Transition in Solution of Polyvinyl Acetate in Toluene

Satoru Mashimo, Yoshio Otsubo and Keniti Higasi

School of Science and Engineering, Waseda University, Shinjuku, Tokyo

(Received July 29, 1970)

The dielectric properties of polyvinyl acetate in toluene were studied over a frequency range of 1—150MHz at various temperatures. Molecular weights of the polyvinyl acetate were determined by intrinsic viscosities to be 7900, 17200, 43000, 165000, and 387000. Dielectric measurements[1] on these five samples were carried out at the same concentration, *viz.*, 5% by weight.

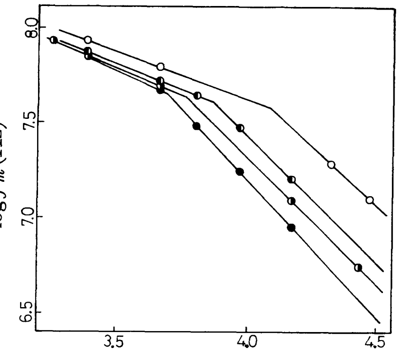
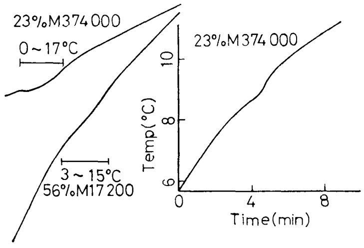


Fig. 1. Plot of $\log f_m$ *vs.* $1/T$.
○: 5%M 7900; ◐: 5%M 17200; ◑: 5%M 43000
●: 5%M 165000, 5%M 387000.

When the logarithm of the frequency of maximum dielectric absorption is plotted against the reciprocal of absolute temperature, two straight lines are obtained (Fig. 1). The point at which two lines intersect is taken tentatively as transition temperature. The apparent activation energy is 2.8 kcal/mol above this temperature, and 6.3 kcal/mol below it. The dielectric behavior of the sample changes at this temperature. This is similar to the transition temperature of solid hydrogen halides[2] or of solid polymers.[3] The values of ε_0, ε_∞ obtained from the Cole-Cole plot change at this temperature; above it Cole's distribution parameter α decreases with increasing temperature, while it remains constant below.



DTA Heating curve

Fig. 2. Results of heat capacity measurements.

The results of differential thermal analysis are shown in Fig. 2. A small but abrupt change of heat capacity could be observed in all the samples having sufficiently high concentrations. The change is detected also in the heating curve (Fig. 2).

The transition temperature determined from heat capacity measurements slightly differs that of dielectric measurement. However, it appears certain that they would approach each other, if the solution of the same concentration could be employed for the two sorts of measurements.

The transition phenomenon thus depends on the concentration and also the molecular weight of the solute. When the transition temperature is plotted against $1/M$, the following equation for a straight line appears to be valid:

$$T_{\text{transition}} = 272 - 2.2 \times 10^5/M \quad (^\circ\text{K}) \qquad (1)$$

This equation is very similar to that between the glass transition temperature T_g and the molecular weight M of polyvinyl acetate in the solid state

$$T_g = 310 - 1.8 \times 10^5/M \quad (^\circ\text{K}) \qquad (2)$$

which is obtained from studies on nuclear magnetic resonance.[4]

---

[1] S. Mashimo and K. Higasi, to be published.

[2] S. Havriliak, Jr., and R. H. Cole, *Discuss. Faraday Soc.*, **23**, 78 (1957).

[3] S. Saito and T. Nakajima, *J. Appl. Polymer Sci.*, **2**, 2455 (1959).

[4] K. Hattori and A. Nojiri, unpublished results. Regarding polystyrene *cf.* T. G. Fox, Jr., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).