Effect of sample history on ionic aggregate structures 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
(Received 7 November 1989; accepted 22 April 1990)

The effects of thermal treatment and of solvent (dimethyl formamide (DMF)) history on the ionic aggregate structures of lightly sulphonated polystyrene ionomers were studied by dynamic mechanical measurements. It was shown that thermal treatment of the ionomers with 2.5 mol% ion content enhanced cluster formation. It was also found that DMF worked as a 'dual' plasticizer that not only destroyed ionic aggregates but also decreased the T_g of matrix materials. Thermal treatment of cast samples from DMF recovered ionic aggregate structures that were comparable to those seen in compression-moulded samples.

(Keywords: sulphonated polystyrene ionomers; dimethyl formamide; ionic aggregate structures; dynamic mechanical measurements)

INTRODUCTION

Ionomers, ion-containing polymers having relatively small amounts of ionic groups (up to 10–15 mol%) along backbone chains, have been studied widely because the presence of ionic interactions produces large changes in physical properties[1–3]. These changes are due to formation of ionic aggregates in the medium of low dielectric constant. These ionic aggregates may be regarded as phase separated domains. Therefore, as in the case of block copolymers, various sample histories, such as cast-solvent history and thermal history, may influence significantly the structure and properties of ionomers. Researchers working in the ionomer field are encouraged to define the conditions of making their samples[3].

Recently, interesting studies on thermal history of ionomers have been conducted by a University of Connecticut group[4] using small-angle X-ray scattering (SAXS). They found that a solvent mixture (90% THF/10% water) completely destroyed ionic clusters, as indicated by the absence of a SAXS peak. However, after heating the sample to 165°C, clusters were reproduced as evident by the appearance of a SAXS peak comparable to that observed for compression-moulded samples. These results suggest the importance of thermal treatment as a means for providing sufficient mobility for ions in the matrix to form ionic aggregates.

In connection with solvent history, plasticizer effects on ionomers should be mentioned. Recently, several research groups[5–7] have studied the effect of various plasticizers on physical properties of ionomers, such as melt rheology and dynamic mechanical properties. All report two types of plasticizers: backbone plasticizers, such as dioctylphthalate[5,6] and diethylbenzene[7], which preferentially plasticize nonpolar backbone chains; and ionic domain plasticizers, such as glycerol[5–7], which preferentially destroy ionic clusters. These two effects were properly differentiated by using appropriate plasticizers.

In this work, we have used dimethyl formamide (DMF) as a casting solvent for sulphonated polystyrene ionomers (Na salts). The effect of DMF retained in the ionomer samples and the effect of thermal treatment on these samples are major concerns. DMF is known as a good solvent for polystyrene, and also known as a polar solvent that destroys ionic interactions[8]. Therefore, a 'dual' plasticization effect arising from the combination of two plasticization effects is expected.

Another purpose of this study is to examine the effects of thermal history on several samples of sulphonated polystyrene ionomers, including some previously used for the study of deformation and fracture[9–11].

EXPERIMENTAL

Details of preparation of lightly sulphonated polystyrenes[10] and of experimental measurements on their dynamic mechanical properties[12] are described elsewhere. The average molecular weight of the starting polystyrene is $M_w = 3.09 \times 10^5$ and $M_n = 1.41 \times 10^5$ ($M_w/M_n = 2.2$). The ion contents of ionomers used in this study (Na salts) were 2.5 and 8.5 mol%. The ionomer specimens with 2.5 mol% ion content were made by compression moulding at 135°C for 1 h, after heating under vacuum at 120°C for 6 h, followed by cooling to room temperature. The ionomer specimens with 8.5 mol% ion content were made by compression moulding at 190°C for 1 h, after heating under vacuum at 210°C for 7 h, followed by cooling to room temperature. Some samples of 8.5 mol% ion content were made by casting from DMF solution. It was determined that these samples still contained 10.8 wt% of DMF after drying in air for 16 h. Dynamic mechanical measurements (~1 Hz) were made on these samples both before and after heat treatment for 41 h at 200°C under vacuum and pressure.

---

* To whom correspondence should be addressed

0032-3861/91/081380-04

RESULTS AND DISCUSSION

Thermal effect

Figures 1 and *2* show the effects of thermal treatment on the tensile storage and loss moduli, E' and E'', for ionomers with 2.5 mol% ion content. The dashed lines represent the data for the compression-moulded samples, before applying thermal treatment, while the solid lines show the data for the samples after thermal treatment. The heat treated samples were held at 200°C for 24 h under some pressure and vacuum. It is clearly seen that a well developed plateau region appears in the E' data after thermal treatment (*Figure 1*) and, as *Figure 2* shows, a small damping peak appears in the loss modulus data in the high temperature region above 200°C. However, the high temperature loss peak obtained in this sample by heat treatment is not as well developed as those previously observed in higher ion content samples[12], and attributed to the presence in the samples of ionic clusters. These results suggest that large ionic aggregates (clusters) can be formed, even in samples of low ion content, by thermal treatment. The low intensity of the higher temperature loss peak may reflect the fact that the amount of cluster formation, obtained in samples having less than the critical ion content of about 5%[12], is small compared with the formation of small ionic aggregates (multiplets)[1]. Recently, Register *et al.*[13] studied the effect of thermal treatment of sulphonated polystyrene ionomers (Mn salts) by SAXS and EXAFS. No SAXS peak, and hence no ionic aggregation, was observed in samples cast from THF/H_2O solution but, after annealing at 120°C for 4 days, an 'ionic aggregate' peak was developed. A peak was also observed in compression moulded samples having 7.6 mol% ion content while, for a 2.6 mol% sample, having a slower rate of aggregation of ionic groups, only a shoulder was observed in the SAXS spectrum. Our results on the effects of thermal treatment in the development of ionic aggregates seem to be consistent with these findings.

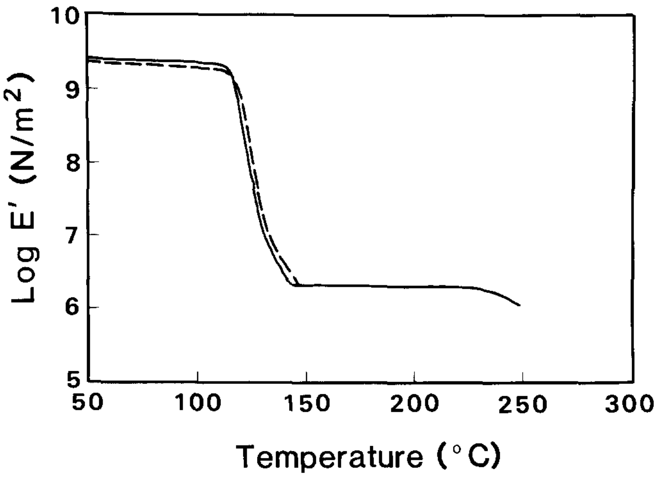

Figure 1 Tensile storage modulus, E', against temperature for 2.5 mol% ionomers before (dashed line) and after (solid line) heat treatment

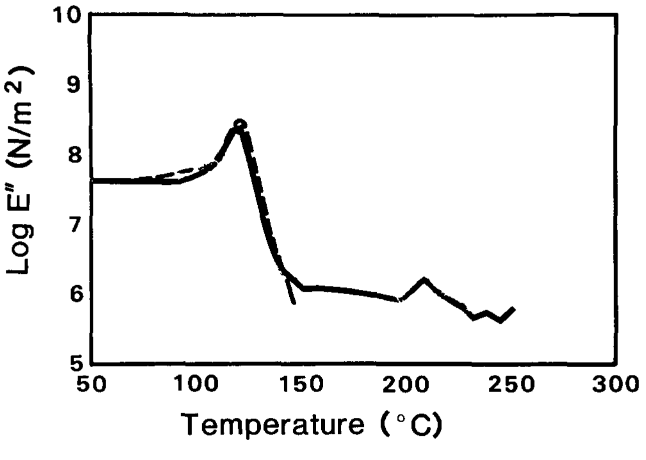

Figure 2 Tensile loss modulus, E'', against temperature for 2.5 mol% ionomers before (dashed line) and after (solid line) heat treatment

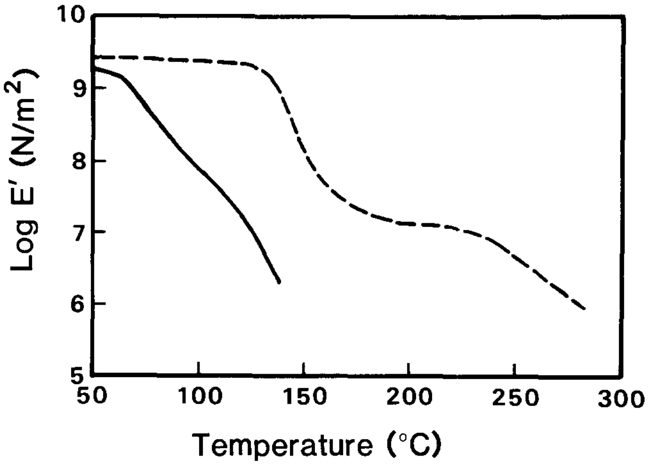

Figure 3 Tensile storage modulus, E', against temperature for 8.5 mol% ionomers with 10.8 wt% of DMF before (solid line) and after (dashed line) thermal treatment

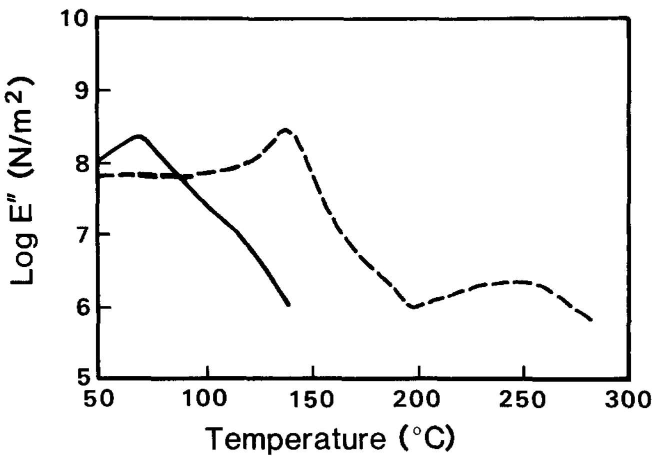

Figure 4 Tensile loss modulus, E'', against temperature for 8.5 mol% ionomers with 10.8 wt% of DMF before (solid line) and after (dashed line) thermal treatment

Solvent (DMF) effect

Figures 3 and *4* show the effects of thermal treatment on the tensile moduli for DMF cast ionomers with 8.5 mol% ion content. The solid lines represent the data for the sample containing 10.8 wt% of DMF, while the dashed lines show the data for the sample after heating at 200°C for 41 h under pressure and vacuum. From weight measurements, it was determined that little DMF remained in the sample after the heat treatment. During the heating, two processes may be involved: evaporation of DMF and thermal treatment. As a reference, tensile

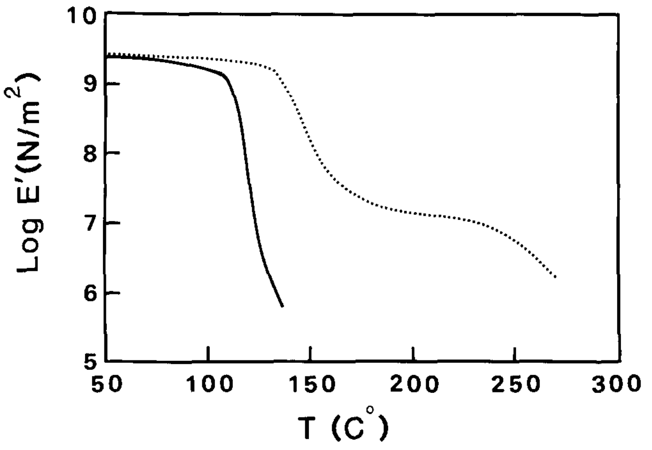

Figure 5 Tensile storage modulus, E', against temperature for PS (solid line) and 8.5 mol% ionomer made by compression moulding (dotted line)

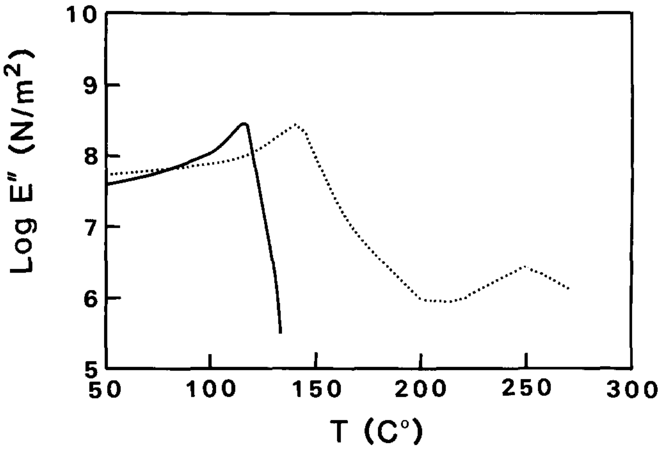

Figure 6 Tensile loss modulus, E'', against temperature for PS (solid line) and 8.5 mol% ionomer made by compression moulding (dotted line)

moduli for the starting polystyrene and for an unheat-treated compression-moulded sample of 8.5 mol% ion content are shown in *Figures 5* and *6*. *Figures 3* and *4* show that for the sample containing 10.8% DMF not only is the second high temperature relaxation process absent but the low temperature relaxation (T_g) process shifts to lower temperatures than that of PS. Also, it is seen that the low temperature relaxation is much broader for the sample with DMF. These results confirm a 'dual' plasticizer effect: DMF works not only as a polar plasticizer destroying ionic clusters but also as a nonpolar plasticizer shifting the T_g of the matrix to considerably lower temperatures. Although the effects of polar plasticizers and nonpolar plasticizers have been actively studied recently by several research groups$^{5-7}$, a strong dual plasticizer effect has not been reported. Bazuin and Eisenberg^7 recently studied the effects of polar (glycerol) and nonpolar (ethyl benzene) plasticizers on the dynamic mechanical properties of styrene/methacrylic acid ionomers. They found that the polar plasticizer essentially eliminated the higher temperature modulus transition, associated with ionic domains, caused the modulus transition to become as sharp as that noted in PS, and slightly suppressed the matrix T_g. On the other hand, the nonpolar plasticizer shifted to lower temperatures and broadened both the higher temperature ionic domain transition and the lower temperature matrix T_g transition.

Another important point which should be mentioned is that, after heat treatment of the 8.5 mol% sample cast from DMF solution, both the storage and loss modulus *versus* temperature curves, as depicted in *Figures 3* and *4*, return to the original curves obtained for compression-moulded samples (*Figures 5* and *6*). This result has an important implication for sample making procedure by solvent casting because DMF is a very effective solvent for ionomers. Although ionic aggregate structures are completely destroyed by DMF, as is seen in polyelectrolyte behaviour of ionomers in this solvent^8, the ionic aggregate structure can be recovered by a proper thermal treatment after the solvent casting. Thus similar samples can be obtained by compression moulding and by solvent casting with proper thermal treatment.

CONCLUSIONS

Dynamic mechanical measurements were used to study the effect of sample history, such as thermal treatment and cast-solvent history. Thermal treatment for ionomers with low ion content (2.5 mol%) enhances cluster formation. DMF is found to be a useful dual plasticizer that not only destroys the ionic aggregates but also decreases the T_g of matrix hydrocarbon chains. Thermal treatment of solvent (DMF)-cast samples with high ion content (8.5 mol%) produces an ionic aggregate structure of the ionomers, which is comparable to that observed in compression-moulded samples. The possibility of further enhancing cluster formation for the ionomers with high ion contents by additional thermal treatment has been considered but the high temperatures needed for thermal treatment cause degradation of samples, making analysis difficult. Our results have an important implication in that cast samples from DMF give the same ionic aggregate structures as those seen in compression-moulded samples when proper thermal treatment is applied. Therefore, one can compare results obtained on very thin films made by solvent casting (for example, deformation mechanisms observed by TEM) to those obtained on samples made by compression moulding (for example fatigue behaviour). We will report these results in future papers.

ACKNOWLEDGEMENT

We thank Professors J. Scheinbeim and B. A. Newman for kindly allowing us to use a Piezotron. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the US Army Research Office is also gratefully acknowledged.

REFERENCES

1 Eisenberg, A. and King, M. 'Ion-Containing Polymers', Academic Press, New York, 1977
2 MacKnight, W. J. and Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 41
3 Pineri, M. and Eisenberg, A. (Eds) 'Structure and Properties of Ionomers', NATO ASI Series C, 198, D. Reidel, Dordrecht, 1987
4 Galambos, A. F., Stockton, W. B., Koberstein, J. T., Sen, A., Weiss, R. A. and Russell, T. P. *Macromolecules* 1987, **20**, 3091

5 Lundberg, R. D., Makowski, H. S. and Westerman, L. *ACS Symp. Ser.* 1980, **187**, 67

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

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

8 Lundberg, R. D. and Phillips, R. R. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 1143

9 Hara, M. and Jar, P. *Polym. Comm.* 1987, **28**, 52

10 Hara, M., Jar, P. and Sauer, J. A. *Macromolecules* 1988, **21**, 3183

11 Hara, M. and Jar, P. *Macromolecules* 1988, **21**, 3187

12 Hara, M., Jar, P. and Sauer, J. A. *Polymer* in press

13 Register, R. A., Sen, A., Weiss, R. A. and Cooper, S. L. *Macromolecules* 1989, **22**, 2224