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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 Morawetz²⁴ 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 estimated²⁶ 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 observed²⁶ in stress relaxation, an x-ray pattern typical of a completely amorphous material is observed,²⁹ and water saturation occurs at ca. 1 H₂O 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 H₂O 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 region²⁹ 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 MacKnight⁸ 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

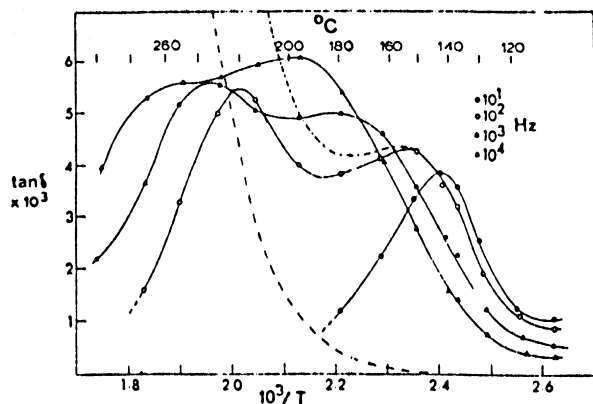


Figure 1. Typical dielectric loss tangents vs. reciprocal temperature for 6.5% NaMA at the indicated frequencies, after subtraction of the conductivity contribution. Also shown are the total observed loss (---) and conductivity loss (---) at 10^2 Hz. High-temperature losses at 10^1 Hz are not shown because 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. $\pm 5\%$, 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 $\pm 10\%$.

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 $\sim 10\%$, 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 (γ) 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

$$\epsilon'' = \epsilon''_{\text{obsd}} - (\sigma_0 / \epsilon_0 \omega) \quad (1)$$

where ϵ_0 is the permittivity 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-

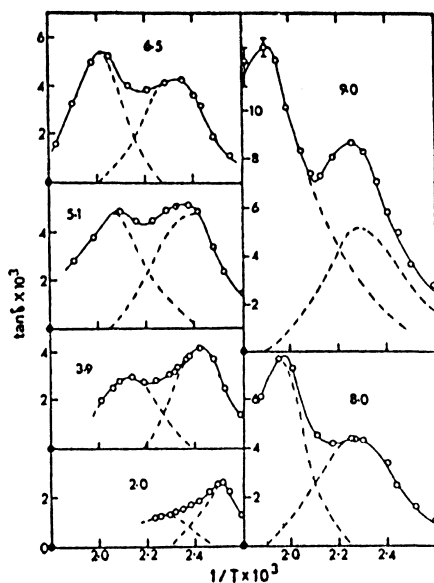


Figure 2. Loss tangents at 10^2 Hz for the compositions studied. Numbers refer to mol % sodium methacrylate. The dotted lines illustrate the resolution into two symmetric peaks (see text).

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 δ plots) and obtaining the dielectric strength and effective dipole moment for each component from the relations

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

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

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

In these equations ϵ'_0 and ϵ'_∞ are the limiting low and high frequency values of the relative permittivity 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

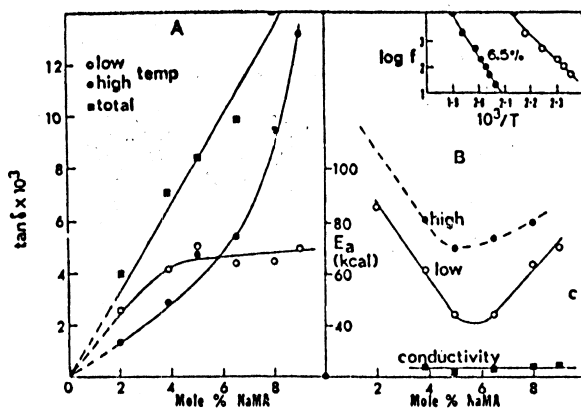


Figure 3. Composition dependences for loss parameters: (A) loss tangent peak heights for the high- and low-temperature relaxations, and their sum; (B) activation energies for dielectric loss and conductivity processes. Inset: Typical Arrhenius plots for 6.5% composition.

Williams,⁴⁰ eq 3 expresses the assumption that the loss spectrum is symmetric, and eq 4 is the Onsager equation.⁴¹

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 group⁴² but three or four times smaller than the estimated 6–7 D for a $\text{COO}^- \text{Na}^+$ 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 permittivity, 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 earlier²⁹ the dielectric peak positions have been extrapolated to 10^{-1} Hz, the

