Dynamic mechanical properties of sulphonated polystyrene ionomers

M. Hara*, P. Jar and J. A. Sauer
Department of Mechanics and Materials Science, Rutgers, The State University of New Jersey, Piscataway, NJ 08855-0909, USA
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Measurements have been made of the dynamic mechanical properties of a series of partially sulphonated polystyrene ionomers. Results obtained indicate that two glass transition temperatures are present, with the lower temperature transition arising from a phase containing only ionic multiplets and the higher temperature transition arising from a phase containing ionic clusters. The loss peak height associated with the multiplet containing phase decreases with increasing ionic content while that associated with the cluster phase rises. The cluster phase appears to become the dominant phase at ion contents of about 6 mol%. The T_g of PS increased linearly with ionic content at the rate of about 3°C per mol%. For each ion content, the average molecular weight between ionic crosslinks was determined from values of the rubbery plateau modulus and compared with calculated values, assuming all ion pairs participate in forming crosslinks. It was also observed that the rubbery plateau region extended over a considerably wider temperature range when samples were prepared with a divalent metal ion, such as Ca, instead of a monovalent ion.

(Keywords: sulphonated polystyrene ionomers; dynamic mechanical properties; glass transition temperature)

INTRODUCTION

The method of introducing a small amount of ionic groups into polymer chains is increasingly becoming useful for modifying the properties of polymers[1–4]. It is now well established that profound changes in various physical properties of these ionic polymers (i.e. ionomers) are due to the clustering of ion pairs in the medium of low dielectric constant. Two types of ionic aggregates are proposed to exist according to ion content[1]: below a certain ion content, multiplets consisting of a small number of ion pairs, which work as physical crosslinks, dominate; above that critical ion content, clusters consisting not only of ion pairs but also of portions of hydrocarbon chains, which bear many of the characteristics of microphase separation, dominate.

In order to investigate ionic aggregate structures, various methods have been used. One of the most widely used techniques is a dynamic mechanical measurement, which is relatively easy to conduct over a wide range of temperatures[5,6]. Systematic studies have been conducted for polyethylene ionomers[3] and polystyrene ionomers[1,2]. In the latter, the ionomer from styrene-methacrylic acid was extensively studied[7]. However, dynamic mechanical properties of partially sulphonated polystyrene (SPS) ionomers[8,10] have not been systematically studied, although these ionomers have received some attention in recent investigations. Strong evidence for the presence of an ionic cluster phase in SPS ionomers comes from SAXS data, which show a maximum in scattered intensity at low angle, whose magnitude increases with ion content[9].

Recently, we reported test results concerning the deformation/fracture behaviour of SPS ionomers[11–13]. It was shown that the deformation mechanisms under both simple tension and cyclic loading changed significantly at a certain ion content (*c*. 4–6 mol%). Also, it was shown that ionomers containing divalent ions exhibited better mechanical properties than those with monovalent ions. It was suggested that these changes were closely related to changes in ionic aggregate structure.

In this work, to investigate and obtain more information concerning ionic aggregate structure, we have conducted a systematic dynamic mechanical study on SPS ionomers of increasing ionic content. We have also studied the effect of varying the type of counterion on the ionic aggregate structure. Test samples used in these studies were similar to those investigated in the study of the deformation/fracture behaviour.

It is well known that sample history, such as the nature of a cast-solvent and of thermal treatment can have a significant effect on the microstructure of ionomers. For example, Galambos *et al.*[14] showed that solvent-cast samples of SPS ionomers from THF/water did not contain clusters; however, after heating samples at 165°C, ionic clusters were formed. In this study, data were acquired on samples that were given no additional thermal treatment. However, for samples of low ion content (2.5 mol% or less) moulded at comparatively low temperatures (135–140°C), a rubbery modulus plateau region was only developed by giving these samples an additional thermal treatment at elevated temperature.

EXPERIMENTAL

Materials

Lightly sulphonated polystyrene was prepared by solution sulphonation of polystyrene (PS) using the procedure described by Makowski *et al.*[15]. Details of sample preparation were described elsewhere[11–13]. A steam stripping method was used to recover polymers after the neutralization of acid samples by NaOH. The starting PS (Mobil PS 1800) had a weight-average

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* To whom correspondence should be addressed

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molecular weight of 3.09×10^5 and a number-average molecular weight of 1.41×10^5 ($M_w/M_n = 2.2$). Ion contents of ionomers, which were controlled by the amount of sulphonating agent, were 1.7, 2.5, 3.5, 4.8, 6.1 and 8.5 mol%.

Specimens

Samples for dynamic mechanical measurements were prepared by compression moulding. They were machined from the same specimens used previously for fatigue experiments[12]. Therefore, the sample history for the samples used in this work was the same as that for samples used in the fatigue studies. The test specimens were rectangular sheets of 12 mm × 2.5 mm × 0.5 mm.

Measurements

Dynamic mechanical studies of the ionomer samples were undertaken by use of a Piezotron (Toyoseiki, Japan). Values were recorded for the storage modulus, E', the loss modulus E'', and the loss tangent, $\tan\delta = E''/E'$. The frequency was 1 Hz and the heating rate was $4°\text{C min}^{-1}$ with a temperature control of ±0.5°C. Reproducibility of the data was good (T_g values for several samples within ±1°C) except at temperatures well above T_g.

RESULTS AND DISCUSSION

Ion content effect

Figure 1 shows an example of the original data points obtained by means of the Piezotron on the Na salt of an 8.5 mol% ion content sample. The data points of storage modulus, E', give a smooth curve, while those of loss modulus E'', are rather scattered, especially at temperatures above 180°C. This is a general trend for all the samples studied. Smoothing of the data was done by using a computer, and only smoothed data are shown in subsequent figures.

Figures 2 and *3* show some results of the dynamic mechanical measurements on the Na salt ionomers as a function of ion content. Two modulus dispersion regions and two mechanical loss peaks are clearly observed for ion contents of 4.8 mol% or higher. Both peaks move to higher temperatures with increasing ion content. Also, as indicated in *Figure 4*, the intensity of the low-temperature peak decreases with ion content, while the intensity of the high-temperature peak increases. It is suggested, as noted also by others[2,9], that the low-temperature peak corresponds to the glass transition of the matrix material containing small ionic aggregates (i.e. multiplets) and the high-temperature peak corresponds to the relaxation of large ionic aggregates (i.e. clusters). From *Figure 4* it appears that the cluster phase becomes the dominant phase at ion contents of about 6 mol%. It is interesting to note that double T_g transitions have also been observed on poly(styrene-*co*-sodium methacrylate) ionomers and there too, based on both measurement of peak heights and peak areas, it was observed that the cluster phase became dominant at an ion content of about 6 mol% (ref. 16). Data somewhat similar to that shown in *Figure 3*, except that it was acquired on SPS ionomers based on an anionic PS, with molecular weight of 115 000, have been recently reported[17].

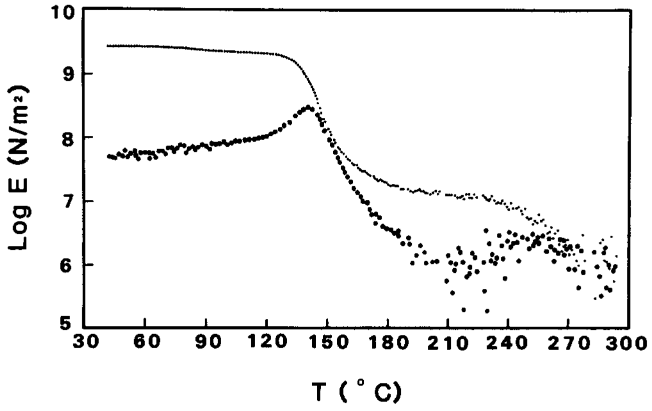

Figure 1 Original data points of storage tensile modulus E', and loss tensile modulus, E'', for the Na-SPS ionomer with 8.5 mol% ion content

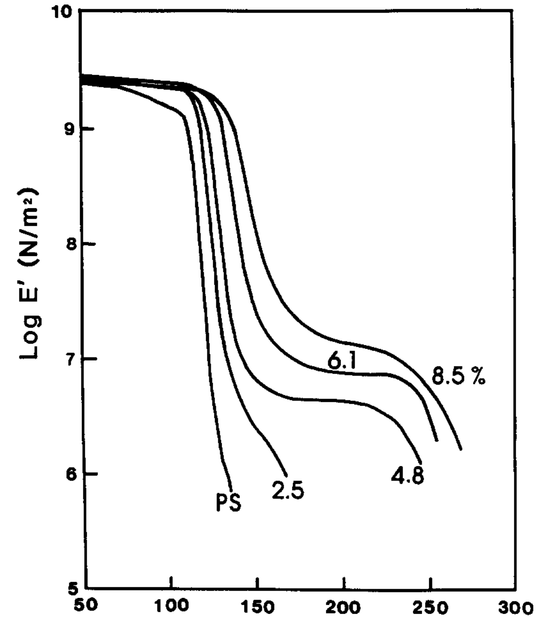

Figure 2 Storage tensile modulus, E', against temperature for Na-SPS ionomers of various ion content

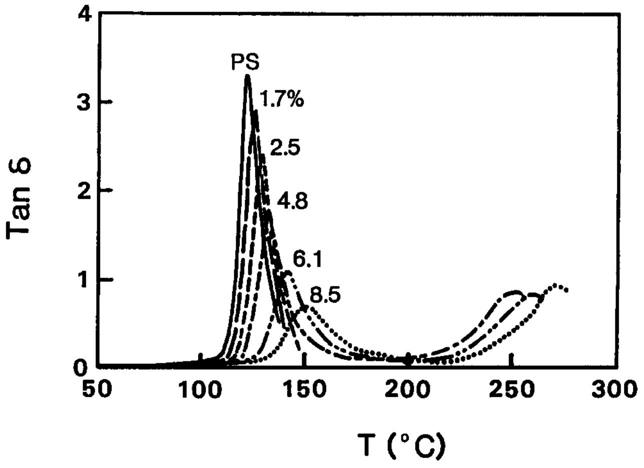

Figure 3 Loss tangent, $\tan\delta$, against temperature for Na-SPS ionomers of various ion content

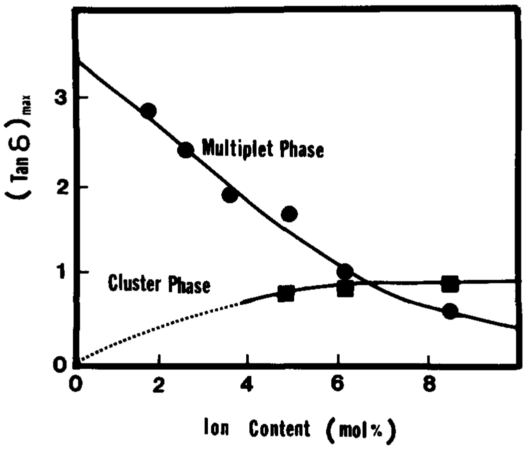

Figure 4 Tan δ peak heights *versus* ion content for both the multiplet phase transition and the cluster phase transition

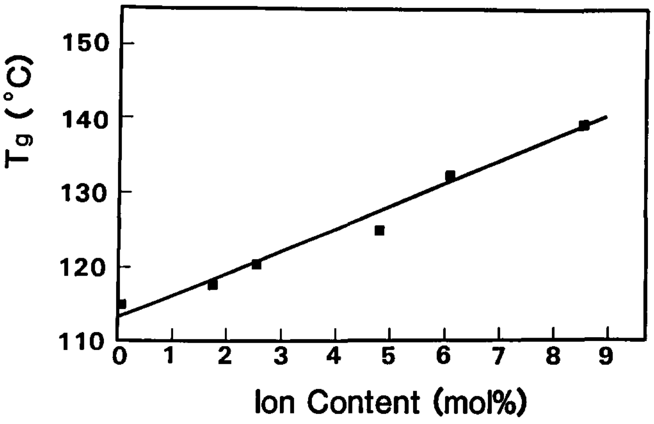

Figure 5 Glass transition temperature (peak in E'' *versus* T curves) of Na-SPS ionomers against ion content

In *Figure 5*, we show how the glass transition temperature of the multiplet-containing matrix phase, taken as the temperature at the peak of the loss modulus curves, varies with ion content. The increase is a linear one at the rate of about 3.2°C per mol% of ionic groups. This value is comparable to values reported in the literature: for example, 1–4°C per mol% for polypentenamer-based ionomers[3]. More recently, the glass transition temperatures of various PS-based ionomers have been reported[18]. In these ionomers the increase of the matrix T_g was 3.4 ± 0.3°C per mol%, in good agreement with our value of 3.2. The T_g values of this study were obtained at a heating rate of 4°C min^{-1} and at a frequency of 1 Hz. Hence values are somewhat higher than would be obtained under more static conditions.

The extensive rubbery plateau region that is evident in *Figure 2*, especially for high ion content samples, is a strong indication of ionic crosslinking. The higher the ion content, the higher the plateau modulus, as the distance between crosslinking points decreases with ion content. To show this effect more clearly, the molecular weight between crosslinking points is shown as a function of ion content in *Figure 6*. The data point for the 2.8 mol% sample was based on the measured rubbery modulus for a sample given an additional thermal treatment (24 h at 200°C). The calculated curve was obtained by assuming that all ion pairs are participating in forming ionic crosslinking and also taking into consideration the number of molecular entanglements in PS. The experimental points are obtained by using the theory of classical rubber elasticity[19]:

$$E' = 3\rho RT/M_c$$

where ρ is the density of the polymer (g cm^{-3}), R is the gas constant, T is the absolute temperature, and M_c is the average molecular weight between crosslinking points. The two curves exhibit the same general trend with increasing ion content but there are some differences. At low ion content levels, the experimental points are higher than the theoretical curves. One of the reasons for this deviation is that there may be some isolated ion pairs which do not form ionic crosslinks. Near 6 mol%, the two curves intersect and, at higher ion content level, the experimental curve is lower than the theoretical curve. Similar behaviour was observed in the stress relaxation data for styrene–methacrylic acid ionomers[20]. This reflects the domination of ionic clusters over multiplets at high ionic contents.

The rubbery plateau modulus is plotted against ion content in *Figure 7*. Again, the experimental point for the 2.5 mol% sample represents data obtained on a heat-treated sample while the other data points have been obtained directly from compression-moulded samples.

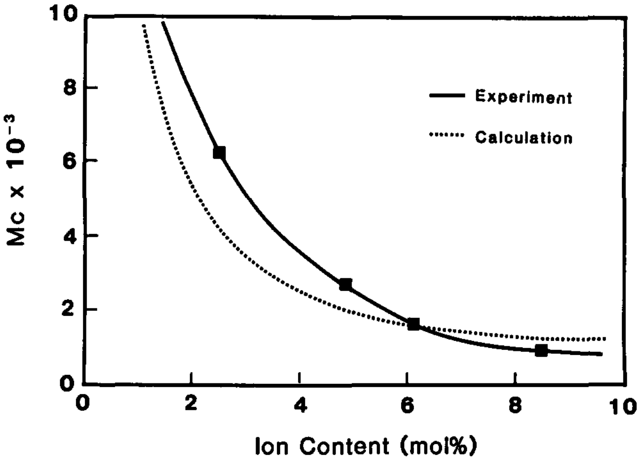

Figure 6 Average molecular weight between crosslinking sites, M_c, against ion content for Na-SPS ionomers

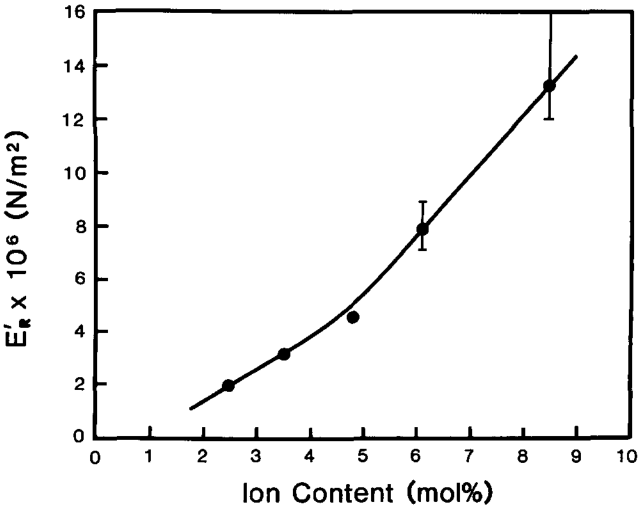

Figure 7 Rubbery plateau modulus, E'_R, against ion content for SPS ionomers

The slope of the curve in *Figure* 7 begins to increase at about 5–6 mol% or approximately at the critical ion content where the cluster phase becomes dominant. Thus the cluster phase has a more significant effect on the plateau storage modulus than does the multiplet phase. Also, as noted previously[12], when the cluster phase becomes dominant at about 6 mol%, there is a dramatic rise in the resistance of bulk specimens of Na-SPS ionomers to fatigue fracture.

Counterion effect

In recent tests in this laboratory, it has been observed[21] that the nature of the counterion in SPS ionomers can have an appreciable effect on mechanical performance. For example, it has been noted that, for a 4.1 mol% SPS ionomer, specimens containing the divalent Ca ion could endure almost three times as many alternating cycles of loading prior to fracture than samples containing monovalent ions, such as K or Cs. It is desirable therefore to obtain additional information as to the effect of divalent *versus* monovalent ions on the mechanical relaxation behaviour and on ionic microstructure. Here we simply note how such changes of the metal counterion in SPS ionomers affects the storage modulus–temperature relation. Results obtained on a 4.1 mol% SPS ionomer having respectively K, Cs and divalent Ca ions are shown in *Figure 8*.

The marked drop in modulus near 125°C, which is a manifestation of the glass transition of the multiplet-containing phase, and the values of the storage modulus at the onset of the rubbery plateau region, are essentially the same for all three ionomer systems. This suggests that the number of ionic crosslinks is about the same for the monovalent ion and the divalent ion systems. However, the length of the rubbery plateau region is relatively short for both the K and Cs ionomers but it extends over a very wide temperature range for the divalent Ca ion system. This suggests that the strength of the ionic interactions in the ionic aggregates is greater when divalent Ca ions are present. The order of the interaction strength or stability observed here is $Cs < K < Ca$. This is an example of a quite general phenomenon noted in various ionic solids. It has been observed, for example, in the strength of small ionic salts[22], in an increase of T_g of some ionic polymers[23] and in the strength of ion-dipole interaction in polymer blends[24].

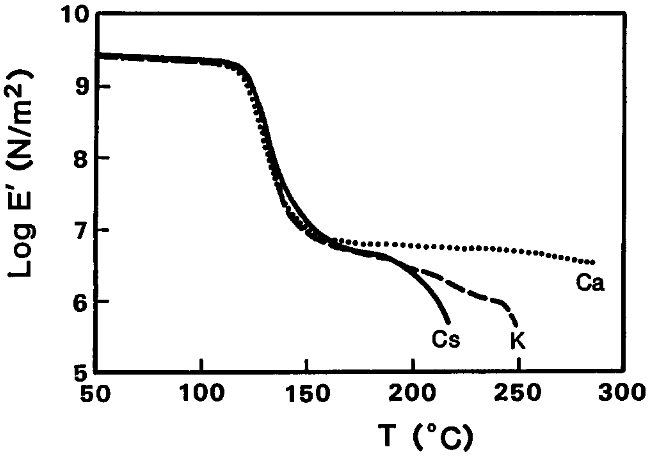

Figure 8 Storage tensile modulus, E', against temperature for SPS ionomers (4.1 mol% ion content) with various counterions

CONCLUSIONS

In compression-moulded samples of Na-SPS ionomers having an ionic content of 3.5 mol% or higher, both a multiplet-containing phase and a cluster phase are developed, even though the samples are not given any additional thermal treatment. For smaller ion contents, it appears that additional thermal treatment is necessary to develop ionic clusters and an extended modulus plateau region above T_g.

Based on respective values of the heights or areas of the two mechanical loss peaks that are observed in PS ionomers in the temperature region above the T_g of PS, it appears that the cluster phase becomes dominant at ionic contents of about 6 mol%.

At ion contents where the cluster phase becomes dominant, there is an appreciable increase in the value of the storage plateau modulus and also in the resistance of SPS ionomers to fatigue fracture.

The T_g of the multiplet-containing phase increases essentially linearly with ion content and the rate of increase for the Na-SPS ionomers studied here is about 3.2°C per mol%.

Ionomers prepared with divalent Ca ions show a much more extended rubbery plateau region than do corresponding SPS ionomers prepared with monovalent K or Cs ions. The increase in strength and stability of ionic interactions when divalent Ca ions replace monovalent ones is probably also responsible for the observed large increase in fatigue lifetime of bulk specimens of SPS ionomers.

Values of M_c, the average molecular weight between ionic crosslinks, were determined for various ion contents from the value of the rubbery plateau modulus. These experimental values, as well as calculated values, fall with increasing ionic content but at a steadily decreasing rate.

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