

NOTES

Glass Transitions in Polymers

In a recent publication Saito and Nakajima¹ presented extensive data on the dielectric loss of polymeric materials over a large range of frequency and over a range of temperature in the neighborhood of the glass transition. On the basis of the variation of the intensity of the loss the authors divided the polymers into two classes, those polymers for which the intensity of loss rose greatly over a range of temperature, and those for which the intensity was essentially constant. They then assigned transition temperatures to these polymers: for the first group (which included the crystallizable polymers) on the basis of the intensity change and for the second group (which included the noncrystallizable polymers) on the basis of high-speed dilatometry. They called these temperatures glass-transition temperatures, T_g .

On the basis of the frequency variation of the dielectric loss as measured by Saito and Nakajima, all these polymers indeed go through a glass transition at a well-defined glass-transition temperature. This transition temperature has, however, no relation to the transition temperature observed by Saito and Nakajima for the crystallizable polymers; indeed, their temperature refers to a different transition. In the case of the noncrystallizable polymers there is only an indirect relation between the value derived from dilatometry and that found from the frequency variations.

On the basis of the WLF theory² of a glass transition a plot of $-\log f_{\max}$ versus T should be superimposable on a plot of

$$\log a_T = -17.44(T - T_g)/(51.6 + T - T_g) \\ 0 \leq (T - T_g) \leq 100^\circ\text{C.} \quad (1)$$

where f_{\max} is the frequency at which the dielectric loss reaches a maximum and a_T is the ratio of relaxation times at temperatures T and T_g . For this superposition to be valid it is necessary only that the relaxation involves an internal

motion governed by the available free volume, a condition which is satisfied for an extensive variety of systems.² The temperature T_g , the glass-transition temperature in the WLF sense, is the temperature at which such motions are stopped, and is, in fact, the only parameter available for fitting the experimental relaxation time ratios to the theoretical equation. The values of T_g determined by this superposition process are listed in Table I, and the fit obtained between the data and the theoretical curve is shown in Figure 1. Significantly worse fits are obtained for T_g 's differing by more than 2°C. from those listed for PVAc, PS, PMMA, and PAN. The region of overlap between the PET data and the region of validity of eq. (1) is so small that this value of T_g is probably good only to about 5°C. The data for PVDC does not fit the theoretical curve as well as might be expected; the fit presented in Figure 1 is about the best that can be done. The most probable explanation would seem to be that the copolymer tested is essentially a block copolymer, and two distinct glass transitions are overlapping.

The values of T_g reported in Table I, column a, for the case of PVAc and especially for PMMA are significantly lower than those reported by Williams, Landel, and Ferry² in their original paper (column b). Since T_g is a function of molecular weight, purity, dryness, etc., we shall not be concerned further with the differences between the values obtained for the samples of Saito and Nakajima and those of other workers. Of much more interest is the difference between the values we obtain here from a WLF plot of Saito and Nakajima's dielectric loss data and the values they deduced from cooling curves on the same samples. With cooling at the rate of 0.3°C./min., they observed breaks in the specific volume-temperature curves at the temperatures shown in Table I, column c, roughly 10°C. higher than the values of T_g deduced here (column a). In the case of PVAc they noted that they could not reach volume equilibrium in 10 hr. for temperatures below 30°C., the point corresponding to their break. This corresponds to the behavior near a glass transition found by other investigators.³ One expects the position of the break to depend on the cooling rate, as the rate is reduced one expects the break to become sharper and the position to approach the thermodynamic second-order glass-transition temperature.* In the case of PVDC, Saito and Nakajima prove that their entire specific volume vs. temperature curve is an equilibrium one, at least for $T > -20.5^\circ\text{C.}$, yet the change of slope they observe is a gradual one, centering at -11°C. The variation of the intensity of the dielectric loss occurs in the same region. The conclusion is inescapable that the same process causes both effects, and that this process is, in fact, an isothermal phase change, a point already made by Saito and Nakajima. By the time the temperature reaches -23°C. , the WLF glass-transition temperature, the majority of the sample has already gone through the phase change and there is not enough amorphous polymer left to affect the specific volume vs. temperature slope at the glass transition.

One would deduce that dilatometry is a poor way to measure glass-transition temperatures. If the glass transition is overlapped by a phase transition reducing the amorphous phase, as is apparent here for PVDC, it is preferable

TABLE I

Polymer	T_g , °C.			
	a	b	c	d
PVAc, polyvinylacetate	19	26	30	—
PS, polystyrene	85.5	85	—	—
PMMA, polymethyl methacrylate	88	110	—	—
PVDC, copolymer of polyvinyl chloride and polyvinylidene chloride	-23	—	-11	-10
PET, polyethylene terephthalate	75.5	—	—	68
PAN, polyacrylonitrile	39	—	—	96

* From fitting Saito and Nakajima's data to a WLF plot (Fig. 1).

^b Data of Williams, Landel, and Ferry.²

^c Same samples as in column a, break in the density-temperature curve, at a cooling rate of 0.3°C./min.¹

^d Same samples as in column a, temperature at which half the intensity change has occurred.

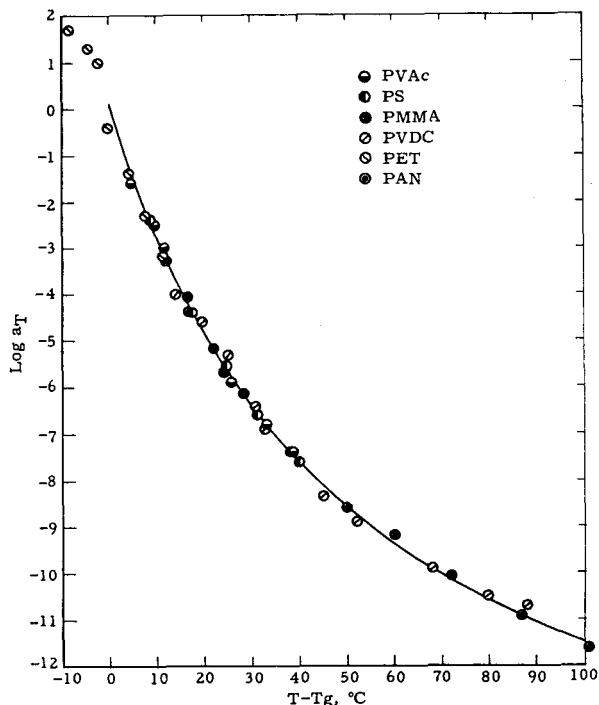


Figure 1.

to observe a variable (e.g., dielectric loss) which is sensitive to changes in the amorphous phase only, instead of the specific volume which reflects the behavior of the entire sample.

Conclusions. Each of the six polymers treated by Saito and Nakajima undergoes a glass transition with relaxation times whose temperature dependence is given by the WLF equation. For the case of the three crystallizable polymers an additional transition occurs at a nearby temperature. This additional transition reduces the amount of the sample that undergoes the glass transition. This second transition, at least for the case of PVDC, can also be observed by dilatometry. In the case of noncrystallizable PVAc, high-speed dilatometry yields a value of T_g which is too high.

We should like to thank our colleague, Dr. D. O. Schissler, for bringing the paper of Saito and Nakajima to our attention.

References

1. Saito, S., and T. Nakajima, *J. Appl. Polymer Sci.*, **2**, 93 (1959).
2. Williams, M. L., R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
3. Fox, T. G., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

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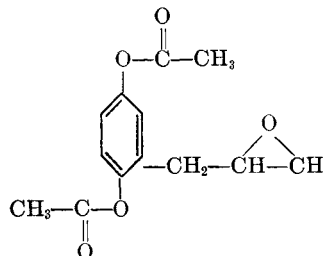
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* This thermodynamic temperature is precisely the glass transition temperature of WLF within an additive constant, the value of which must be the same for all systems.

Poly-3-(2,5-Diacetoxyphenyl)Propylene Oxide

There are a number of polymers described in the scientific and patent literature which are known as electron exchange polymers, redox polymers, or sometimes as nondiffusible reducing agents. Examples of these are polyvinyl hydroquinone,¹⁻³ copolymers of vinyl hydroquinone,^{4,5} polyvinyl gentisal,⁴ polyacrylyl ascorbic acid,⁴ and some acylated polyvinyl hydroquinones.⁶ We have prepared and studied briefly a new hydroquinone-type monomer whose structure is given below:



Monomer Preparation

Allyl hydroquinone (m.p. = 90–91°C.) was dissolved in a slight excess of acetic anhydride and a catalytic amount of concentrated sulfuric acid was added. After the reaction mixture had cooled it was poured onto crushed ice. The crystalline diacetate, after recrystallization, had a melting point of 47–48°C. Results of analysis⁷ were as follows: Calcd. C, 66.6; H, 6.0. Found: C, 66.4; H, 5.8.

Allyl hydroquinone diacetate (29 g., 0.124 mole) and 24.6 g. (0.2 mole) of perbenzoic acid were dissolved in 200 ml. of chloroform. The reaction was maintained at 0°C. for 24 hr. and then extracted three times with cold, aqueous, dilute sodium carbonate solution. After washing with water, drying over anhydrous magnesium sulfate, and removal of the chloroform by distillation, the residue was fractionated through a short distillation column. A small forerun of solid distillate (2 g., boiling range 100–110°C./0.6 mm.) was obtained, followed by 18 g. of product (b.p. 161°C./0.6 mm.). The epoxide of allyl hydroquinone diacetate is a crystalline, almost colorless solid, m.p. = 32°C. Analysis⁷ for C and H gave: Calc'd: C, 62.4; H, 5.6. Found: C, 62.3; H, 5.5. The molecular weight, measured by the freezing point depression of benzene, was determined as 266 as against a theoretical value of 250. The infrared spectrum of the pure epoxide is presented in Figure 1.

Polymerization

In some preliminary polymerization experiments it was found that typical epoxide polymerization catalysts such as anhydrous ferric chloride, boron trifluoride etherate and zinc chloride-aluminum isopropoxide yield oily and semisolid polymers when the pure monomer is treated with these catalysts at 80°C.

In a controlled polymerization, a small reaction vessel, equipped with a stirrer and protected from atmosphere moisture, was charged with 5 g. of pure epoxide, 0.038 g. of freshly prepared aluminum isopropoxide and 0.038 g. of Matheson ACS zinc chloride. The polymerization was carried out at 80°C. with continuous stirring for 6 days. The resulting orange-colored solid was dissolved in 5 ml. of