Solubility of a styrene oligomer in a polystyrene ionomer*

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A dynamic mechanical analysis of a microphase-separated polystyrene ionomer blended with a styrene oligomer (molar mass = 800) is presented. In particular, the extent of plasticization by the oligomer of the ionomer glass transition (T_g) and of the so-called ionic transition (T_i) as a function of blend composition and three ion contents was examined. It was noted that, with increasing oligomer concentration, the T_g (which represents the less polar regions of the ionomer) initially decreases rapidly compared to T_i (which represents the more polar microphase-separated regions of the ionomer), and then more slowly at a rate comparable to T_i. The T_g decrease is less than that predicted by the Fox equation (in contrast to a lower molar mass non-polar diluent); furthermore, it deviates more strongly with oligomer concentration the higher the ion content of the ionomer. At high oligomer concentrations, gross phase separation of the oligomer from the plasticized ionomer occurs. These results are discussed in terms of the solubility of the oligomer in the two ionomer phases.

(Keywords: plasticization; oligomer; ionomer; polystyrene; dynamic mechanical analysis; microphase separation; phase separation)

INTRODUCTION

The concept of selective plasticization of ionomers has been established for some time. It was specifically invoked in the report of Lundberg *et al.*[1] describing the contrasting effects of a polar and a non-polar diluent on the melt viscosity and glass transition temperature of a sulphonated polystyrene ionomer. The polar diluent was shown to be much more effective in reducing the melt viscosity of the ionomer (up to a certain level), whereas the non-polar diluent is the more effective by far in reducing the glass transition temperature. It was postulated that the non-polar diluent acts as a plasticizer of the polystyrene matrix, whereas the polar diluent, through solvation of the ionic groups, interferes with the ionic interactions which are responsible for the high melt viscosities of ionomers.

The phenomenon was subsequently probed through dynamic mechanical[2,3] and rheological[4] studies of plasticized polystyrene-based ionomers. It was found that, in the range of diluent concentrations investigated, the non-polar diluents are effective in reducing both the glass transition temperature, T_g, and what will be called here the ionic transition temperature, T_i (the latter being associated with what are commonly believed to be microphase-separated aggregates, or clusters, composed of polar or ionic material as well as entrained matrix material). The decrease in T_g due to plasticization by diethylbenzene[2] follows the Fox equation remarkably well for all the samples studied (various ion contents, sulphonated and carboxylate materials). The degree of influence on the ionic transition, however, was observed to be greater for the carboxylate material than for the sulphonated material; in the former, the degree of plasticization of the clusters parallels that of the matrix. On the other hand, the polar diluent completely destroys the effect of the clusters on the mechanical properties.

A preliminary study[4] of the plasticization of the polystyrene ionomer by a styrene oligomer revealed indications that there is a limit to the effect of non-polar diluents on at least the ionic transition. This paper presents results of a more in-depth analysis of this aspect of plasticization of ionomers. The effect of the oligomer on the T_g and the T_i of the ionomer are specifically examined. In other words, the extent of solubility of the oligomer in the ionomer, with respect to both the matrix and the ionic aggregates, is investigated through a study of the dynamic mechanical properties of the ionomer/oligomer blend system. Both the ion content of the ionomer and the ratio of the two components of the blend are variables.

Reference has been made above only to the specific studies which have inspired the present investigation. Other studies of plasticization of ionomers (including the above) have been extensively reviewed in ref. 5. To these must be added very recent work, involving internal as well as external plasticization of specific ionomer systems[6,7]. None of these studies are immediately related to the present one, and so will not be summarized.

EXPERIMENTAL

The poly[styrene-co-(methacrylic acid)] (PS-MAA) copolymers were synthesized, and the acid contents determined, in the classical manner[8]. Percentage conversions in the free-radical polymerizations were well below 10%. Molar masses obtained by gel permeation

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chromatography were in the range of 100 000 to 200 000 with a polydispersity of ~ 2. The PS-MAA were stoichiometrically neutralized in benzene/methanol solution by adding calculated amounts of a standardized solution of sodium hydroxide in methanol, to give the ionomers PS-MAA-Na; these were then freeze-dried followed by further drying under heated vacuum. Ion contents studied were 3.2, 4.8 and 7.9 mol%, to be referred to as 3, 5 and 8 mol% and indicated as x in PS-0.0xMAA-Na. The styrene oligomer (8S) of molar mass 800 ($M_w/M_n = 1.2$) was purchased from Pressure Chemicals. The blends were prepared by dissolving together the freeze-dried ionomer and the oligomer in the desired ratio by weight in benzene/methanol (95/5 v/v), and freeze-drying, followed by further drying under vacuum for several days at temperatures of 70°C or less; samples were then compression-moulded into suitable forms (either rectangular rods or disks), and further dried under heated vacuum, as in ref. 4. Blend ratios were 100/0, 80/20, 60/40, 40/60 and 20/80 (w/w) ionomer/oligomer. It was ascertained that there was no significant oligomer loss under the experimental conditions employed.

The Polymer Laboratories dynamic mechanical thermal analyser (d.m.t.a.) in the dual cantilever bending mode was used to measure the dynamic mechanical properties as a function of temperature and frequency. The samples, in the form of rectangular rods, were typically 10.0 mm wide, ~ 2.5 mm thick, and usually had a free length of 5.0 mm. For the low ion content samples as well as the higher oligomer-containing samples, the free length was usually reduced to 2.0 mm. In a number of cases, the experiments were repeated more than once on the same blend composition, with good reproducibility. It was also ascertained that the exact dimensions of the sample did not affect the results. Operation in the shear mode (on disk samples, typically 11 mm in diameter and 2 mm average thickness) was employed to ascertain the bending mode data in the region above T_g where the loss peaks associated with T_i were not always easy to discern. Measurements were performed at five frequencies (0.3, 1, 3, 10 and 30 Hz) at a heating rate of 0.8°C min^{-1} and a deflection of 64 μm. The experimental chamber was constantly flushed with a light flow of prepurified nitrogen.

RESULTS

Representative dynamic mechanical data as a function of temperature for various ionomer/oligomer ratios are shown in *Figures 1–3*. The dynamic storage moduli for the blends with the 5 mol% ionomer are plotted in *Figure 1*. The plasticizing effects of the oligomer on the glass transition zone and rubbery flow zone in the ionomer are clearly evident, thus confirming the similar but more limited results of ref. 4. It is also apparent that the rubbery plateau is extended, and its modulus decreased, with increasing 8S concentration.

The loss tangents in the glass transition zone of 8 mol% ionomer/oligomer blends are shown in *Figure 2*, illustrating their variation not only in the temperature position of the peak maximum but also in its intensity and width. As oligomer concentration is increased, the intensity initially decreases, reaching a minimum at an ionomer/oligomer ratio of $\sim 60/40$, and then increases again; this trend was observed for all three ion contents studied. On the other hand, the widths and surface areas generally increase with increasing oligomer concentration. The ionic transition was best observed in the loss moduli data, where a shallow maximum above the T_g could usually be distinguished. An example of this data is shown in *Figure 3* for the 5 mol% ionomer, where both the glass transition loss zone and the higher temperature ionic transition loss zone are apparent.

The variation in temperature of the glass transition (as determined from the loss tangent maxima) and of the ionic transition (as determined from the loss modulus

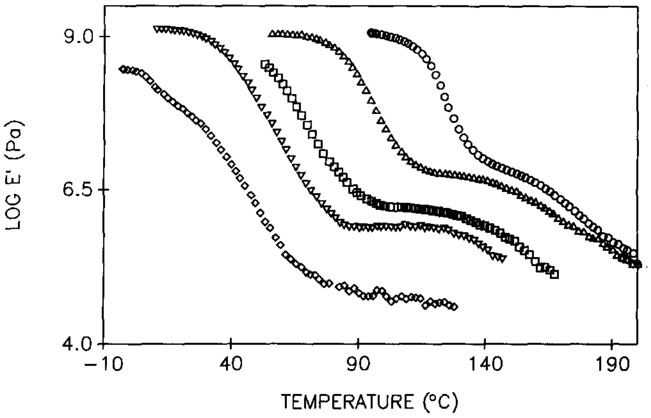

Figure 1 Young's storage modulus *versus* temperature at 1 Hz for various compositions of PS-0.05MAA-Na/8S. Compositions (w/w): ○, 100/0; △, 80/20; □, 60/40; ▽, 40/60; ◇, 20/80

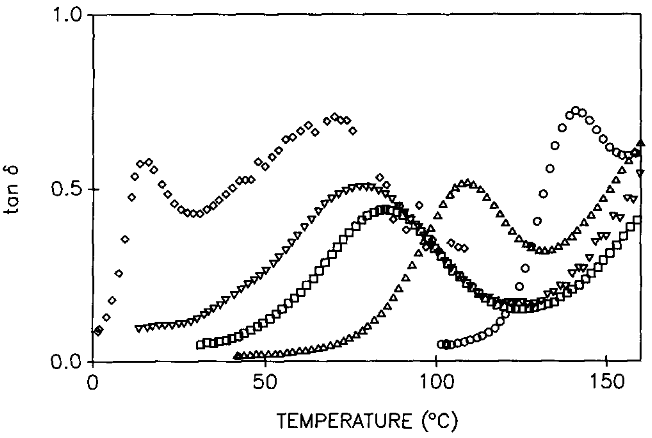

Figure 2 Loss tangent *versus* temperature at 1 Hz for various compositions of PS-0.08MAA-Na/8S. Symbols as in *Figure 1*

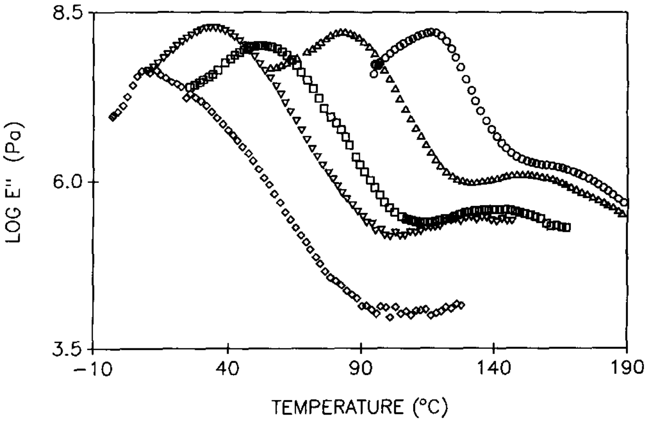

Figure 3 Young's loss modulus *versus* temperature at 1 Hz for various compositions of PS-0.05MAA-Na/8S. Symbols as in *Figure 1*

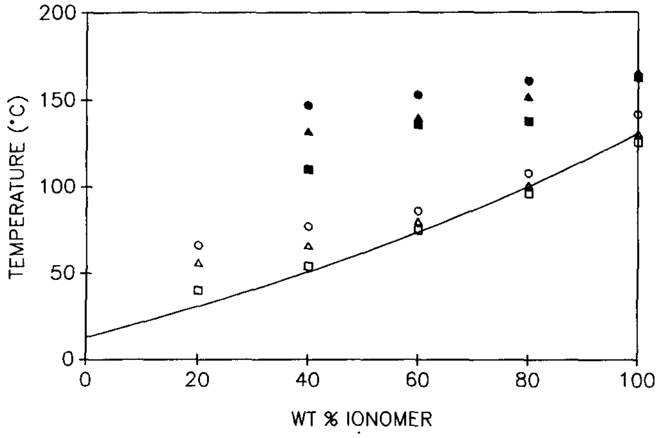

Figure 4 Glass transitions (unfilled symbols; from loss tangent maxima) and ionic transitions (filled symbols; from loss modulus maxima) at 1 Hz as a function of wt% ionomer for the PS-MAA-Na/8S blends at three ion contents (□, ■ 3; Δ, ▲ 5; ○, ● 8 mol% MAA). The line represents the Fox equation[9] for the 5 mol% MAA blend

maxima) at a frequency of 1 Hz is illustrated in *Figure 4* as a function of wt% ionomer in the blends, for the three ionomers studied. Also plotted are the T_gs that would be expected for the blend series involving the 5 mol% ionomer, if the Fox equation[9], given as follows, were obeyed:

$$1/T_g = w_A/T_{g_A} + w_B/T_{g_B}$$

where w_A, w_B and T_{g_A}, T_{g_B} refer to the weight fractions and the glass transitions in the pure state of the blend components A and B, respectively. For these calculations, an oligomer T_g of 13°C was used, for reasons that will be clear shortly. The Fox equation is generally valid for completely miscible polymer/plasticizer systems. There are a number of observations to be made from *Figure 4*.

First of all, it is clear that, with increasing 8S concentration, the experimental T_gs increasingly deviate from those calculated using the Fox equation. Furthermore, the higher the ion content of the ionomer, the greater the deviation. This is all the more evident when it is noted that, if the Fox equation were applicable, the T_gs for the ionomers of different ion contents should approach one another as oligomer is increased; in fact, the reverse is seen. It should be mentioned that all of the samples were measured by differential scanning calorimetry (d.s.c.) as well: the T_g behaviour was observed to be qualitatively identical to that described above. Thus, it appears that the efficiency of the oligomer in plasticizing the ionomer decreases with increasing oligomer concentration and with increasing ion content of the ionomer.

As for the ionic transition, although it shows a regular decrease in temperature, it is clearly less plasticized overall by the oligomer than is the T_g. (This necessarily results in a lengthening of the rubbery plateau, as seen in *Figure 1*.) In fact, it seems that the decrease in T_i over the whole composition range is similar to the decrease in T_g in the higher oligomer concentration range (above ~40 wt%). Again, it appears that the higher the ion content, the less the addition of oligomer decreases this transition temperature. (It should be remarked that the uncertainties associated with the T_is are significantly greater than those of the T_gs; however, the trends are clear.)

The Arrhenius apparent activation energies that were determined for the two transitions (based on five frequencies, in most cases) are shown in *Figure 5*. In the case of the matrix glass transition, there is a rapid decrease in activation energy at the lowest oligomer concentrations; at greater than ~40 wt% oligomer, there is only a small additional decrease. The activation energies for the ionic transition, on the other hand, do not vary significantly with blend composition over the entire range; in fact, they appear to decrease slightly at roughly the same rate as the T_g activation energies at high oligomer concentrations. This parallels the observations for the transition temperatures in *Figure 4*.

One further result must be described. In *Figure 2*, an additional loss tangent peak at low temperatures (~13°C) is clearly evident for the 8 mol% ionomer blended with 80 wt% of oligomer. A hint of this transition also appears in the 40/60 blend. This transition can be identified as the glass transition of phase-separated oligomer that appears in the blends of high oligomer concentration. The d.m.t.a. T_g of 13°C for 8S in the blends corresponds very well to the d.s.c. T_g (20°C min^{-1} heating rate) of ~0°C for pure 8S. As shown in *Figure 6*, the higher the ion content of the ionomer, the more pronounced the extent of phase separation of oligomer in the 20/80 blends. This correlates with the physical appearance of the samples, as described in *Table 1*. Gross phase separation in the blends is clearly indicated by the lack of transparency of the samples at higher 8S concentrations; this is accentuated with increasing ion content of the ionomer.

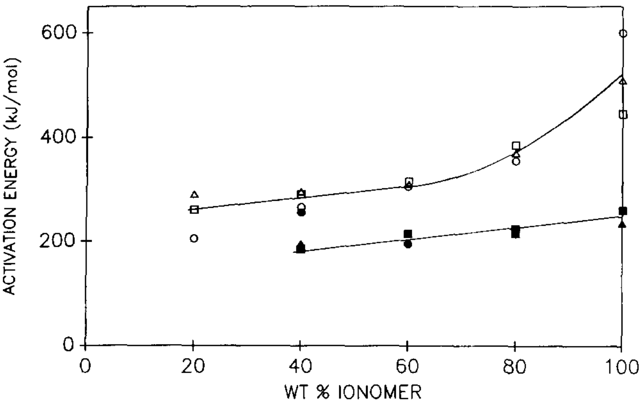

Figure 5 Apparent Arrhenius activation energies of the glass transitions and ionic transitions (as determined from loss tangent maxima and loss modulus maxima, respectively, at five frequencies) as a function of wt% ionomer for the PS-MAA-Na/8S blends at three ion contents. Symbols as in *Figure 4*

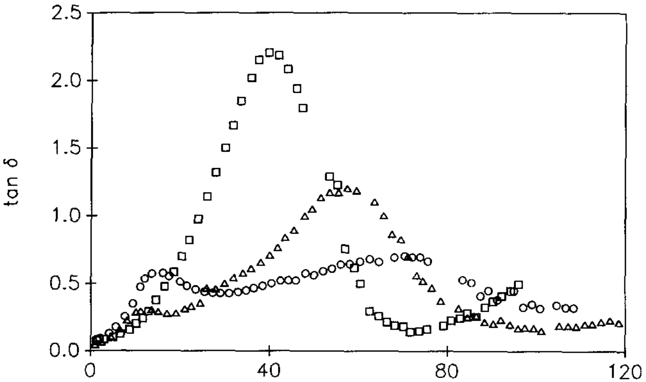

Figure 6 Loss tangent *versus* temperature at 1 Hz for the 20/80 (w/w) PS-MAA-Na/PS blends at three ion contents: □, 3; Δ, 5; ○, 8 mol% MAA

Table 1 Physical appearance of the non-transparent PS-MAA-Na/8S blends

Ionomer/oligomer (w/w)	MAA content (mol%)	Appearance
20/80	3	Slightly translucent
20/80	5	Translucent
20/80	8	Opaque
40/60	8	Slightly translucent

DISCUSSION

The plasticization, by the oligomer, of the microphase-separated ionic domains and of the matrix phase of the ionomer can be considered in terms of the solubility of the oligomer in the two phases. When the oligomer is soluble in a phase, it increases the free volume of the phase and thereby decreases its T_g. The data above indicate that the oligomer is soluble to a limited extent in the ionic domains (or clusters) of the ionomer. That the ionic domains are plasticized at all is most likely related to the non-polar material that has all along been presumed to be a component of the clusters[10]. On the other hand, it is significant that the T_i decrease due to 8S is considerably less than was observed for the same ionomer due to diethylbenzene[2], where the decrease in T_i parallels the decrease in T_g. This is probably related to the relatively large size of the oligomer (eight styrene repeat units) compared to diethylbenzene, making it less soluble in the cluster phase; the high concentration of associated ionic groups in the clusters makes it more difficult for larger non-polar molecules to find a suitable (non-polar) microenvironment. Explanations other than solubility may also be evoked to rationalize the T_i decrease[7]; however, without a more precise idea of the nature of the cluster domains than is currently available in the literature, it is difficult to be more specific about the mechanism leading to the T_i decrease.

Not unexpectedly, the oligomer is much more soluble in the less polar ionomer matrix. At the lower oligomer concentrations, where the T_g decreases much more rapidly than the T_i, the oligomer is preferentially (but not exclusively) dissolved in the matrix phase. Above ~40 wt% 8S concentration, the T_g decreases less rapidly; that is, the additional 8S seems to partition itself more equally between the more polar and the less polar phases.

Finally, at high oligomer concentrations, a solubility limit is reached, leading to phase separation of the oligomer from the ionomer. This is manifested in dynamic mechanical measurements by a loss tangent maximum in the region of the glass transition of the oligomer, and physically by increasing opacity of the samples. The solubility limit is attained more quickly, the higher the ion content of the ionomer. In fact, that is consistent with the copolymeric nature of the ionomer, where the plasticizer or diluent is miscible with only one component of the copolymer, in this case the styrene component. From the point of view of the solubility of the ionomer in the diluent (rather than vice versa), this is also consistent with the fact that higher ion content ionomers cannot be dissolved in (but only swollen by) non-polar solvents such as benzene, diethylbenzene, and, no doubt, 8S.

The variation in intensity and half-width of the T_g with increasing oligomer concentration may reflect a variation in concentration gradient of the oligomer in the matrix, which causes local T_g differences. Initially, the gradient may become increasingly wide as oligomer is added, perhaps because of an uneven distribution of the polar aggregates in the matrix (which in turn is due to the random distribution of the ionic groups along the polymer chain). That is, the oligomer distributes itself according to the local concentration of ionic groups in a way that causes increasingly large local T_g differences. Thus the T_g loss tangent width increases at the expense of maximum peak intensity. At some point, the gradient in oligomer concentration reaches its maximum width, following which additional oligomer simply leads to increased peak intensity. A similar variation in intensity has been observed for plasticized poly(vinyl chloride)[11], where the spatial and size distribution of the crystalline domains may affect the dispersion of the plasticizer.

CONCLUSION

The glass (T_g) and ionic (T_i) transitions of poly[styrene-co-(sodium methacrylate)] ionomers plasticized by a styrene oligomer were investigated through dynamic mechanical thermal analysis. The T_i, representing the more polar regions of the ionomers, decreases only slowly with increasing oligomer concentration. The T_g, representing the less polar regions of the ionomers, initially decreases rapidly, and then more slowly at a rate comparable to the T_i. As the ion content is raised, there is increasing deviation from the T_gs predicted by the Fox equation. At high oligomer concentrations, there is gross phase separation between oligomer and plasticized ionomers; furthermore, the samples become increasingly opaque.

These observations can be interpreted as follows. The solubility of the styrene oligomer in the polar microphase-separated regions of the polystyrene ionomer is strictly limited. Its solubility in the matrix is considerably greater, but also reaches a limit, leading to phase separation at high oligomer concentrations; the higher the ion content, the sooner this limit is attained.

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REFERENCES

1 Lundberg, R. D., Makowski, H. S. and Westerman, L. *Adv. Chem. Ser.* 1980, **187**, 67

2 Bazuin, C. G. and Eisenberg, A. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1137

3 Fitzgerald, J. J., Kim, D. and Weiss, R. A. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 263

4 Bazuin, C. G., Eisenberg, A. and Kamal, M. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1155

5 Bazuin, C. G. in 'Multiphase Polymers: Blends and Ionomers' (Eds L. A. Utracki and R. A. Weiss), ACS Symposium Series 395, Washington, 1989

6 Gauthier, M. and Eisenberg, A. *Macromolecules* 1989, **22**, 3751, 3756

7 Wollmann, D. PhD Thesis, Department of Chemistry, McGill University, 1989

8 Eisenberg, A. and Navratil, M. *Macromolecules* 1973, **6**, 604

9 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **2**, 123

10 Eisenberg, A. *Macromolecules* 1970, **3**, 147

11 Schmieder, K. and Wolf, K. *Kolloid. Zeit.* 1952, **127**, 65