 3.8(Na)h. $T_{\text{ref}} = T_g$ for each sample.

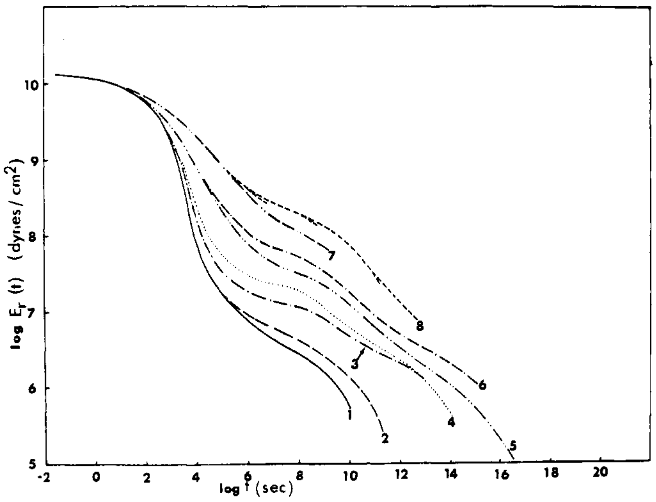
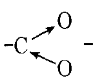
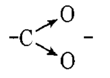


Figure 3. Stress relaxation master curves for eight different samples: curve 1, PS; 2, 0.65(Na)h; 3, 1.9(Na)h; 4, 2.5(Na)h; 5, 3.8(Na)h; 6, 4.6(Na)h; 7, 5.5(Na)l; 8, 6.2(Na)h.

1700 cm^{-1} -C=O stretching vibrations are absent in the salt. Instead of these, two new peaks appeared; one at 1560-1570 cm^{-1} interpreted as a


$$-\mathrm{C}\overset{\nearrow \mathrm{O}}{\underset{\searrow \mathrm{O}}{}}\ -$$

asymmetrical vibration and second at 1410 cm^{-1} corresponding to the


$$-\mathrm{C}\overset{\nearrow \mathrm{O}}{\underset{\searrow \mathrm{O}}{}}\ -$$

symmetrical stretching vibration.[29] The polymers are therefore considered to be 100% neutralized.

C. Glass Transition Temperature (T_g). Figure 1 shows the T_g's of the styrene-sodium methacrylate copolymers. The T_g of the copolymer is a function of ion concentration and, as might be expected, also of the molecular weight. The lines are drawn for low and high molecular weight samples for concentrations up to 6 mol %, where the increase is linear. The increase in T_g was found to be of the order of 2°/mol % of ions in the region below 6 mol %, which is lower than that given by Otocka[30] for lithium salt and Fitzgerald and Nielsen.[23] The results of all these studies are shown on the same figure.

D. Stress Relaxation. The results of the stress relaxation runs are shown in Figures 2-11. A computer program[31] was used to obtain the master curves, shift factors and relaxation spectra from the individual curves of modulus *vs.* time. All the master curves are plotted with their T_g's as the reference temperatures.

The master curve for the polystyrene (PS) sample (Polystyrene was prepared by anionic polymerization as a part of a previous project of A. E.) (M_n = 230,000, M_w = 330,000) and one for the polymer 3.8(H)h are shown in Figure 2. These curves are similar in shape, with the height of the inflection point (log E_i = 6.5) unaffected by the presence of the carboxylic groups. The effect of the hydrogen bonding which is observed in the transition region thus seem to diminish with increasing temperature. The difference in the flow region for these two samples is probably due to the difference in molecular weights only. It should be mentioned that the master curve for PS presented here agrees within experimental error with that given by Takahashi *et al.*[32]

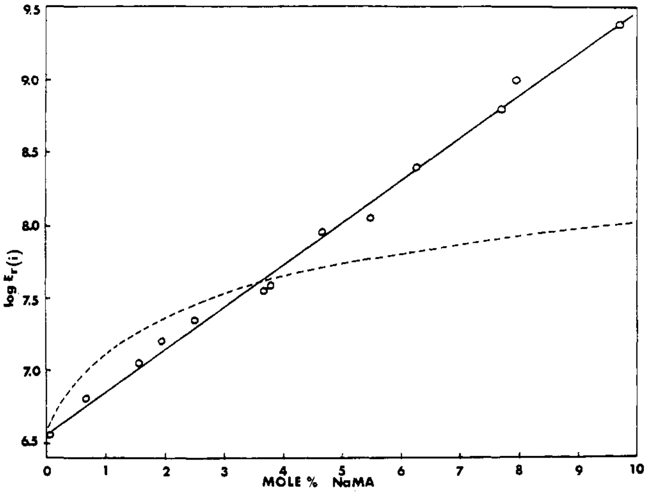


Figure 4. Dependence of the height of the upper inflection point of the stress relaxation master curves (or pseudo-master curves) on the concentration of sodium methacrylate (NaMA) in a copolymer.

In the same figure (Figure 2) the master curves for the polymers 3.8(Na)h and 3.7(Na)l are also shown. These two curves are identical up to log E equal 6.5, below which a molecular weight effect becomes observable. Both curves exhibit an inflection point at log E_i = 7.5 independent of the molecular weight.

The shift factors for both samples 3.8(Na)h and 3.7(Na)l follow the WLF type of equation with the constants C_1 = 23, C_2 = 72 while both PS and the polymer 3.8(H)h follow the WLF equation with C_1 = 14 and C_2 = 46, close to the values presented for PS in the literature.[33,34]

A family of master curves for high molecular weight copolymers containing different amounts of sodium ions is shown together with that for the polystyrene sample in Figure 3. Two features are noteworthy. A broadening of the transition and flow regions can be observed with increasing ion content, and two inflection points are visible on each master curve with the excption of that for PS and

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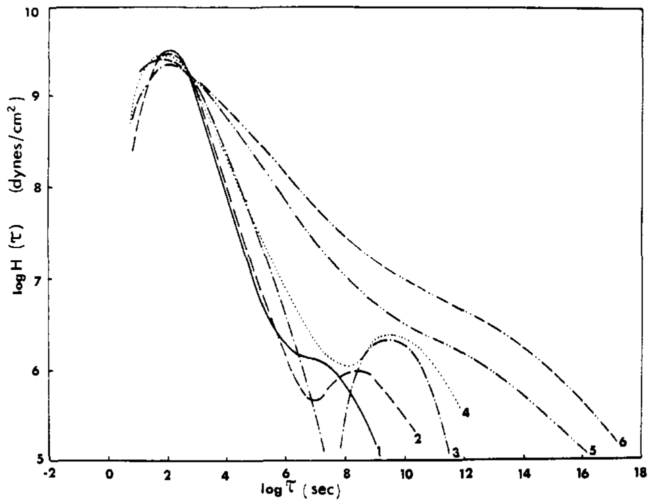

Figure 5. Distribution of relaxation times: curve 1, PS; 2, 0.6(Na)h; 3, 1.9(Na)h; 4, 2.5(Na)h; 5, 3.8(Na)h; 6, 4.6(Na)h.

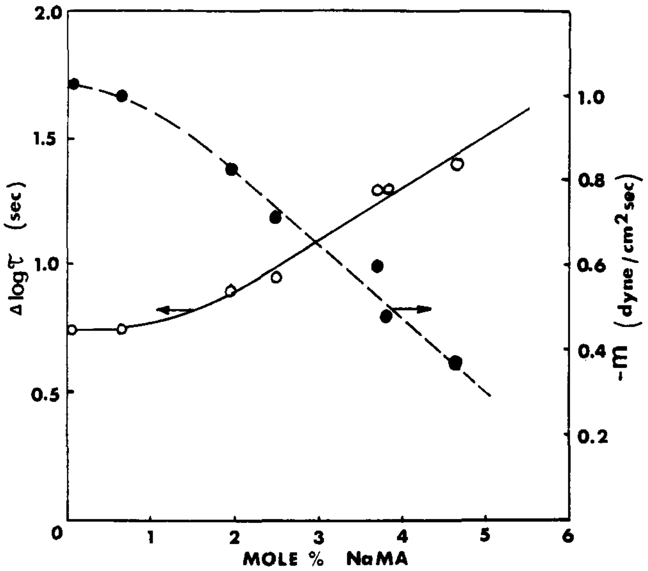

Figure 6. Slope (m) of the linear portion and half-width ($\Delta \log \tau$) of the distribution of relaxation times plotted as a function of ion concentration.

the copolymer 0.65(Na)h. The experimental values of the upper inflection points are plotted in Figure 4, against the ion concentration, with the dashed line representing the rubbery modulus as calculated from the theory of ideal rubber elasticity with the assumption that each ion pair is incorporated in a cross-link. It can be seen that the height of the upper inflection point is a linear function of the ion content, and can be expressed by the equation $\log E_i = 30c + 6.5$, where c is the mole fraction of the neutralized carboxylic groups and 6.5 is the log of the rubber-like modulus of pure polystyrene. The lower inflection point remains unchanged at *ca.* $\log E = 6.5$ [dyn cm^{-2}]. One can also see that the upper inflection points appear at a relatively constant time region, corresponding to the 10^7 sec if modulus of each polymer is measured at its T_g.

At this point it is necessary to mention that the four points corresponding to the highest ion concentrations in Figure 4 do not correspond to the inflection points on the real master curves (because of the impossibility of obtaining these (see ref 15) but are determined from "pseudo-master curves" obtained by superposing only the short time regions (2–100 sec) of the individual modulus *vs.* time data. The purpose of presenting these four points is to show the continuous trend in stress relaxation behavior from the region where time–temperature superposition is obeyed into the "nonsuperposable" region above the critical ion concentration.

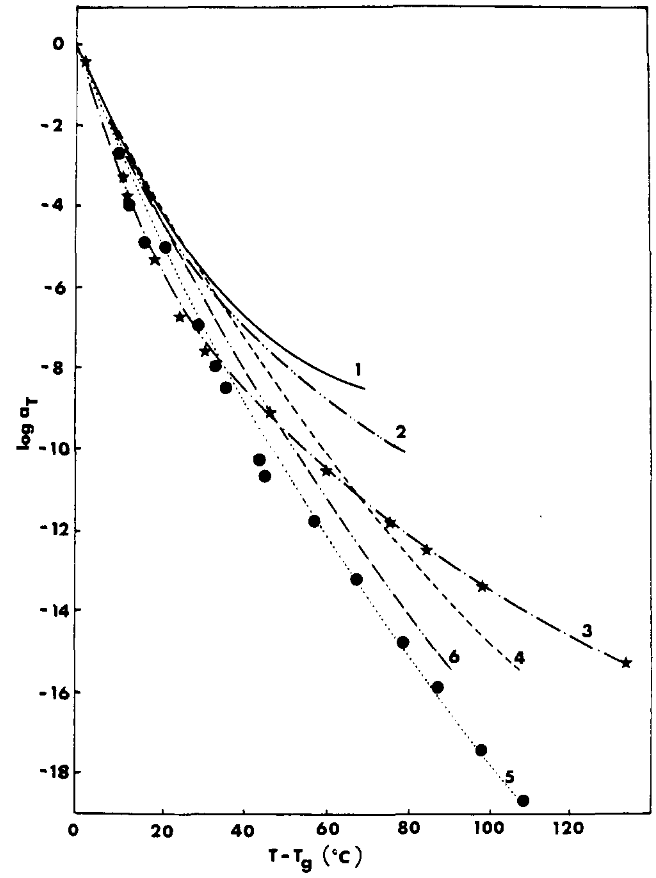

Figure 7. Shift factors *vs.* $T - T_g$: curve 1, PS, 0.6(Na)h, and 3.8(H)h; 2, 1.9(Na)h and 2.5(Na)h; 3, 3.7(Na)l, 3.8(Na)h (★), and 4.6(Na)h; 4, 6.2(Na)h and 7.9(Na)l; 5, 7.7(Na)m (●); 6, 9.7(Na)m. Experimental points were omitted from lines 1, 2, 4, and 6 for the sake of clarity.

The distribution of relaxation times for the polymers for which time–temperature superposition is valid are plotted in Figure 5. They show a considerable broadening with increasing ion concentration implying that new relaxation modes are introduced by the presence of ions. As can be seen from Figure 6 both the slope $(m)^{18}$ of the linear portion of the distribution of relaxation times and half-width $(\Delta \log \tau)^{1}$ of the relaxation spectrum became a fairly linear function of ion concentration for samples above 1 mol % of salt.

The shift factors of the master curves from Figure 3 follow the WLF type of equations fairly well as can be seen in Figure 7 (curves 1, 2, and 3). Both C_1 and C_2 increase with the increasing ionic concentration (Table II). It is interesting to see that even in the case of polymers with more than 6 mol % of ions, where only pseudo-master curves can be obtained the "pseudo-shift factors" employed in the construction of those pseudo-master curves still tend to follow the WLF type of equations but with much higher C_1 and C_2 parameters (Table II). This is also evident in Figure 7 (curves 4, 5, and 6). Thus, two distinct families of curves are obtained, one for samples which are subject to time–temperature superposition (lines 1, 2, and 3) and another for samples above the critical ion concentration (lines 4, 5, and 6). In the first publication it was shown that by taking different time segments for the same sample of high ion content, different master curves can be

Table II
WLF Constants C_1 and C_2

Sample Designation	C_1	C_2	Line No. in Fig. 7	Remarks
PS	14	46	1	s[a]
3.8(H)h	14	46	1	s
0.6(Na)h	13	40	1	s
1.9(Na)h	19	71	2	s
2.5(Na)h	19	71	2	s
3.7(Na)l	23	73	3	s
3.8(Na)h	23	73	3	s
4.6(Na)h	23	73	3	s
6.2(Na)h	47	227	4	n[b]
7.9(Na)l	47	227	4	n
7.7(Na)m	60	240	5	n
9.7(Na)h	66	300	6	n

[a] s means that time-temperature superposition is applicable. [b] n means that time-temperature superposition is not applicable.

obtained all of which look perfectly reasonable. At this point it is worth noting for the sake of completeness that the shift factors obtained by this procedure are different for different time segments. This is shown in Figure 8 where curves 5a, 5b, 5c, and 5d refer to shift factors obtained by utilizing progressively longer time segments for the same polymer sample.

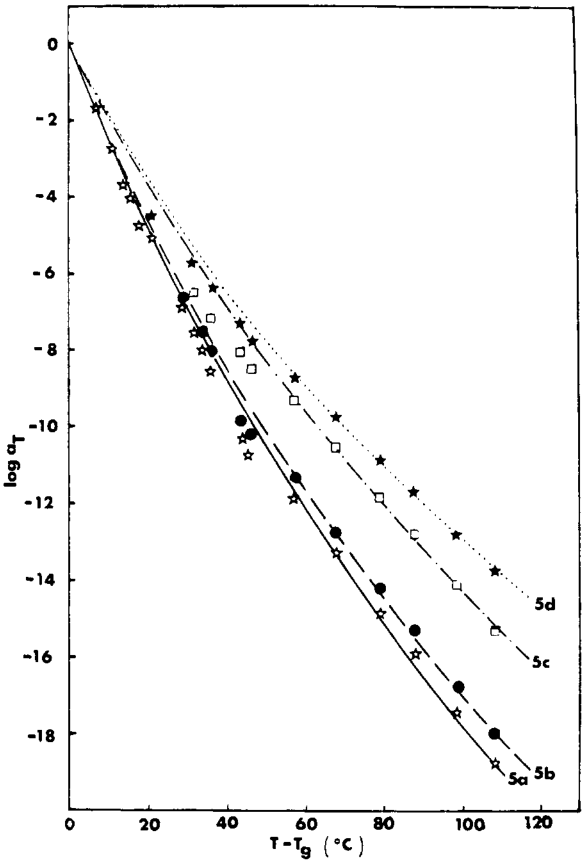

Figure 8. Dependence of shift factors (log a_T) on temperature ($T - T_g$) for four different time segments employed in constructing pseudo-master curves for sample 7.7(Na)m. Curves are of the WLF form with various constants C_1 and C_2: curve 5a (C_1 = 60, C_2 = 240) and points (☆) 2–100 sec; curve 5b (C_1 = 54, C_2 = 218) and points (●) 10–1000 sec; curve 5c (C_1 = 54, C_2 = 278) and points (□) 100–10000 sec; curve 5d (C_1 = 41, C_2 = 217) and points (★) 1000–100,000 sec.

An attempt was made to correlate the rate of relaxation with the ion concentration. If the stress relaxation master curve is plotted with T_g as the reference temperature, one can find, by inspection, the time required for the modulus to reach a certain value. For instance, in case of polystyrene (Figure 3) the stress relaxation modulus of 3 × 10^6 dyn cm^{-2} is obtained at *ca.* 5 × 10^7 sec if the stress relaxation run is performed at the T_g of polystyrene (102°). For the sample 3.8(Na)h the same modulus is obtained after *ca.* 10^{12} sec if measured at its T_g (112°). By plotting the master curves at their T_g's, the effect of ions on T_g is eliminated and the only observed effect is the slowing down of the primary diffusional relaxation mechanism caused by the presence of ions. In this particular example it would take 20,000 times longer to reach the same modulus for sample 3.8(Na)h than for PS. One can expect that the slowing down factor will be a function both of the chosen modulus and the ion concentration. Thus, if one plots the relative displacement along the time axis of the master curves (all measured at their T_g's) for different modulus values against the ion concentration one can obtain a semiquantitative idea of the slowing down of the primary relaxation mechanism caused by the presence of ions for different values of modulus. This is shown in Figure 9; the concentration of ions is expressed both in mole per cent and as an average number of styrene units between two consecutive sodium methacrylate groups. The points corresponding to the highest ion concentration (6.2 mol %) are already those for the pseudo-master curves. Between two extremes of the glassy state where only short range motions are possible, and the low viscosity liquid, where molecules can move as a whole, a wide region of different moduli exist. One can expect that the lower the modulus, the longer the chain segment involved in cooperative motions causing stress relaxation to the modulus value. It appears from the finite intercept of the curves with the concentration axis in Figure 9 that the slowing down becomes effective only if an average interion distance is less than an average length of chain segments involved in cooperative motion at this particular modulus. Thus, for a modulus of 3 × 10^9 (log E = 9.5) no slowing down becomes observable until the ion concentration reaches *ca.* 3%, corresponding to 30–40 styrene units between ions. By contrast for a modulus 10^8, the slowing commences at *ca.* 1.5%, corresponding to *ca.* 60–70 styrene units between ions. The slowing down of the diffusional relaxation mechanism will be described further in the Discussion section.

It was found that in polymers of low molecular weight above 6 mol % time–temperature superposition was reestablished at temperature *ca.* $T = T_g + 60$. This is illustrated in Figure 10 for polymer 7.9(Na)l, which clearly indicates the failure of time–temperature superposition up to 180° and its applicability above that temperature. Phenomena of this type were not observed in any polymer of high molecular weight. This will also be discussed in the last section.

Finally, the 10-sec moduli (E_{10}) for samples of different ion concentration obtained in stress relaxation experiments are plotted as a function of temperature in Figure 11, showing the increase of T_g with increasing ion concentration and also the enhanced rubber-like plateaus. The molecular weight effect also becomes quite apparent if one compares the samples 3.8(Na)h and 3.7(Na)l (curves 5 and 6).

E. Water Uptake. The results of the water uptake experiments, shown in Figure 12, illustrate the different type of behavior encountered in those polymers containing more than *ca.* 6 mol % Na ("nonsuperposable") and those of lower ion concentration which obey time–temperature superposition.

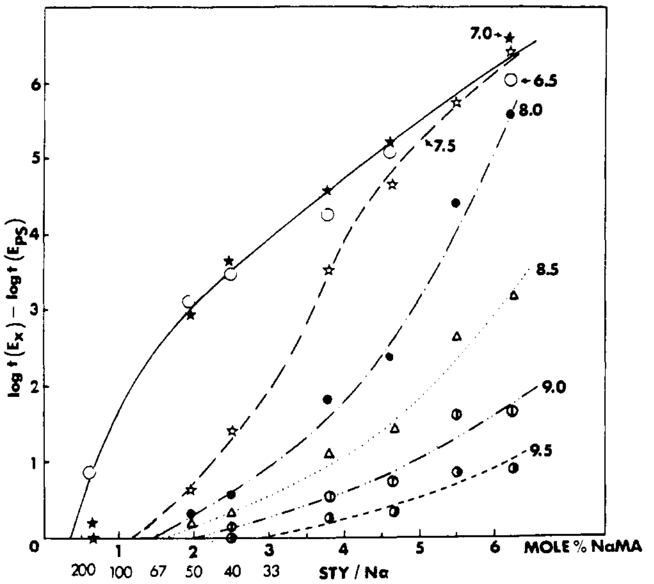

Figure 9. Slowing down of primary stress relaxation mechanism as a function of ion concentration. Numbers on each curve refer to the logarithm of values of modulus considered in slowing process, as described in the text.

In case of polymers containing less than 6 mol % ions, equilibrium swelling was obviously reached after *ca.* 300 hr, and the polymers contain *ca.* 1 H_2O molecule/Na ion. The polymers containing more than 6 mol % Na show a much higher water content, and some of the samples probably do not reach equilibrium even after 4000 hr.

III. Discussion

The simplest way of interpreting the data presented in the previous section is by postulating that below 6% the ions form simple multiplets which act as transient cross-links and slow down the primary relaxation mechanism, while above that concentration cluster formation is observed, which bears many of the characteristics of microphase separation. In this section the data will be interpreted with this postulate in mind, and the most important consequences will be discussed. The first part of the discussion will be devoted to a justification of the postulates regarding the state of aggregation. The second will concern itself with the relations between polymer morphology and viscoelastic properties above the critical ion concentration, in other words, with the effect of ionic clusters and with their structure. The third will pursue in some detail the slowing down of the primary diffusional relaxation mechanism by the presence of simple ionic multiplets in the region of low ion concentration.

A. State of Ion Aggregation. Figures 3, 4, and 11 provide the most clear-cut rheological justification for the existence of some type of ionic aggregates in the material. The presence of a secondary inflection point in the relaxation modulus (Figure 3) which correlates with the ion concentration cannot be interpreted as anything but some type of temporary cross-linking or microphase separation.

In spite of the drastic change in some of the material properties at 6 mol % salt, notably the values of C_1 and C_2 (see Table II), no such change occurs in the value of the upper inflection point. The reason for this is not clear, but may well be related to the fact that the concentration of clusters builds up only gradually as the 6% point is exceeded; thus, no drastic discontinuities are to be expected. Figure 11 bears all of the hallmarks of a system of polymers of increasing cross-link density, at least at low ion concentrations. At high ion concentrations these curves strongly resemble an incompatible polyblend system.[35]

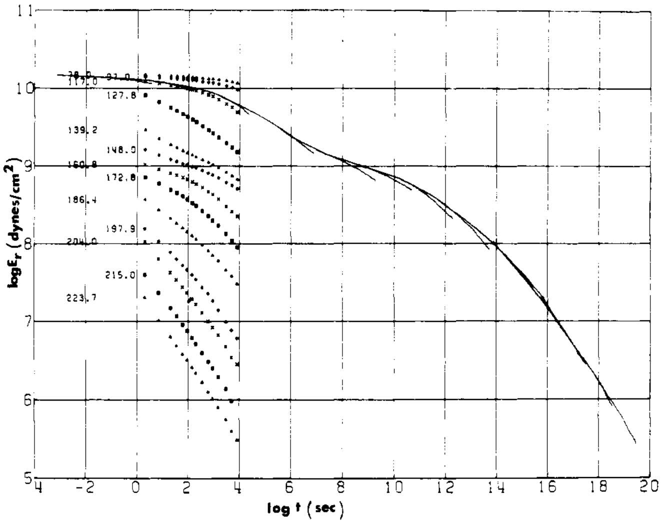

Figure 10. Original stress relaxation curves and attempted master curve for copolymer 7.9(Na)l $T_{ref} = T_g$.

The fact that time–temperature superposition is obeyed below 6% whereas it is not above that point, the fact that WLF parameters differ considerably (Figure 7 and Table II) and that results of water uptake experiments are also different in these two regions suggests that the morphology of the ionic aggregates is quite different. Furthermore X-ray diffraction experiments (to be published separately) indicate that above 6 mol % Cs salt new scattering centers appear with periodicities of 70–80 Å, further reinforcing the concept of microphase separation in that region. Finally the fact that up to *ca.* 6 mol % salt the observed upper inflection points on the stress relaxation master curves agree within a factor of two with values calculated from the simplest theory of rubber elasticity, suggests that simple temporary cross-links are present in that concentration region.

B. Nature of Clusters and Their Effect. 1. Structure of Clusters. In addition to the rheological evidence, the most striking indication for the existence of clusters comes from X-ray evidence. Unlike the ethylene ionomers, no crystallinity is present in styrene copolymers so that the observed periodicities from 70 to 80 Å for materials above 6 mol % can be assigned unambiguously to a new phase consisting mostly of the ionic material, *i.e.*, the ionic clusters.

The presence of ionic clusters has been mentioned by several investigators[6-10] and has also been treated theoretically.[11] From the periodicity found in the styrene iononomers (7–10% salt), we can conclude that if all the ions were incorporated into the clusters, each cluster would contain approximately 150–300 ion pairs. However, it is highly probable that a considerable fraction of ion pairs is present outside of the clusters. First, the intercluster distance of 70 Å is considerably larger than that of the fully stretched segment between ionic groups. Thus, unless all sequential ion pairs along any chain are incorporated into the same cluster, which is unlikely, a substantial fraction of the ionic material must be present between the clusters. Another line of evidence that leads to the same conclusion is provided by the glass transition behavior of the material. As is seen in Figure 1 the glass transition temperature increases continuously with increasing ion concentration over the entire range studied. If all the ions are

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(35) See ref 18, p 82.

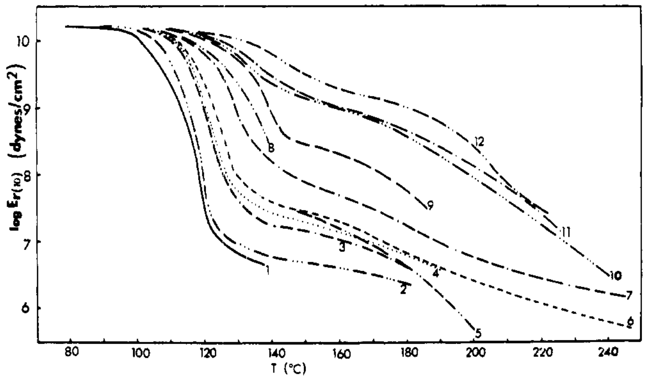

Figure 11. 10-sec modulus *vs.* temperature for samples of different ion concentration: curve 1, PS; 2, 0.6(Na)h; 3, 1.9(Na)h; 4, 2.5(Na)h; 5, 3.7(Na)l; 6, 3.8(Na)h; 7, 4.6(Na)h; 8, 5.5(Na)l; 9, 6.2(Na)h; 10, 7.9(Na)l; 11, 7.7(Na)m; 12, 9.7(Na)h.

contained in the clusters, then all we should observe is one value of T_g for the polystyrene phase (independent of the ion concentration) and another for the ionic phase. This is obviously not the case.

In a previous theoretical discussion[11] it was shown that multiplets (*i.e.*, structures containing ionic material exclusively) could have maximum sizes of only *ca.* 8–10 ion pairs unless unusual structural features are present. Since there is no evidence for such unusual features, we must assume that the cluster of 150–300 ion pairs consists of large number of multiplets of anywhere from 2 to 10 ion pairs per multiplet. The multiplets in turn must be separated from each other by organic material, so that the clusters contain both ionic and organic regions. The organic phase by contrast contains only a small percentage of ions.

2. **Time–Temperature Superposition.** As was pointed out before, there are some ion pairs present in the organic phase and they serve to slow down the primary relaxation mechanism. The temperature dependence of this process is given by the WLF relation. On the other hand, the relaxation processes occuring within the cluster are undoubtedly much more complex. It might be possible to regard the cluster perhaps as a filler particle, the structure of which is continuously changing, with some ions leaving and others entering. The temperature dependence of this later process is likely to be quite different from that of the primary diffusional mechanism; therefore, time–temperature superposition is not likely to hold.

As Figure 10 shows, time–temperature superposition is reestablished above 180° for low molecular weight samples above 6 mol % ions. This most probably indicates that the cluster lifetimes at that temperature are very much shorter than the relaxation times due to the retarded polymer motions; the former therefore do not contribute appreciably to the relaxation. The reestablishment of time–temperature superposition is not observed at high molecular weights, suggesting that even if the residence time of any one ion pair in a cluster is very short, a chain of very high molecular weight has so many ion pairs that the effect of clusters is not dissipated until presumably very much higher temperatures.

3. **Glass Transition.** In one considers curve 12 of Figure 11, *i.e.*, the modulus–temperature plot for the sample containing 9.7% NaMA one finds that the curve looks very much like that for a phase separated material with the T_g's of two phases being approximately 130 and 180°, respectively. Given that the T_g of polystyrene is *ca.* 100°, a knowledge of the T_g of poly(NaMA) would allow a very approximate calculation of the composition of two phases.

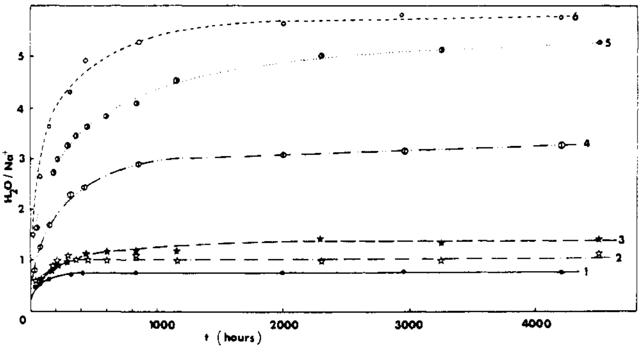

Figure 12. Number of water molecules per sodium ion absorbed by polymer as a function of time: curve 1, 3.7(Na)l; 2, 1.9(Na)h; 3, 5.5(Na)l; 4, 7.9(Na)l; 5, 9.7(Na)h; 6, 9.1(Na)m.

Otocka estimates the T_g of poly(NaMA) to be approximately 310°.[12] Another estimate can be obtained by taking the value for poly(sodium acrylate), (250°, ref 36) and adding approximately 100° due to the presence of the methyl group. This difference is the same as that between acrylic acid and methacrylic acid.[36] Thus 400° seems to be a reasonable upper limit for the T_g of poly(NaMA).

Using the equation[37]

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

we find that the composition of the first phase is 19 mol % NaMA while that of the second phase is 44 mol %. Using any of the other common equations for the T_g of copolymers, even higher NaMA contents would be obtained. These results are patently unreasonable if one recalls that the total NaMA content is 9.7 mol %. Thus we see that the simple copolymer equations are inapplicable in this case, which further confirms that one is dealing with a material the structure of which is quite different from that of a random copolymer without phase separation.

It might be more useful to regard the material of low T_g as a cross-linked copolymer with a large $\mathrm{d}T_g/\mathrm{d}C$ due to the high cross-linking efficiency of the ions. No detailed explanation can at this time be given for the high T_g of the clusters since their detailed geometry is unknown.

It is worth noting at this time that the thermal diffusivity change accompanying the upper T_g is so small that it is below the limit of detectability of DSC runs. It is, however, clearly visible in tan δ experiments as will be shown in a subsequent publication.

4. **Water Uptake.** The water uptake experiments yield results which are consistent with this model. While dispersed ionic multiplets in the region below 6 mol % salt take only *ca.* 1 water molecule/sodium ion, a value indicating that a very limited number of binding sites is available in a predominantly hydrocarbon environment of low dielectric constant, the presence of ionic clusters creates regions of high dielectric constant which are favorable for water.

5. **Comparison with Previous Studies of Clustered Ionic Systems.** It is interesting to note that our results on modulus temperature curves bear a striking resemblance to those of Moacanin and Cuddihy[38] indicating that even in a system consisting of a low molecular weight salt dissolved in a nonionic polar organic polymer (poly(propyl-

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(36) A. Eisenberg, H. Matsuura, and T. Yokoyama, *J. Polym. Sci., Part A-2*, 9, 2131 (1971).

(37) T. G. Fox, *Bull. Amer. Phys. Soc.*, 1, 3, 123 (1956).

(38) J. Moacanin and E. F. Cuddihy, *J. Polym. Sci., Part C*, 14, 313 (1966).

Table III

Log E (dyn cm^{-2})	Segment Length (No. of Monomer Units)
9.5	30
9.0	50
8.5	60
8.0	70
7.5	80
7.0	170
6.5	300

ene oxide) and $LiClO_4$) microphase separation seems to be encountered. This suggests that in the above system the cation is bound so strongly to the polymer that it behaves like an ion-containing polymer in which the ions are bound to the chain.

McKnight *et al.*[6] studied the ethylene-sodium acrylate copolymers and found ion clustering even at low ion concentrations (*i.e.*, below 6 mol %). This seemingly contradicts our results, but in view of the partial crystallinity of their copolymers, it might be expected that the ion concentration in the amorphous portion of the material is actually higher than the overall concentration because of the exclusion of the ions from the crystalline phase.

C. Dispersed Ionic Multiplets and Their Effects. The fact that below 6 mol % the WLF equation is generally applicable suggests that the relaxation mechanism is quite similar to that in normal polymers. However, it is also clear that the presence of ions slows down the diffusional mechanism, the slowing down increasing with increasing ion concentration and the size of a moving segment. Thus it would seem that a certain degree of cooperation in the ion hopping process is essential. This also explains the broadening of the distribution.

The lifetime of the ionic cross-links is finite. The multiplets can dissociate, the ion pairs can diffuse and new temporary multiplets may be formed. This would be expected to lead to a partial relaxation of stress if the sample is deformed.

The WLF parameters C_1 and C_2 were found to be increasing with increasing ion concentrations (Table II) implying that both free volume at T_g and expansion coefficient decrease. This seems intuitively correct since the presence of additional electrostatic attraction increases the cohesion of the material.

In the final part of this section an attempt is made to evaluate semiquantitatively the effect of ions on the rate of chain slippage. Figure 9 shows the slowing down of the relaxation as a function of ion concentration and modulus. The detailed description of how this figure was obtained was given in part E of the Experimental Section.

As one can see the effect is not a simple one; it even appears as if two mechanisms might be operating, one at low modulus, and another at high modulus values. Any speculation along these lines is probably not justifiable, therefore we limit ourselves in this discussion to the relatively simple case in which only one ion pair is attached to the moving segment of a polymer chain. It is assumed that the slowing down first appears at the ion concentration at which the length of the moving segment becomes longer than the average interion distance. This manifests itself as the finite intercepts on the concentration axis (Figure 9) of the lines showing the slowing down for different values of modulus between $10^{9.5}$ and $10^{6.5}$ dyn cm^{-2}. It is assumed that by this procedure the average length of the segment which is involved in reducing the modulus to a particular value is established. Thus, for a modulus of $10^{9.5}$ dyn cm^{-2}, the slowing down becomes apparent at *ca.* 3 mol % of the ions, implying that in order to reach a modulus of $10^{9.5}$, a cooperative motion of *ca.* 33 units is required. Table III shows the length of the moving segment needed to reduce the modulus to a particular value.

At this particular value of the modulus and the corresponding ion concentration, the average interion distance and the length of the moving segment are just equal; therefore, a rearrangement of ion multiplets is not required for the relaxation of the segment. Therefore in relaxing down to this modulus value, the presence of ions does not cause any deviation from the behavior of pure polystyrene. However, if, on the average, more than one ion is attached to the moving segment, it will manifest itself in a slowing down of the relaxation because this ion, being incorporated into a multiplet, has to be released from the multiplet to allow the segment to move and contribute to the overall relaxation.

Let us here consider the case of putting one additional ion pair onto each moving segment and see by how much the relaxation is slowed down. This can be estimated by doubling the ion concentration and observing the slowing down at the same value of the modulus (same length of moving segment) (Figure 9). This procedure is illustrated below. It can be seen from Figure 9, that if we choose, for example, a modulus of $10^{9.5}$ dyn/cm^2, slowing down becomes apparent at a concentration of *ca.* 3 mol %, corresponding to a moving segment of *ca.* 33 monomer units. If the ion concentration is then doubled to 6 mol % and the length of moving segment is unchanged ($\log E = 9.5$), we can see that the slowing down is equal *ca.* 10 ($\log t = 1$). If this procedure is repeated for several modulus values it can be seen that the slowing down is equal to 1 ± 0.3 log time units. This implies that by putting one sodium methacrylate group on a moving segment of polystyrene the rate of chain diffusion is slowed down *ca.* ten times. An attempt to repeat this procedure for more than one ion pair segment was unseccessful since the rate of slowing down becomes in addition also a function of the modulus.

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