SHORT COMMUNICATION

Glass Transition in Aliphatic Ionenes

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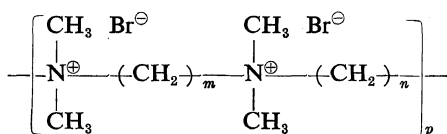
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The synthesis of aliphatic ionenes has been studied by Rembaum, *et al.*[1,2] Only a few investigations, however, have been reported on their physical properties, owing to their high hygroscopic property. Eisenberg, *et al.*,[3] measured the glass transition temperatures (T_g) of the aliphatic ionene—plasticizer systems by using DSC, and obtained T_g for nonplasticized polymers by extrapolation. By the use of a torsional braid analysis (TBA) instrument, we succeeded in observing directly the dynamic mechanical properties of several ionenes and the T_g values of nonplasticized polymers.

The structure of the aliphatic ionenes studied is as follows:

$$\left[\begin{array}{c} \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{-N^{\oplus}}}}} \overset{\displaystyle Br^{\ominus}}{} -(CH_2)_m- \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{N^{\oplus}}}}} \overset{\displaystyle Br^{\ominus}}{} -(CH_2)_n- \end{array} \right]_p$$

A polymer with this structure is called an m, n ionene. Six different ionenes were prepared by the method described by Rembaum.[2] The intrinsic viscosities of these polymers were 0.04—0.10 dl/g in 0.4-M KBr aqueous solutions. The dynamic mechanical properties were measured by a Chemical Instrument Co. torsional braid analyser, Model 100-B1. A glass-fiber braid was immersed in a *ca.* 30% aqueous solution of the polymer and dried under vacuum. Then the braid was set in an environmental chamber of the TBA instrument, and dried again under vacuum at a temperature above T_g. This procedure insured that the measurements were made on perfectly dried states. After the

introduction of dry N_2 gas, the measurements were performed at a heating rate of 1°C/min.

Figure 1 shows the temperature dependence of the relative rigidity and the damping index of four ionenes. A dispersion was observed in the region of 90—140°C for each polymer, except 6, 6 ionene. Each dispersion was observed at the same temperature for both heating and cooling runs. The 6, 6 ionene, which had no dispersion in its TBA measurement, showed a very distinct X-ray diffraction pattern in com-
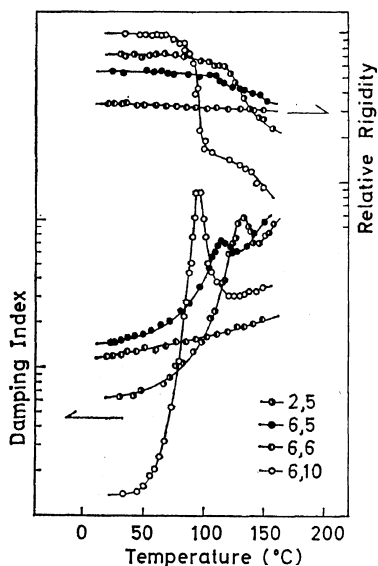
Figure 1. Temperature dependence of the relative rigidity and the damping index of aliphatic ionenes. Curves are arbitrarily vertically shifted. (m, n) in the figure refers to m, n ionene.

parison with the other ionenes, which indicated high crystallinity. From these results, the dispersion can be attributed to the initiation of micro-Brownian motions of the chains in the amorphous regions. Since the measuring frequency of TBA, which varies from 0.4 Hz (room temperature) to 0.2 Hz (absorption maximum), is very low, we can regard the absorption maximum temperatures as the static T_g's. Thus the absorption maximum temperatures are called T_g's in this communication.

Our directly measured T_g values lie between 90 and 140°C, whereas the values of T_g reported previously for the same ionenes, which were obtained by extrapolations from the H_2O plasticized ionene systems, fell between −20 and 0°C.[3] The effects of H_2O on T_g in 6, 10 ionene were examined with the TBA method in order to clarify the causes of discrepancy. Figure 2
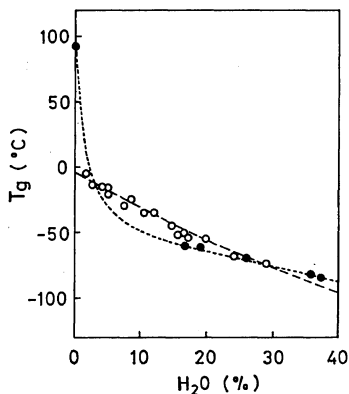

Figure 2. Variation of T_g with H_2O content for 6, 10 ionene (filled circles). Data reported by Eisenberg, *et al.*,[3] for 6, 8 ionene (open circles); broken line indicates their extrapolation.

shows the variation of T_g with H_2O content in 6, 10 ionene. In the same figure, the values of 6, 8 ionene from the paper of Eisenberg, *et al.*, are included. There is no significant difference between the data except in the region of extremely low H_2O content. Eisenberg and his coworkers used the equation of T_g of plasticized systems for extrapolating to zero H_2O content. Their extrapolation now seems rather to give estimates for the amorphous and ionized state of the ionenes. The abnormal plasticizing effects

on the ionenes in the region of low plasticizer content seem to be related to the change of polymer conformations.

In Figure 3, the effects of molecular weight on T_g are shown. It is clear that the T_g values obtained in this study are not influenced by the chain ends. Following the $[\eta]$—M_w relation of 6, 6 ionene reported by Casson,[4] the weight-average molecular weight of 6, 5 ionene with $[\eta]=0.05$ dl/g is estimated to be about 2000. It is quite characteristic that the molecular-weight dependence on T_g is much smaller than that for nonionic organic polymers.

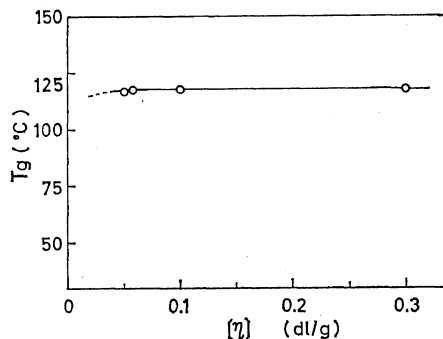In Figure 4, the T_g values determined are

Figure 3. The effects of molecular weight on T_g (6, 5 ionene). $[\eta]$ was measured in 0.4-M KBr aqueous solution.
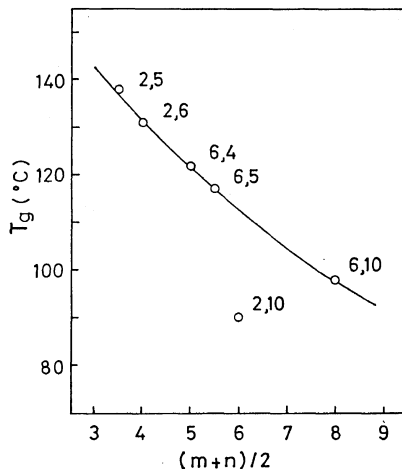

Figure 4. Variation of T_g with average spacing of the ions. (m, n) in the figure indicates m, n ionene.

plotted as a function of $(m+n)/2$, which is the average spacing of the ions. T_g increases systematically as $(m+n)/2$ decreases, except for 2, 10 ionene. Because $(m+n)/2$ is approximately proportional to the inverse of the ionic concentration in polymers, this behavior can be understood as an effect of the strong ionic fields. The reason why the behavior of 2, 10 ionene differs from the others is not very clear, but in this particular ionene the lack of uniformity of the ionic spacing may have made $(m+n)/2$ an unsuitable measure. The work to get more extensive data and to interpret those results from the view point of molecular structures is in progress.

REFERENCES

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2. A. Rembaum, H. Rile, and R. Somano, *ibid. Part B*, **8**, 457 (1970).
3. A. Eisenberg, H. Matsuura, and T. Yokoyama, *Polymer J.*, **2**, 117 (1971).
4. D. Casson and A. Rembaum, *Macromolecules*, **5**, 75 (1972).