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## The study of Transition in High Polymers by Photoelastic Method

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In the present study, it is reported that the transition point of high-polymers can be determined by observing the dependency of photoelasticity of that materials upon temperature, and that the value determined by this method agrees with the one by thermal expansion method for P. V. C. but for polystyrene it is larger and rather near to the value by magnetic resonance method.

### § 1. Introduction

The second order transition temperature of high-polymer has been investigated by measuring the effect of temperature upon the coefficient of thermal expansion, specific heat and elastic constant. Recently it has also been measured by the nuclear magnetic resonance method. The present workers investigated it by observing the connection between temperature and photoelasticity of high polymer.

Nowadays for molecular theoretic explanation of the second order transition temperature of high polymer there are two possible approaches; the one is from the view point of rate process, and the other is from the view point of thermodynamical phase change. But in view of the dynamical properties of high-polymer, the latter may be better, because below the transition point, the elasticity is about  $10^{10}$  dyne/cm<sup>2</sup>, which is solid-like and energetic, while above that point, the elasticity becomes about  $10^7$  dyne/cm<sup>2</sup>, which seems to be due to entropy. That fact seems to indicate that the transition process is due to thermodynamical phase change and that above the transition point the micro-Brownian motion is released. If the micro-Brownian motion is released, it may be directly observed by birefringence, because the birefringence

appears in accordance with the motion of molecule. So at the transition point the birefringence may be expected to change from solid-like character to rubber-like character, that is, above that point the birefringence may decrease proportionally to reciprocal absolute temperature,  $1/T$ . In this study the workers ascertained this phenomenon for polystyrene and P.V.C.

## § 2. Experimental Method

The strips of polystyrene and P.V.C. were measured off, whose size was 3.5 cm long, 1.5 cm wide and 0.25 mm thick for P.V.C. and 0.05 mm thick for polystyrene. These strips were cut out from thin films of polystyrene and P.V.C. These films were cast from solution, benzene solution for polystyrene and nitrobenzene solution for P.V.C. They were carefully dried in drier at 30°C. Specimen for observation was hung in furnace which had two windows and whose temperature was raised at the rate of 0.5° C/min during observation.

The specimen was put under tension by hanging a weight at the lower side of it, where it was devised that uniform tension was maintained in specimen. The birefringence of those specimen was measured by the well known Szivessy-Dierkesmann's compensation method through the windows of furnace. The source of light used here was  $D_{Na}$ .

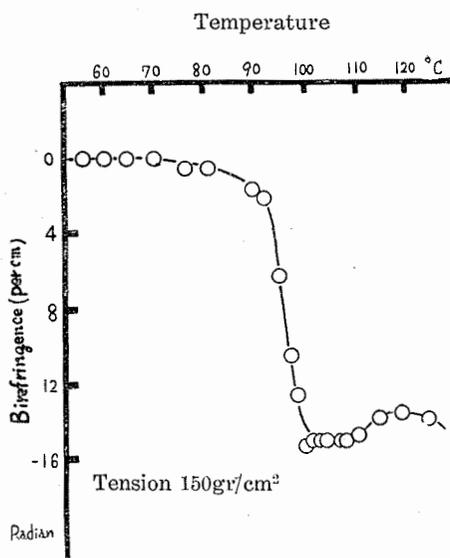


Fig. 1. Dependency of birefringence of polystyrene under 150 gr/cm<sup>2</sup> tension upon temperature.

## § 3. Results and Discussion.

- 1) The effect of temperature upon birefringence under constant tension.

### a) Polystyrene.

The results with polystyrene under 150 gr/cm<sup>2</sup> tension are plotted in Fig. 1, where

the birefringence suddenly increases at about 80°C, and after it attains to the maximum at about 100°C, it slightly decreases with temperature. At about 120°C it again increases with temperature. Fig. 2. shows the results with polystyrene under 100 gr/cm<sup>2</sup> tension and indicates the same tendency as Fig. 1.

The large birefringence below 90°C in Fig. 2 seems to take place because of inner strain of the specimen. It did not seem to appear if the specimen was more carefully annealed. These figures indicate that they can be divided to four regions; the first is solid-like region where the birefringence is small, the second is the transition region where the birefringence abruptly increases with temperature, the third is rubber-like region where the birefringence slightly decreases with temperature, and the last is a region of flowing where the

birefringence increases larger and larger in accordance with temperature. These phenomena agree with the expectation. If the transition temperature is assumed to be a inflexion point of the second region, it becomes 95°C for 150 gr/cm<sup>2</sup> tension and 103°C for 100 gr/cm<sup>2</sup> tension. That indicates that the larger the tension is, the lower the transition point is. It agrees with the results of experiments of elastic properties.<sup>1)</sup> The transition point determined by this method seems to become larger than that measured by the thermal expansion method, but by the magnetic resonance method the transition point becomes about 110°C<sup>2)</sup> and measuring of elastic properties indicate that the transition point is about 100°C.<sup>1)</sup> So the value obtained here seems to be rather reasonable for polystyrene.

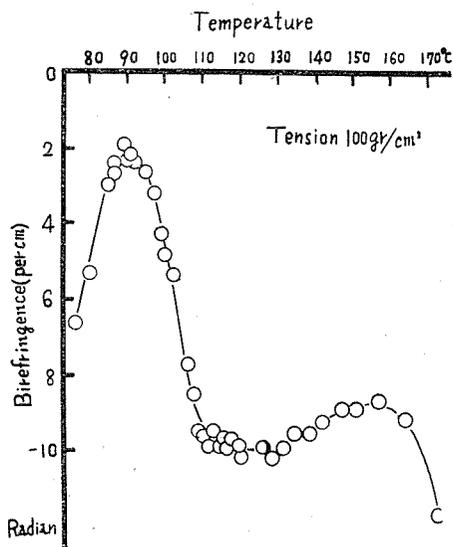


Fig. 2. Dependency of birefringence of polystyrene under 100 gr/cm<sup>2</sup> tension upon temperature.

## b) P.V.C.

The same method as for polystyrene is used for P.V.C. The results are plotted in Fig. 3 for 200 gr/cm<sup>2</sup> tension and in Fig. 4 for 100 gr/cm<sup>2</sup> tension. These figures show the same tendency as the case of polystyrene. The transition temperature determined in the same way as for polystyrene is 70°C for 200 gr/cm<sup>2</sup> tension and 74°C for 100 gr/cm<sup>2</sup> tension. In this case the increase of

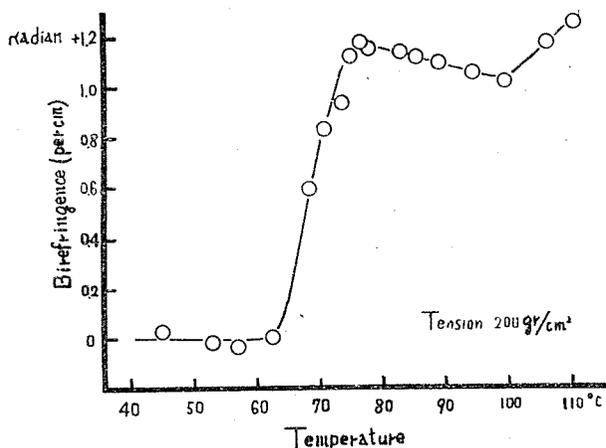


Fig. 3. Dependency upon temperature of birefringence of P.V.C. under 200 gr/cm<sup>2</sup> tension.

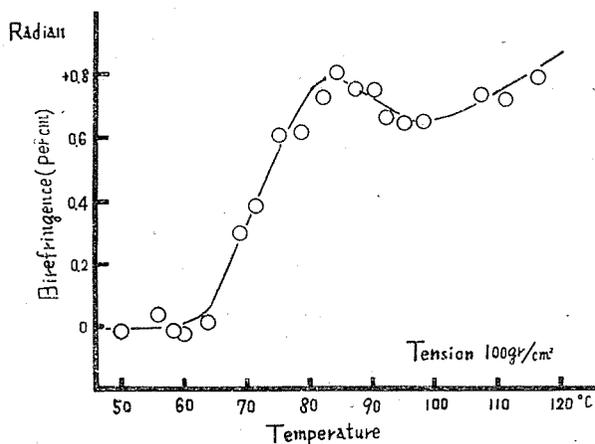


Fig. 4. Dependency upon temperature of birefringence of P.V.C. under 100 gr/cm<sup>2</sup> tension.

tension also tends to lower the transition point. In this case, the transition point is the same as the value determined by other method.

2) The effect of plasticizer upon transition temperature.

The results of observations of P.V.C. with slight nitrobenzene under  $200 \text{ gr/cm}^2$  tension are plotted in Fig. 5. In this case the nitrobenzene plays the role of plasticizer for P.V.C. and the transition point is lowered by about  $10^\circ\text{C}$ . These phenomena agree with the expectation for plasticized materials.

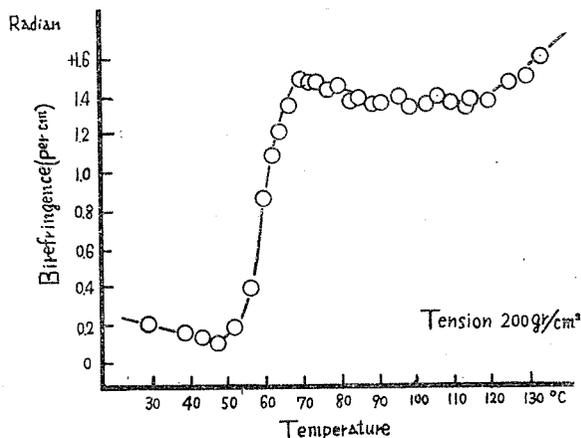


Fig. 5. Dependency upon temperature of birefringence of P.V.C. with slight nitrobenzene.

3) The relation of birefringence to temperature and tensile loads above transition point.

Fig. 6. shows the connection between birefringence and tensile loads at constant temperature. The corrected values of the birefringence and tensile load, under the assumption that the volume of specimens was constant, are plotted in this figure. It indicates that the birefringence is proportional to tensile load. The tangents of these curves are plotted against reciprocal absolute temperature,  $1/T$ , in Fig. 7. The curve of Fig. 7. is a nearly straight line. This agrees with the birefringence expected from rubber elastic theory<sup>3)</sup> and seems to indicate that polystyrene is rubber-like above transition point. E. KLEIN says that polystyrene does not show

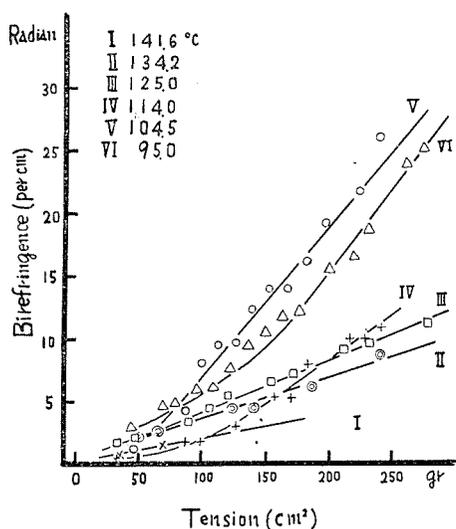


Fig. 6. The connection between birefringence of polystyrene and tensile load.

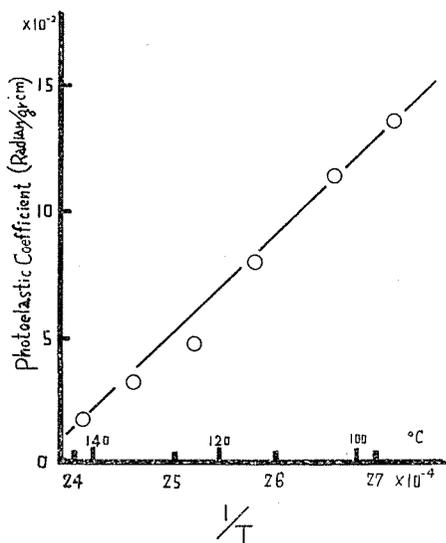


Fig. 7. The connection of birefringence of polystyrene and reciprocal absolute temperature.

rubber elasticity and suddenly flows above the transition point.<sup>4)</sup> The present results seem to disagree with his result. But the present workers think this discrepancy is due to the difference of tensile load used. In the present study the rubber-like stage may be observed because the effect of the cross linkage due to second order bonding effectively appears, as the tension is low.

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