NOTES

Cluster Formation in Plasticized Poly(phenylene oxide) Ionomers

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Ionomers are polymers containing relatively small amounts of ionic groups, attached to nonionic polymer backbone chains.[1,2] Ionic groups form ion aggregates, or multiplets,[3] which influence the properties of polymers significantly. In many ionomer systems, a small-angle X-ray scattering (SAXS) peak[4–8] and two glass transitions (T_gs)[9] have been observed. In 1990, the multiplet-cluster model, the Eisenberg–Hird–Moore (EHM) model,[10] was proposed to interpret SAXS and mechanical data of random ionomers. According to the model, the multiplet acts as a physical crosslink which induces reduction in chain mobility surrounding the multiplet. The size of the restricted mobility region is not large enough to show its own T_g. However, as ion concentration increases, the restricted mobility regions start to overlap. Eventually, regions become large enough to have their own T_g. These regions are called clusters, and the ionomers behave as two-phase material.

Hseih and Peiffer[11] investigated the miscibility of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPhO)-polystyrene (PS), sulfonated PPhO (NaSPPhO) ionomer-PS, PPhO-sulfonated PS (SPS) ionomer, and NaSPPhO ionomer-SPS ionomer. They found that the miscibility of blends depends on the sulfonation of ionomers. The unfunctionalized polymer blends are miscible over the whole composition range, but miscibility is reduced upon functionalization. The miscibility of blends of similar polymer pairs was investigated by Register and Bell,[12] Bazuin et al.,[13] Tomita and Register,[14] and Pan et al.[15] Vulkovic et al.[16] studied the phase-behavior of sulfonated PPhO ionomer blends with poly(styrene-co-bromostyrene).

Lee and Lee[17] investigated the properties of sulfonated PPhO ionomers. The glass transition temperature of the ionomer was found to increase with sulfonation, and that there is a β-transition at 40°C below the matrix T_g. They reported that the NaSPPhO ionomer shows a thermal decomposition at ca. 230 to 260°C. In this temperature range, the bonds between a benzene ring of a polymer chain and a sulfonate group may break. They observed a weak SAXS peak of the ionomer, and proposed that the ionomer forms only weak ion aggregates because of the rigidity of PPhO polymer chains.

In some ionomer systems, clustering is induced by plasticization. Examples include plasticized systems of poly(styrene-co-4-vinylpyridinium methyl iodide)[18] and poly(methyl methacrylate-co-cesium methacrylate)[19] ionomers. Thus, in the present study, we investigated the effects of plasticization on cluster formation in the NaSPPhO ionomer system and determined whether we can observe a cluster T_g by lowering the glass transition temperature of the NaSPPhO ionomer via plasticization. This study was carried out to answer to the question as to why the unplasticized ionomer having multiplets does not show a cluster glass transition.

EXPERIMENTAL

Sulfonation

A poly(2,6-dimethyl-1,4-phenylene oxide) (PPhO) sample of $M_w = ca.$ 200000 was obtained from Aldrich. The method of Makowski et al.[20] for homogeneous sulfonation was used to produce the sulfonated PPhO (NaSPPhO) sample. To determine ion concentration, the sample was dissolved in a benzene–methanol (9 : 1, v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic sodium hydroxide to the phenol-phthalein end point. Ion content was ca. 5.7 mol%. Neutralization of the acid groups was achieved by adding a predetermined quantity of methanolic sodium hydroxide to 5% (w/v) ionomer solution in a benzene–methanol (9 : 1, v/v) mixture. The solution was freeze dried and then dried further under vacuum at 175°C for 1 day.

Plasticization

Plasticized ionomers were obtained by dissolving the ionomers in a mixed solvent of benzene–methanol (9 : 1, v/v) and adding dioctyl phthalate (DOP) to the ionomer solution. The ionomer-plasticizer blends were freeze-dried and further dried under vacuum at 80°C for 2 days.

Sample Preparation

For DMTA measurement, the samples were compression molded at 30 MPa. Sample notations and molding temperatures are listed in Table I. The samples molded at high temperatures were quenched to remove crystallinity which might influence mechanical properties. Sample notation for the plasticized sodium sulfonated PPhO ionomer is NaSPPhO-x, where x indicates wt% of DOP in a sample. The dimensions of the molded

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Table I. Sample notations and molding temperature

Sample notation	Molding temperature/°C
PPhO	290
NaSPPhO	270
PPhO-33	150
NaSPPhO-4	250
NaSPPhO-9	220
NaSPPhO-17	200
NaSPPhO-24	180
NaSPPhO-31	170

samples were approximately $2.5 \times 6.5 \times 30$ mm.

Dynamic Mechanical Thermal Analysis (DMTA)

Mechanical measurement was performed using a Polymer Laboratories Mark II dynamic mechanical thermal analyzer (DMTA) in the dual cantilever bending mode, at frequencies of 0.3, 1, 3, 10, and 30 Hz and heating rate of $1°C \min^{-1}$. For each sample, the storage modulus (E') and loss modulus (E'') were obtained as functions of temperature.

RESULTS AND DISCUSSION

Figure 1 shows the storage and loss moduli of PPhO and NaSPPhO samples as functions of temperature at 1 Hz. For the PPhO sample, the polymer shows a glassy modulus up to 210°C, and above that temperature the modulus starts to drop rapidly. For the NaSPPhO sample, drop in the modulus starts at *ca.* 220°C. The rubbery moduli at 270°C are 6.3×10^6 Pa for the NaSPPhO and 0.8×10^6 Pa for the PPhO. This is due to the presence of multiplets which act as physical cross-links. Similar results were observed for poly(styrene-*co*-sodium methacrylate) ionomers.[21]

We determined the peak in the $\log E''$ curve as a glass transition temperature (T_g); the T_g of the NaSPPhO is *ca.* 228°C, which is *ca.* 6°C higher than that of the PPhO polymer. The higher T_g of the ionomer is owing to the presence of multiplets and copolymerization effect.[22] The increase in T_g by ionization is larger for the SPS case than for the NaSPPhO ionomers at a comparable ion content. This is due to the fact that the PPhO polymer chain has a higher T_g (*ca.* 210°C by DSC) than PS polymer (*ca.* 100°C by DSC),[23] and thus the PPhO polymer chain has some difficulty in forming multiplets. The NaSPPhO ionomer should thus have smaller and fewer multiplets than the SPS ionomer does.[2]

The mechanical properties of DOP-plasticized PPhO and NaSPPhO samples are shown in Figure 2. The storage modulus for the plasticized NaSPPhO samples starts to decrease at lower temperatures as the plasticizer content increases. When one looks at the $\log E''$ curves, one sees one peak at *ca.* 80°C and a shoulder at *ca.* 100°C for the plasticized homopolymer, while two peaks are observed for the plasticized NaSPPhO ionomers. The shoulder is thought to be associated probably with crystallization behavior in the PPhO polymer. The temperatures of the peak at lower temperatures are 126, 119, and 109°C, and those at higher temperatures are 220, 216, and 211°C for the ionomers containing 17, 24, and 31 wt% of DOP, respectively. The high-
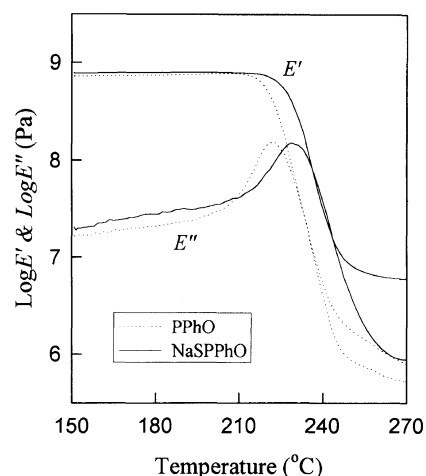

Figure 1. Storage modulus (E') and loss modulus (E'') as functions of temperature for PPhO and NaSPPhO samples, measured at 1 Hz.
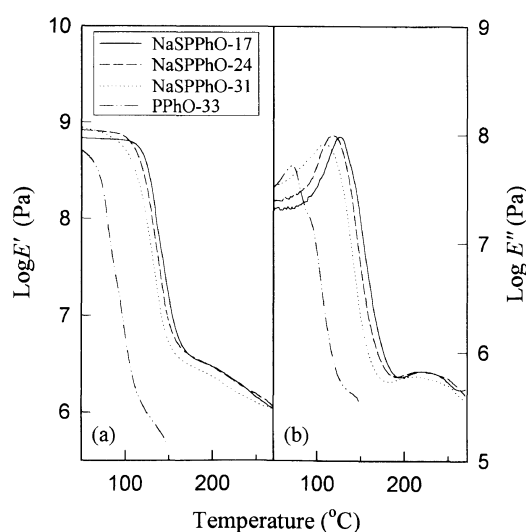

Figure 2. (a) Storage modulus (E') and (b) loss modulus (E'') as functions of temperature for plasticized PPhO and NaSPPhO samples, measured at 1 Hz.

temperature peak is probably due to the cluster T_g, and similar results were observed for the plasticized SPS ionomer system.[24] The nonpolar plasticizer, DOP, molecules reside in nonpolar matrix and cluster regions, but not in polar multiplets. With increasing plasticizer content, the matrix T_g decreases, and cluster T_g drops. If the plasticizer is added sufficiently, the cluster T_g is observed below the thermal decomposition temperature (*ca.* 270°C: This temperature in DMTA experiments is relevant to *ca.* 250°C in DSC and TGA studies). As the matrix T_g drops, the kinetic energy of the polymer chains, kT_g, decreases. Thus, the flexibility of polymer chains increases to facilitate multiplet formation. These two factors contribute to cluster T_g peak formation at *ca.* 220°C.

Matrix and cluster T_gs are shown as functions of the amount of plasticizer in Figure 3. In the figure, the matrix T_g decreases rapidly with increasing DOP content from 0 to 10 wt% [*ca.* $-8.5°C/(wt\%$ of DOP)]. Above that plasticizer content, T_g decreases gently [*ca.* $-1°C/(wt\%$ of DOP)]. For samples containing below 10 wt% of plasticizers, reliable cluster T_g data were not obtained
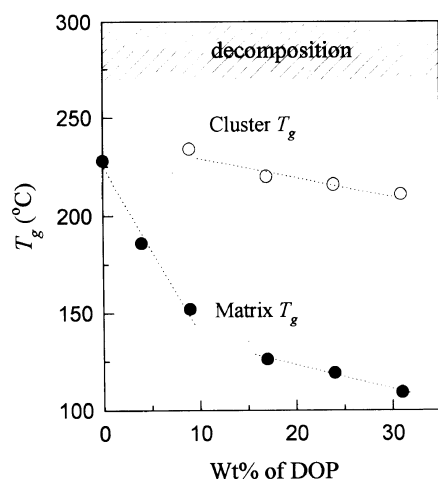
Figure 3. Matrix and cluster glass transition temperatures measured from peaks of $\log E''$ curve (at 1 Hz) for unplasticized and plasticized ionomers as functions of wt% of DOP.

Table II. Activation energies (E_a) of matrix and cluster T_gs

Sample notation	E_a for the matrix T_g kJ mol^{-1}	E_a for the cluster T_g kJ mol^{-1}
PPhO	1280	—
NaSPPhO	980	—
PPhO-33	980	—
NaSPPhO-17	650	250
NaSPPhO-24	500	240
NaSPPhO-31	460	230

because T_g was very close to and even above the thermal decomposition temperature. When plasticizer content is ca. 10 to 30 wt%, the cluster T_g decreases with increasing DOP content at ca. $-1°C/(\text{wt}\% \text{ of DOP})$. Cluster T_g as a function of wt% of DOP is similar to that of matrix T_g. One can obtain the cluster T_g of an unplasticized ionomer by extrapolation to 0 wt% of plasticizer. The extrapolated cluster T_g is $>300°C$, which is far above the bond-breakage temperature of the ionic groups from the benzene rings. Thus, we cannot obtain cluster T_g of the unplasticized ionomer.

Activation energies $(E_a$s) for matrix and cluster glass transitions were calculated using Arrhenius plots of log frequency vs. inverse temperature. Activation energies are listed in Table II.

E_a for matrix T_g of PPhO is ca. 1280 kJ mol^{-1}, while that of the PPhO polymer containing 33 wt% DOP (PPhO-33) is ca. 980 kJ mol^{-1}. For the unplasticized ionomer, E_a for the matrix glass transition is ca. 980 kJ mol^{-1}. For the plasticized ionomers, E_as for the matrix T_g are ca. 460—650 kJ mol^{-1}, while those for the cluster T_g, 240 kJ mol^{-1}. These activation energies are similar to those of the plasticized Na neutralized SPS ionomers, in which E_as for the matrix and cluster T_gs

were ca. 500 kJ mol^{-1} and ca. 200 kJ mol^{-1}, respectively.[25] This implies that activation at T_gs may be similar in the two plasticized ionomer systems. The very similar E_as for the cluster T_g suggest that ion-hopping of sodium sulfonate groups, possessed by these two systems, is involved strongly in cluster glass transition mechanisms of the two ionomer systems.[2,26,27]

REFERENCES AND NOTES

1. A. Eisenberg and M. King, "Ion-Containing Polymers, Physical Properties and Structure," Academic Press, New York, N.Y., 1977.
2. A. Eisenberg and J.-S. Kim, "Introduction to Ionomers," Wiley, New York, N.Y., 1998.
3. A. Eisenberg, *Macromolecules*, **3**, 147 (1970).
4. F. C. Wilson, R. Longworth, and D. J. Vaughan, *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*), **9**, 505 (1968).
5. C. L. Marx, D. F. Caulfield, and S. L. Cooper, *Macromolecules*, **6**, 344 (1973).
6. W. J. MacKnight, W. P. Taggart, and R. S. Stein, *J. Polym. Sci., Polym. Symp.*, **45**, 113 (1974).
7. M. Fujimura, T. Hashimoto, and H. Kawai, *Macromolecules*, **14**, 1309 (1982).
8. R. B. Moore, D. Bittencourt, M. Gauthier, C. E. Williams, and A. Eisenberg, *Macromolecules*, **24**, 1376 (1991).
9. B. Hird and A. Eisenberg, *J. Polym. Sci., Polym. Phys., Ed.*, **28**, 1665 (1990).
10. A. Eisenberg, B. Hird, and R. B. Moore, *Macromolecules*, **23**, 4098 (1990).
11. D. T. Hseih and D. G. Peiffer, *Polymer*, **33**, 1210 (1992).
12. R. A. Register and T. R. Bell, *J. Polym. Sci., Part B, Polym. Phys.*, **30**, 569 (1992).
13. C. G. Bazuin, L. Rancourt, S. Villeneuve, and A. Soldera, *J. Polym. Sci., Part B, Polym. Phys.*, **31**, 1431 (1993).
14. H. Tomita and R. A. Register, *Macromolecules*, **26**, 2796 (1993).
15. Y. Pan, Y. Huang, B. Liao, M. Chen, G. Cong, and L. M. Leung, *J. Appl. Polym. Sci.*, **65**, 341 (1997).
16. R. Vukovic, G. Bogdanic, A. Erceg, D. Fles, F. E. Karasz, and W. J. MacKnight, *Polymer*, **39**, 2847 (1998).
17. Y.-K. Lee and C. H. Lee, *Polymer* (*Korea*), **20**, 191 (1996).
18. D. Wollmann, C. E. Williams, and A. Eisenberg, *Macromolecules*, **25**, 6775 (1992).
19. J.-S. Kim, H.-S. Kim, and A. Eisenberg, *Bull. Korean Chem. Soc.*, **19**, 623 (1998).
20. H. S. Makowski, R. D. Lundberg, and G. L. Singhal, U. S. Patent 870841 (1975).
21. J.-S. Kim, R. J. Jackman, and A. Eisenberg, *Macromolecules*, **27**, 2789 (1994).
22. The glass transition temperatures for random copolymers change with composition between those of the homopolymers, which is a copolymerization effect.
23. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," John Wiley & Sons, New York, N.Y., 1988.
24. R. A. Weiss and J. J. Fitzgerald, *J. Polym. Sci., Part B, Polym. Phys.*, **24**, 1064 (1991).
25. J.-S. Kim, S. B. Roberts, A. Eisenberg, and R. B. Moore, *Macromolecules*, **26**, 5256 (1993).
26. B. Hird and A. Eisenberg, *Macromolecules*, **25**, 6466 (1992).
27. J.-S. Kim, K. Yoshikawa, and A. Eisenberg, *Macromolecules*, **27**, 6347 (1994).