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Dielectric Properties of Styrene–Sodium Methacrylate Copolymers in the Glass Transition Region

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ABSTRACT: Dielectric loss measurements have been conducted on high molecular weight copolymers containing 2.0, 3.9, 5.1, 6.5, 8.1, and 9.0 mol % of sodium methacrylate over a temperature range of ca. 100–200 °C at frequencies from 10^1 to 10^4 Hz. After subtraction of the large conductivity loss, two overlapping loss tangent peaks are observed whose relative heights depend on composition and measurement frequency and whose positions are in agreement with torsion pendulum data. The dielectric data indicate that although clustering of multiplets occurs at all compositions, it is not clearly manifested until the number of ions in clustered multiplets exceeds the number of ions in isolated multiplets in the surrounding matrix, which occurs at compositions containing more than ca. 5% salt. There is evidence for cluster dissociation at higher temperatures, and it is shown that this may account for the unusually high values of the WLF parameters C_1 and C_2 and other rheological anomalies.

In the last decade or so there has been a steadily increasing interest in copolymers containing an ionic component. Among the systems which have received considerable attention are the copolymers based on ethylene,[1-13] rubbery materials,[13-23] and styrene.[24-29] The literature on these ion-containing polymers is now quite extensive, two review articles[30,31] and two books[32,33] having been devoted to the field; accordingly, only that work which is of direct relevance to the present investigation will be discussed here.

Copolymers of styrene and methacrylic acid, and the corresponding salts of several ions, have received extensive attention. Preliminary stress relaxation measurements have been made on both neutralized and acidic forms of these materials by Erdi and Morawetz[24] and Fitzgerald and Nielson.[25] The result of principal interest was the observed slow down in the rate of relaxation in going from the acid, to the sodium salt, to the barium salt. Similar results were obtained by Eisenberg, Navratil, and others as part of their comprehensive study of the mechanical and other properties of these materials. The latter included studies of stress relaxation,[26-28] dynamic mechanical relaxation,[29] melt viscosity,[34] x-ray diffraction,[29] and water uptake,[26] principally of the sodium salts. Their results may be summarized as follows:

(1) In the glass transition region the stress relaxation master curves are very broad, as they are for most ion-containing polymers.[33] It has been estimated[26] that the addition of one sodium methacrylate group to a polystyrene segment slows down the rate of chain diffusion by a factor of ca. 10.

(2) There are distinct changes in many of the properties at 5–6% NaMA. At ion concentrations below this figure time–temperature superposition is observed[26] in stress relaxation, an x-ray pattern typical of a completely amorphous material is observed,[29] and water saturation occurs at ca. 1 H_2O per ion pair.[26] On the other hand, at concentrations greater than ca. 6% time–temperature superposition is not observed,[26] an extra small angle x-ray peak corresponding to a Bragg distance of ca. 70 Å is observed,[29] and water saturation occurs at more than 3 H_2O per Na^+.[26]

(3) All of the observed changes in properties at ca. 6% NaMA are consistent with the onset of the clustering of ions as opposed to small multiplet formation, a theoretical account of which has been given before.[35]

(4) The dynamic mechanical loss tangent exhibits two peaks in the glass transition region[29] which are attributed to the glass transitions of the clustered material and the matrix. The intensity of the lower temperature relaxation is a weak function of composition, in contrast to the high temperature relaxation which increases steadily in intensity with increasing ion content.

(5) The stress relaxation master curves exhibit a pronounced inflection point at temperatures slightly above the glass transition region,[27] with the modulus value at the inflection point increasing steadily with ion content.

There have been no dielectric studies made on styrene ionomers. Dielectric studies have been made, however, on partially neutralized copolymers of methacrylic acid and ethylene by Read et al.[4] and by Phillips and MacKnight[8] as part of a comprehensive study of those materials. Two peaks were observed in the glass transition region, corresponding to ionic domains and the surrounding polyethylene matrix. A sub-T_g relaxation due to water, and another attributed to methylene sequences in the amorphous phase, were also reported.[4] These ethylene ionomers are partially crystalline, in contrast to the corresponding styrene copolymers which are completely amorphous.

The present study was undertaken with the purpose of establishing the dielectric properties of styrene–sodium methacrylate (NaMA) copolymers and to correlate these with the anomalous mechanical properties. The dielectric manifestations of the clustering phenomenon were of particular interest. To this end, dielectric measurements have been made in the glass transition region for high molecular weight styrene–sodium methacrylate copolymers, containing 0–9% salt, in the frequency range 10^1–2×10^4 Hz.

Experimental Section

The samples were kindly prepared by D. Holden and D. Nonnenman using previously described methods.[27] Samples were compression

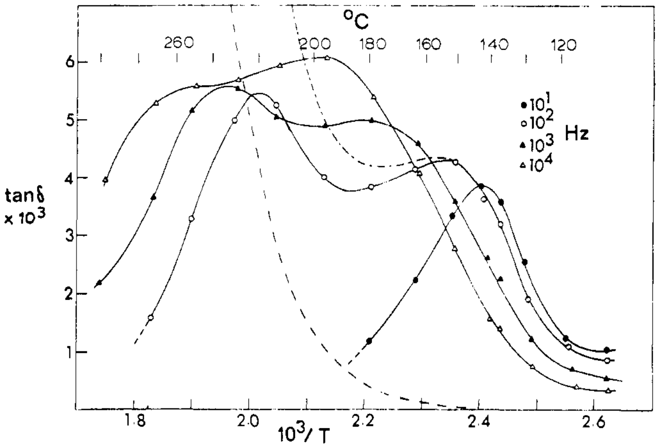

Figure 1. Typical dielectric loss tangents vs. reciprocal temperature for 6.5% NaMA at the indicated frequencies, after subtraction of the conductivity contribution. Also shown are the total observed loss (– – –) and conductivity loss (- - -) at 10^2 Hz. High-temperature losses at 10^1 Hz are not shown because of dominant conductivity losses (see text).

molded into disks of ca. 1-cm diameter and ca. 0.05-cm thickness, and aluminum foil electrodes were pressed onto the samples during the molding procedure. The dielectric cell was of the three-terminal type, with stainless steel electrodes contained in a brass cup to reduce thermal gradients. The cell could be evacuated and used up to ca. 300 °C, attainment of higher temperatures being prevented by thermal degradation of the Teflon insulation. The samples were inserted between the spring loaded freshly sanded electrodes, and the temperature was raised to above the softening temperature (ca. 160 °C) under vacuum, to ensure a close contact of the aluminum foil with the electrodes. This procedure was essential for noise-free data (particularly at low frequencies), but because of physical distortions arising from the softening process the cell constant could not be determined directly. Also, the cell constant changed continuously in the glass transition region, so that only loss tangent data could be accurately measured. However, the room temperature dielectric constants could be evaluated in separate experiments to within ca. ±5%, and these were used to determine the nominal cell constant for each experimental run. The apparent dielectric constant changed by ca. 10% in the glass transition region for all compositions, and thus the loss tangent data reflect the actual loss to within ±10%.

Apart from a water-dependent relaxation, which will be described separately,[36] no sub-T_g dielectric relaxations were found above −196 °C at frequencies up to 2×10^4 Hz. The water peak invariably disappeared after the sample was heated to 160 °C under vacuum and kept there for an hour or longer; it can therefore be asserted with some confidence that water does not contribute to the observed losses in the glass transition region.

Measurements were made under vacuum from ca. 80 °C to ca. 250 °C in most cases, although at the higher ion concentrations the upper temperature limit could be extended to ca. 300 °C without serious physical distortion of the sample. Evacuation also prevented degradation by oxidation, and the samples were not visibly degraded at the end of any of the experiments. Data on the 2% sample were not reliable above ca. 160 °C because of rapid softening.

A General Radio 1621 capacitance measuring system was used at measuring frequencies ranging from 10^1 to 2×10^4 Hz at intervals of 1, 2, 5, and 10 per decade. Samples containing 2.0, 3.9, 5.1, 6.5, 8.1, and 9.0 mol % sodium methacrylate were studied.

Results

To within a scatter of ~10%, the room temperature dielectric constant increased from ca. 2.7 to ca. 3.2 as the concentration of NaMA increased from 2 to 9%. These data are in accord with the literature value of the dielectric constant of atactic polystyrene, 2.85.[37] The changes with frequency were ca. 0.1% per decade.

The sub-$T_g(\gamma)$ relaxation for polystyrene, which occurs at −170 °C at 10^4 Hz,[37] was not observed. This is in keeping with recent data[38,39] which demonstrate that the dielectric activity of this relaxation is due to oxygen which is weakly bonded to the benzene rings, since evacuation at 160 °C would almost certainly remove this oxygen. The dielectric loss tangent at −100 °C and 10^3 Hz for the dry 9% sample (3.8×10^{-4}) is in good agreement with the corresponding loss observed under vacuum for polystyrene (4.2×10^{-4}),[39] compared with 6.8×10^{-4} for oxygen equilibrated polystyrene.[39]

In the glass transition region the conductivity losses were high and completely dominated the lowest frequency data. Fortunately the limiting low-frequency conductivity could be evaluated directly from the data at the highest temperatures (to within ca. 10%) from the low-frequency invariant values, or from short extrapolations to lower frequencies, and could be subtracted out. The conductivity determined in this way was found to exhibit the Arrhenius temperature dependence for all the compositions studied (except 2%, for which the conductivity could not be measured), over a necessarily small temperature range (ca. 100 °C). For the purposes of the subtraction procedure this temperature dependence was assumed also to be valid at the lower temperatures and the conductivity contribution calculated and subtracted out for all data points. The residual dielectric loss, ϵ'', was calculated from the observed loss ϵ''_{obsd} and the zero-frequency conductivity, σ_0, from the relation

$$\epsilon'' = \epsilon''_{\text{obsd}} - (\sigma_0/e_0\omega) \qquad (1)$$

where e_0 is the permitivity of free space and ω is the angular frequency.

The observed conductivity activation energies are independent of composition at 26 ± 2 kcal mol^{-1} (see below). At any given temperature the conductivity increases uniformly with increasing salt concentration, the ratio of the conductivities of the 9 and 3.9% samples being ca. 3.

After subtraction of the conductivity contribution, two well-defined peaks are observed at all frequencies greater than ca. 5×10^1 Hz for all compositions except 2%. Representative loss tangent data are shown in Figure 1 as a function of reciprocal temperature for the 6.5% composition at the indicated frequencies; intermediate frequencies are omitted for clarity. To indicate the magnitude of the conductivity contribution, the observed total loss and conductivity loss at 10^2 Hz are also shown. At 10^1 Hz only one peak is observed, because at this frequency the conductivity contribution completely dominates the high-temperature losses. For the 9% composition the conductivity loss tended to mask the high-temperature peak up to ca. 10^2 Hz, resulting in larger uncertainties in the residual loss data at those frequencies. On the other hand at the highest frequencies the two residual peaks merge together. Generally speaking, it was found that the best overall resolution occurred at ca. 10^2 Hz, since this frequency is high enough for the conductivity contribution to be acceptably small at higher temperatures and low enough for a satisfactory resolution of the two residual peaks to be achieved. For the 8 and 9% compositions, however, the best resolution occurred at ca. 10^3 Hz. The loss tangent data at 10^2 Hz for all the compositions studied are shown in Figure 2, from which several qualitative trends are discernable. Both peaks move to higher temperatures as the ion concentration increases. Also, the heights of the low-temperature peak are essentially composition invariant at ion contents greater than ca. 4–5%, whereas the high-temperature peak height increases steadily with increasing ion concentration.

These and other composition variations are illustrated in Figure 3. The heights of each peak, and their sum, are plotted in Figure 3A, and the composition dependences of the activation energies for the two dielectric losses and for the conductivity are shown in Figure 3B. A representative Arrhenius plot, for the 6.5% sample, is given in the inset.

The peak heights are of some importance, and some com-

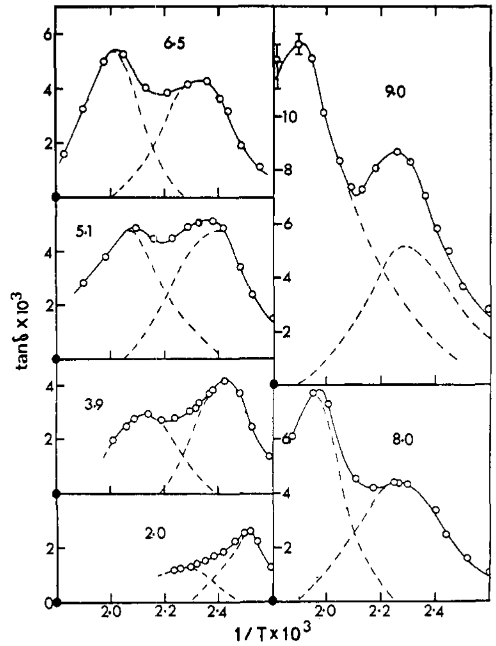

Figure 2. Loss tangents at 10^2 Hz for the compositions studied. Numbers refer to mol % sodium methacrylate. The dotted lines illustrate the resolution into two symmetric peaks (see text).

ments on how they were determined from the data are in order. For the samples containing 3.9–8% NaMA, peak overlap at 10^2 Hz does affect the observed peak heights significantly. For the 2% composition, however, the high-temperature peak occurs only as a shoulder and its height was estimated by assuming the low-temperature peak to be symmetric (dotted lines, Figure 2). The datum in Figure 3A for this composition is thus the *most reasonable* maximum height. For the 9% composition, the reverse situation occurred and it was the low-temperature peak which appeared as a shoulder. In this case, it was difficult to estimate the peak height accurately because only half of the high-temperature peak was observed, and in addition the uncertainties in these high-temperature data were increased because of the greater conductivity background. Although the latter is much smaller at higher frequencies, the increased degree of peak overlap did not permit any reasonable extrapolation of the peak heights from high to low frequencies. Accordingly, the data shown for the 9% composition have relatively large uncertainties, but it is clear that these do not obscure the general trends.

The total integrated intensities of the residual peaks at 10^2 Hz could be estimated for all compositions except 9%. This was accomplished by resolving the loss spectra (plotted as ϵ'' vs. $1/T$) into two symmetric components (as indicated by the dotted lines in Figure 2 for the corresponding tan δ plots) and obtaining the dielectric strength and effective dipole moment for each component from the relations

$$(\epsilon'_0 - \epsilon'_\infty)_{T_{\max}} = \frac{2}{\pi R}\left\langle\frac{1}{E_A}\right\rangle^{-1}\int_0^\infty \epsilon''\, d\left(\frac{1}{T}\right) \tag{2}$$

$$(\epsilon'_0 + \epsilon'_\infty)_{T_{\max}} = 2\epsilon'_{T_{\max}} \tag{3}$$

$$N\mu^2 = \frac{3kT_{\max}}{4\pi}\left(\frac{2\epsilon'_0 + \epsilon_\infty}{3\epsilon_0}\right)\left(\frac{3}{2 + \epsilon'_\infty}\right)^2(\epsilon'_0 - \epsilon'_\infty) \tag{4}$$

In these equations ϵ'_0 and ϵ'_∞ are the limiting low and high frequency values of the relative permitivity at the temperature $T_{\max}$, E_A is the activation energy for the loss process, R is the gas constant, k is Boltzmann's constant, N is the number density of methacrylate groups of dipole moment μ, and $\langle\ \rangle$ denotes an average value. Equation 2 is due to Read and Williams,[40] eq 3 expresses the assumption that the loss spectrum is symmetric, and eq 4 is the Onsager equation.[41]

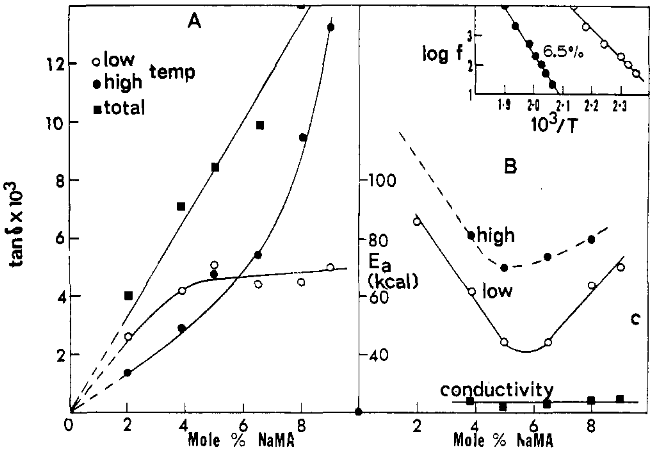

Figure 3. Composition dependences for loss parameters: (A) loss tangent peak heights for the high- and low-temperature relaxations, and their sum; (B) activation energies for dielectric loss and conductivity processes. Inset: Typical Arrhenius plots for 6.5% composition.

The composition dependences of $N\mu^2$ for the two relaxations were found to be the same as those of the peak heights. This indicates that the peak heights give a good indication of the overall intensity, despite the complications of peak overlap and systematic changes in both peak width and $T_{\max}$. The sum of the two values of $N\mu^2$ was used to calculate μ at each composition. For all compositions for which $N\mu^2$ could be evaluated (except 8%), the dipole moment was calculated to be 1.7 ± 0.1 D. This is the same as the COOH group[42] but three or four times smaller than the estimated 6–7 D for a COO^-Na^+ ion pair. This could be a reflection either of multiplet formation or of incomplete relaxation of an ion pair in the glass transition region.

For the 8% composition a value of 2.1 ± 0.1 D was obtained. This discrepancy of ca. 15% in μ is not considered significant, however, since it reflects a combined uncertainty of 30% in the activation energy, the relative permitivity, resolution of the spectrum into two components, the area of the resolved peaks, and the estimated conductivity contribution (which is ca. 50% of the observed total loss at the high temperature peak maximum). Dipole moments could also be evaluated for the 3.9, 5.0, and 6.5% compositions from data taken at 10^3 Hz and were found to be within 10–15% of the 10^2 Hz values. A thorough search was made for a Maxwell–Wagner absorption which might result from highly conducting clusters immersed in a matrix of relatively low conductivity. None was found, indicating that either the clusters are not sufficiently defined for the effect to occur or that their conductivity is too low to give the effect at the measuring frequencies. It is also possible that the effect is present but is hidden under the glass transition dielectric transition absorptions. The latter can be discounted as Maxwell–Wagner absorptions, since their activation energies do not correlate with the activation energy for conductivity (Figure 3b). The glass transition absorptions are also much broader than that observed for Maxwell–Wagner processes.[43,44]

Discussion

Composition Dependence of Peak Positions. The movement of both peaks to higher temperatures with increasing ion contents is illustrated in Figure 4A for data taken at 10^2 Hz. To facilitate comparison of these dielectric data with the dynamic mechanical data reported earlier[29] the dielectric peak positions have been extrapolated to 10^{-1} Hz, the

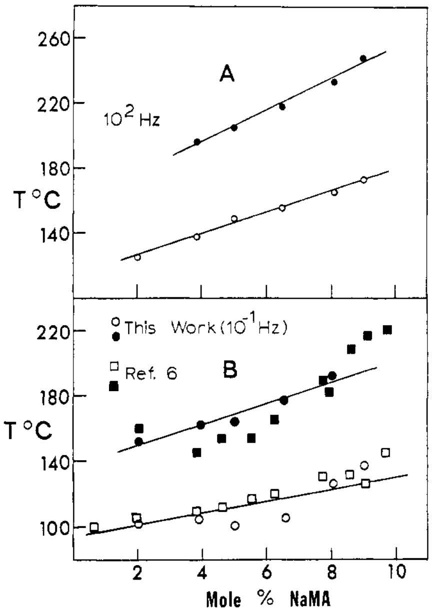

Figure 4. (A) Peak positions at 10^2 Hz as a function of composition. (B) Extrapolated peak positions at 10^{-1} Hz and torsion pendulum peak positions from ref 29.

approximate frequency at which the torsion pendulum operated at these temperatures. A comparison of the two sets of data is shown in Figure 4B. In view of the random errors in each set of data, the systematic errors introduced by the strong temperature dependence of the torsion pendulum frequency in the glass transition region, and the separate sample preparations, the agreement is considered acceptable. There is therefore no doubt that the same two relaxations are being monitored by the two techniques. Because of the lower cohesive energies associated with materials of lower ion concentration, the low-temperature peak is attributed to regions of low ion concentration, and the higher temperature relaxation is attributed to regions of relatively high ion concentration. The latter will be referred to as clusters, and the former as the matrix, in anticipation of the conclusions which are discussed below. This phenomenon corresponds closely to that observed in the ethylene ionomers,[4,8] discussed in the introductory section. In the case of the styrene ionomers, however, the dielectric intensity of the matrix is relatively high, compared with that of amorphous polyethylene, and this is attributed to the presence of isolated multiplets. The latter has also been inferred from the stress relaxation data.[27]

Composition Dependence of Peak Heights and Intensities. The peak heights at 10^2 (Figure 3A), 10^3, and 10^4 Hz and the (limited number of) integrated intensities at 10^2 and 10^3 Hz all exhibit the same trends. For convenience, therefore, these quantities will henceforth be referred to collectively as the dielectric strengths.

The low-temperature loss process is characterized by a dielectric strength which increases up to ca. 5% NaMA and remains more or less independent of composition at higher total ion concentrations (Figure 3). It was found that the break occurs at ca. 5% at all measuring frequencies above ~50 Hz, and this indicates that the break is not some artifact of the composition dependence of the peak position. Thus it appears that the ionically dilute matrix, with which the low-temperature relaxation is associated, becomes "saturated" at total salt contents of ca. 5% and that additional ionic material is taken up by the clusters. The latter is reflected in the greater rate of increase in dielectric strength of the high-temperature peak above ca. 6% (Figure 3A).

Table I
Composition Dependences of Dielectric Strength Parameters

Composition, mol % salt	2	3.9	5.1	6.5	8	9
Observed high-temperature tan $\delta_{max} \times 10^3$	1.4	2.9	4.8	5.4	9.5	12.6
Observed low-temperature tan $\delta_{max} \times 10^3$ (matrix)	2.5	4.2	5.1	4.4	4.4	5.0
Matrix tan $\delta_{max} \times 10^3$ (PS subtracted)	0	1.8	2.7	2.1	2.1	2.7
Observed sum tan $\delta_{max} \times 10^3$	3.9	7.1	9.9	9.8	13.9	17.6
Sum of tan $\delta_{max} \times 10^3$ (PS subtracted)	1.4	4.7	7.5	7.5	11.6	15.3
From obsd peak heights						
Mol % in matrix	1.3	2.3	2.7	2.9	2.5	2.6
Mol % in clusters	0.7	1.6	2.4	3.6	5.5	6.4
From peak heights after PS subtraction						
Mol % in matrix	0	1.5	1.8	1.8	1.4	1.6
Mol % in clusters	2	2.4	3.3	4.7	6.6	7.4

The occurrence of matrix saturation is most clearly demonstrated by expressing the relative heights of the loss tangent peaks at 10^2 Hz in terms of how the total ion concentration is divided between the clustered and unclustered regions. This is readily evaluated, since the sum of the two loss tangent peak heights is strongly correlated with the total salt content (correlation coefficient 0.975). Thus the height of the high-temperature peak can be related directly to the percentage of ions present as clustered multiplets, while the low-temperature peak height reflects both the percentage of ions present as isolated multiplets and the dielectric loss of polystyrene in the glass transition region. Assuming the latter to be proportional to the percentage of polystyrene, and taking $\tan \delta = 2.5 \times 10^{-3}$ for pure polystyrene, the contribution of the isolated multiplets to the observed loss can be estimated. The results are included in Table I. In order to assess roughly the uncertainties in these estimates, a second set of figures was calculated from the observed peak heights from which the polystyrene contribution was not subtracted and these are also included in Table I for comparison. It is apparent that saturation of the matrix at total ion contents in excess of 5% is reflected in both sets of figures. The differences between the absolute values for the two sets of data illustrate just one source of uncertainty in these figures and emphasize clearly that the actual numbers given in Table I should not be taken as anything more than illustrating the general trends.

For all given compositions, apart from 2%, both peak heights increase with increasing measuring frequency, i.e., with increasing T_{max}. This is probably a reflection of the narrowing in peak width, since the integrated intensities are comparable, although this cannot be observed directly because of the increasing overlap with increasing frequency. In addition to this, however, the *relative* strength of the two relaxations also changes systematically with increasing frequency, that of the low-temperature peak increasing more rapidly. This can be seen in the data plotted in Figure 1, for example. Although some of this may result from the accompanying increase in peak overlap, the fact that it is observed in every instance, in particular at 5 and 6.5% where peak overlap is minimal, suggests that the trend is real. This is consistent with the notion of clusters dissociating at higher temperatures and of the ion content of the matrix increasing correspondingly. Such a dissociation has also been suggested to account for the thermorheologically complex response of these materials.[26]

Composition Dependence of WLF Parameters. One of the most striking rheological changes which occur at about 5% NaMA is the rapid increase in the WLF parameters C_1 and C_2 with increasing ion content.[27] Both parameters increase by approximately the same factor, the correlation coefficient between C_1 and C_2 for compositions containing 0–9.7% salt being +0.99. It will now be shown that these features can be accounted for by cluster dissociation which increases the ion content of the matrix with increasing temperature and gives rise to an effectively temperature dependent glass transition temperature.

The WLF expression for the activation energy E_A is

$$E_A = RT^2C_1C_2(C_2 + T - T_g)^{-2} \tag{5}$$

The temperature dependence of T_g is introduced by inserting the expression

$$T_g = T_g^0 + a(T - T_g^0) \tag{6}$$

into eq 5, where T_g^0 is an independently evaluated glass temperature, usually determined from dilatometric or calorimetric measurements. The result is

$$E_A = RT^2C_1C_2(1 - a)^{-2}[C_2(1 - a)^{-1} + T - T_g^0]^{-2} \tag{7}$$

The experimentally observed values of E_A/RT^2 are a relatively weak function of $T - T_g^0$ and of the composition,[27] compared with C_1 and C_2 (see Table II). It is therefore clear from eq 7 that if the observed changes in C_1 and C_2 are due solely to an effectively temperature dependent T_g, then both parameters should increase by the same factor, $(1 - a)^{-1}$. Also, since T_g is not temperature dependent for polystyrene, it is possible to estimate $(1 - a)$ from the changes in C_1 and C_2 relative to polystyrene.

The composition dependences of C_1, C_2, a, and other parameters of interest are tabulated in Table II. The correlation between C_1 and C_2 is demonstrated by the small random variation in C_1/C_2 (±20%) compared with the large systematic changes in C_1 and C_2 separately (a factor of ~5). The variation in E_A/RT^2 is also random and relatively small (ca. ±35%). The values of "a" calculated from the observed increases in C_1 and C_2 relative to polystyrene are given in the last columns of Table II, respectively. The two values agree to within ±15% or better in most cases, an exception being a difference of ca. 30% for the lowest salt concentrations. The steady increase in "a" with increasing ion content is consistent with the corresponding increase in the number of ions released to the matrix for a given degree of cluster dissociation. At ca. 6% total ion content the increase in "a", C_1, and C_2 becomes more rapid, reflecting the more rapid increase in concentration of the clustered multiplets (Figure 3A). It can therefore be concluded that the observed changes in C_1 and C_2 with increasing ion content are primarily a direct reflection of cluster dissociation, which increases the ion content, and therefore the T_g, of the matrix with increasing temperature.

It is important to note that it is the temperature dependence of T_g, given by the parameter "a", which results in the observed changes in C_1 and C_2 and not a step increment in T_g at some temperature above the experimentally determined T_g^0. Insertion of the expression

$$T_g = T_g^0 + \Delta \tag{8}$$

into eq 5 and applying the same constraints on E_A/RT^2 as before results in C_2 *decreasing* by Δ and C_1 *increasing* by the factor $C_2^{PS}/(C_2^{PS} - \Delta)$. This result is clearly incompatible with the observed *positive* correlation between C_1 and C_2.

Activation Energies. The sharp minimum in the dielectric activation energies for both peaks at ca. 6% is quite striking, and is in marked contrast to the corresponding composition dependence of the conductivity activation energy (Figure 3B). It is not at all clear what this is due to. However, its occurrence in the composition region in which clustering begins to predominate, and in which the dielectric strengths of the clusters and matrix become comparable, is presumably not fortuitous. It is possible that localized stresses are set up by the mixing of clusters and matrix and that these are minimized when the total ion contents of each phase approach one another.

Table II

Composition, mol % of NaMa	T_g^0, °C	C_1	C_2	C_1/C_2	E_A/RT^2 for $T - T_g$ = 20	"a" from C_1/C_1^{PS}	C_2/C_2^{PS}
0	102	14	46	0.30	0.148	0	0
0.6	105	13	40	0.32	0.144		
1.9	109	19	71	0.27	0.163	0.26	0.35
2.5	110	19	71	0.27	0.163	0.26	0.35
3.8	112	23	73	0.31	0.194	0.39	0.37
4.6	114	24	73	0.31	0.194	0.39	0.37
6.2	116	47	227	0.21	0.175	0.70	0.80
7.7	118	60	240	0.25	0.213	0.77	0.81
9.7	130	66	300	0.22	0.193	0.79	0.85

Conductivity. Within experimental uncertainty, the conductivity increases linearly with increasing ion content. The uncertainty is quite large, different samples of the same composition giving conductivities differing by a factor of 2 or so in extreme cases. This is probably due to some type of impurity. However, it is emphasized that these differences were not reflected in the residual dielectric spectra, which were reproducible to ±10%.

Assuming all of the ions contribute to the conductivity, the average mobility is estimated to be ca. 2×10^{-14} cm^2 s^{-1} V^{-1} at 220 °C, for all compositions. The corresponding diffusion coefficient, calculated from the Nernst-Einstein equation, is ca. 10^{-15} cm^2 s^{-1} at this temperature. The room-temperature diffusion coefficient is estimated to be ca. 10^{-23} cm^2 s^{-1}, compared with ca. 10^{-9} for diffusing water in these materials.[45] Clearly, the water does not diffuse in association with the ions at room temperature.

The conductivity for the 9% sample at 310 °C is characterized by a single conductivity relaxation time, evidenced by the frequency invariance of the conductivity in the vicinity of the conductivity relaxation frequency f_σ[46] given by

$$f_\sigma = \sigma_0/\epsilon'_\infty e_0 \tag{9}$$

where σ_0 is the zero frequency specific conductivity, e_0 is the permitivity of space, and ϵ_∞ is the limiting high-frequency dielectric constant. (In the case of a single relaxation time ϵ'_∞ is the observed frequency independent dielectric constant in the vicinity of f_σ.[46]) The single relaxation time behavior, and the low activation energy for conductivity, suggest that the structural changes which occur at T_g do not contribute to the long-range ionic mobility, since structural relaxation in the glass transition region is characterized by a broad distribution of relaxation times and a large average activation energy.

In the stress relaxation experiments,[27] a secondary relaxation is observed at higher temperatures which has the hallmarks of a pure viscosity[47] and it is of interest to see how this viscosity is related to the conductivity. Although both reflect ion exchange,[48] the viscosity would be expected to be affected more by motion of the anions, since these are attached rigidly to the backbone, whereas the conductivity is determined by the more mobile ions, undoubtedly the cations in this case. The difference between anion and cation mobilities would then be expected to manifest itself as a difference in the average shear and conductivity relaxation times, $\langle\tau_s\rangle$ and $\langle\tau_\sigma\rangle$, respectively, given by[46,49]

$$\langle\tau_s\rangle = \eta_0/G_\infty \simeq t/D(t)G_\infty \tag{10}$$

$$\langle\tau_\sigma\rangle = e_0\epsilon'_\infty/\sigma_0 \tag{11}$$

where G_∞ is the limiting high frequency (glassy) shear modulus, η_0 is the zero frequency viscosity, and $D(t)$ is the shear compliance at time t. The shear relaxation time can be evaluated at 175 °C from previously reported data[47] as $t/D(t)G_\infty \simeq 10^4/10^{-8.5}10^{10.5} \simeq 10^2$ s, and this is to be compared with ca. 10^0 s for the conductivity relaxation time at the same temperature. These figures indicate that the conductivity is determined by sodium ions whose mobility is ca. 10^2 greater than the mobility of the anions, which is restricted by the cooperative motion of the chains. This difference also accounts for the single relaxation time behavior of the conductivity since the sodium ions move through a lattice which is frozen on the time scale of their motions and which, therefore, does not contribute to the sodium mobility. The activation energy for conductivity is accordingly composition invariant, since the changes in structural relaxation behavior which occur at ca. 5% NaMA, e.g., those responsible for the minima in dielectric activation energies, occur on a much slower time scale than the conductivity.

Summary and Conclusions

The dielectric data reported here confirm most of the earlier conjectures on the structure of these materials made on the basis of the mechanical properties. In addition, however, several new features can now be identified, such as the coexistence of clusters and multiplets at most concentrations, the occurrence of matrix saturation at 5–6% NaMA, and the occurrence of cluster dissociation. The picture of the structure and relaxation properties of these materials which emerges from the dielectric and mechanical data can be summarized by the following points:

(1) Multiplets and clusters appear to be present at all compositions studied here, since two peaks in the glass transition region are observed in both the dielectric and dynamic mechanical data.

(2) The materials may be viewed as clusters of ionically concentrated material immersed in a matrix of low ion concentration. The matrix appears to become saturated when it contains ca. 2.5% salt, which occurs when the total ion content reaches ca. 5%. The most direct evidence for this is the composition invariant dielectric strength of the lower temperature relaxation above this concentration. At higher ion contents, the structural changes required in the matrix to accommodate excess ions are apparently energetically expensive, and additional ions are incorporated solely into the clusters. This results in a very rapid increase in size and/or numbers of the clusters at total ion concentrations in excess of 5–6%, with corresponding large changes in the relaxation behavior.

(3) The clusters appear to dissociate at least partly at higher temperatures. The evidence for dissociation may be summarized as follows: (a) Systematic changes in relative heights of the dielectric loss tangent peaks occur with increasing measuring frequency (higher average temperatures). This constitutes perhaps the strongest evidence. (b) The breakdown of stress relaxation time temperature superposition at ion concentrations of greater than ca. 6% is evidence for an additional relaxation mechanism, possibly cluster dissociation. (c) The WLF parameters C_1 and C_2 increase rapidly with ion concentrations in excess of ca. 6%.[5] This can be explained in terms of an effectively temperature dependent T_g, which arises from the increase in T_g as the matrix incorporates the extra ions released by cluster dissociation.

The precise nature of the clusters remains unclear. Generally, however, the "clusters" appear to be regions of high ion content which are structurally more rigid and whose relaxation properties are characterized by higher activation energies than the relatively dilute matrix material. Such clustering is to be expected in a two-component system where like–like interactions (e.g., Coulomb and van der Waals) are stronger than like–unlike interactions, according to statistical considerations[50,51] and other theoretical considerations.[35] In addition, cluster dissociation has been predicted to occur when the elastic forces of the intercluster polymer chains become comparable with the electrostatic force.[35] All of these theoretical predictions are consistent with the dielectric data.

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References and Notes

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