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Dielectric Transition in a Solution of Linear Poly(vinyl acetate)

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Synopsis. The dielectric constants and losses of linear poly(vinyl acetate) (PVAc) in carbon tetrachloride were measured at various temperatures and frequencies. The results provide proof that dielectric transition in solution occurs for PVAc, irrespective of its sources.

The interesting phenomenon of dielectric transition in solution was first discovered for poly(vinyl acetate) (PVAc) in toluene.[1] Later the same phenomenon was found also for PVAc in carbon tetrachloride,[2] poly(vinyl chloride) in dioxane[3] and poly(*p*-chlorostyrene) in carbon tetrachloride.[3] One interpretation[3] of this transition is that the transition indicates the change in conformation from globular chain molecules (lower temperature) to loosely coiled chain molecules (higher temperature). This new type of transition has also been discussed by several theoreticians, such as Ptitsyn *et al.*,[4] Lifshitz,[5] Edwards,[6] Domb,[7] and Saito.[8]

The purpose of this note is to clear up doubts regarding the polymer samples employed. The samples of PVAc and poly(vinyl chloride) used previously were all from commercial sources, and commercial PVAc is believed to have branched chains. A sample of linear PVAc chains was prepared for this work by the acetylation of linear poly(vinyl alcohol),[9] and its purity was checked by means of the infra-red absorption spectra. The viscosity-average molecular weight of the sample was 6.1×10^4. The carbon tetrachloride was dehydrated and distilled before use. The dielectric measurements[1–3] were carried out by the use of the apparatus described in previous reports.[2,3]

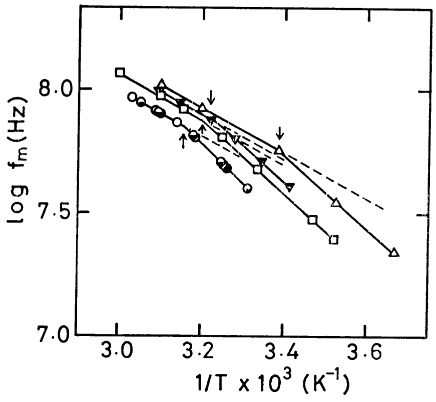

Fig. 1. Plot of $\log f_m$ against $1/T$ for PVAc in carbon tetrachloride.
△: 2.66 wt%, $\overline{M}_n = 0.97 \times 10^4$, $\overline{M}_v = 1.7 \times 10^4$;
▼: 1.93 wt%, $\overline{M}_n = 3.0 \times 10^4$, $\overline{M}_v = 4.3 \times 10^4$;
□: 2.68 wt%, linear PVAc, $\overline{M}_v = 6.1 \times 10^4$;
●: 1.00 wt%, $\overline{M}_n = 1.1 \times 10^5$, $\overline{M}_v = 3.9 \times 10^5$;
○: 2.04 wt%; ◒: 3.20 wt%.

The results of the dielectric measurements are shown in Figs. 1 and 2, together with those for the commercial ones.[2,3] A dielectric transition is observed in the linear PVAc in carbon tetrachloride, too. The plot of $\log f_m$ against $1/T$ gives two straight lines. The transition temperatures (T_t) are obtained from the points at which two lines intersect. The apparent activation energy above T_t is calculated to be 4.2 kcal/mol, while it is 6.9 kcal/mol below T_t. These values

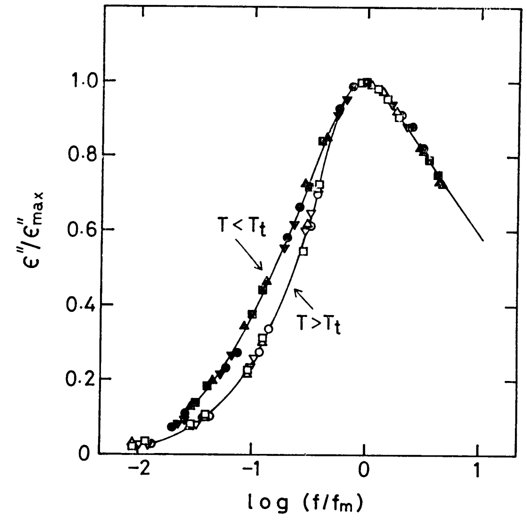

Fig. 2. Master plot of $\varepsilon''/\varepsilon''_{\max}$ against $\log(f/f_m)$ for PVAc in carbon tetrachloride.
▲: 2.66 wt%, $\overline{M}_n = 0.97 \times 10^4$, 0.0 and 13.0 °C; △: 40.0 and 50.0 °C; ▼: 1.93 wt%, $\overline{M}_n = 3.0 \times 10^4$, 19.7 and 25.5 °C; ▽: 44.1 and 50.3 °C; ■: 2.68 wt% linear PVAc, 11.0 and 15.0 °C; □: 50.0 and 60.0 °C; ●: 3.20 wt%, $\overline{M}_n = 1.1 \times 10^5$, 29.0 and 35.0 °C; ○: 50.0 and 55.0 °C.

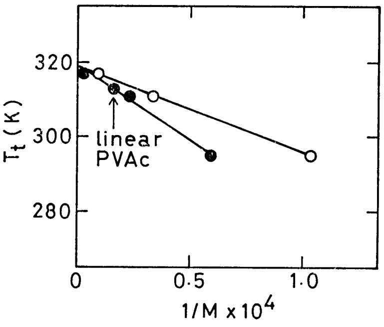

Fig. 3. Plot of T_t against the reciprocal of the molecular weight of PVAc. Open circles refer to the number-average molecular weight and closed circles the viscosity-average molecular weight.

are in complete agreement with those for the commercial PVAc. A slight change in the shape of the two loss curves at T_t is observed, and there is no difference in these curves with the sort of sample, *i.e.*, whether commercial and linear. The temperature, T_t, depends on the molecular weight of PVAc, as is shown in Fig. 3. In conclusion, the effects of the branched chains, and, possibly, of the source of the sample do not appear to play an important role in this kind of transition phenomenon.

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