The Transition Phenomenon of Unsaturated Polyester Resin

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So far, the author has studied the relationship between the structure and the transition phenomenon of high polymers such as polyethylene and polyvinylalcohol by volume dilatometry and the nuclear magnetic resonance absorption method. As to polyethylene[1], a crystalline polymer, investigation was made of the effect of the degree of crystallinity and of the degree of chain branching on its transition temperature, and on polyvinylalcohol[2] a study was made of the relationship between the hydroxyl group and the transition phenomenon. There is a report[3] that the glass transition temperature of non-crystalline polymer such as atactic polystyrene largely depends upon the degree of polymerization and that the mechanism of the transition phenomenon can be made clear from the standpoint of rate process. Unsaturated polyester resin (unsaturated alkyd resin) crosslinked by a vinyl compound is a non-crystalline polymer having a three dimensional network. Therefore it is expected that the mechanism of the transition phenomenon of the resin differs from that of non-crystalline polymer such as atactic polystyrene, even if the polyester resin itself shows some transition phenomenon.

Polyester resin in a broad sense includes all the high molecular compounds in which the ester linkage between the carboxyl group and the hydroxyl group is the principal element for the formation of high polymer. In the present paper, however, it stands for the polyester resin in a narrow sense; that is, the unsaturated polyester resin crosslinked by a vinyl compound such as styrene and vinylacetate. As is well known, the polyester resin has many good points in comparison with other synthetic resins. For example it excels in such chemical properties as resistance against acid, alkali, water, oil and organic solvent, as well as in electrical property. Above all arc resistance is its distinguishing character. The completely crosslinked polyester resin is hard and brittle at room temperature and below at about −5°C it becomes more brittle, but above 60°C it becomes abruptly flexible. It seems that there is scarcely found any paper describing at what temperature and by what transition mechanism such a change of property occurs. The dilatometric study by the authors showed that this resin had two transition points of second order and the upper transition temperature was charged by the amount of vinyl compound, and in addition it was investigated by nuclear magnetic resonance absorption method from what struct ture and molecular motion these transition phenomena arose.

Experimental

Samples.—MD-S-O: This sample was prepared by mixing maleic anhydride and diethyleneglycol in the mole ratio of 1 to 1 and by heating the mixture at 180°C for six hours with stirring under nitrogen atmosphere.

MAD-S-O: This sample was prepared by mixing maleic anhydride, adipic acid, and diethyleneglycol in the mole ratio of 9 to 1 to 10 and by heating the mixture at 180°C for four hours with stirring under nitrogen gas atmosphere.

These two samples were viscous liquids having no crosslinking structure and were used as starting substances for the preparation of other samples, that is, all other samples were prepared by adding styrene to MD-S-O or MAD-S-O in the ratio shown in Table I and by heating at 80°C for three hours between glass plates, and in addition after-cure treatment was performed at about 100°C for three hours.

TABLE I. THE AMOUNT OF STYRENE IN THE SAMPLES OF POLYESTER RESIN

Sample	Styrene monomer wt. %	The ratio of C=C group to styrene monomer
MD-S-0	0.0	1 : 0
MD-S-1	10.0	1 : 0.20
MD-S-2	20.0	1 : 0.45
MD-S-3	30.0	1 : 0.77
MD-S-4	35.9	1 : 1
MAD-S-0	0.0	1 : 0
MAD-S-1	10.0	1 : 0.22
MAD-S-2	20.0	1 : 0.50
MAD-S-3	30.2	1 : 1
MAD-S-4	40.0	1 : 1.35

Volume Dilatometry.—The details about this procedure were omitted as they had been described already[1]. Mercury was used as a confining liquid and the temperature range covered was from the

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1) K. Tanaka, This Bulletin, 33, 1060, 1133 (1960).

2) K. Tanaka et al., This Bulletin, 29, 843 (1956); 30, 197, 428 (1957).

3) T. G. Fox and P. J. Flory, *J. Appl. Phys.*, 21, 581 (1950).

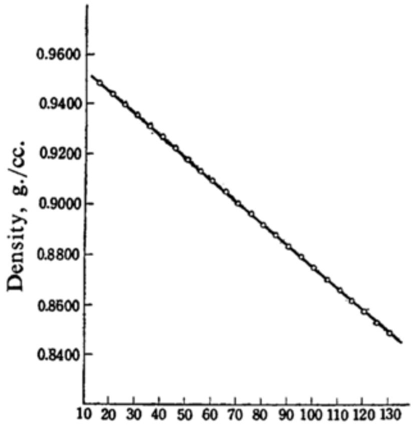

Fig. 1. The density-temperature relationship of silicone oil.

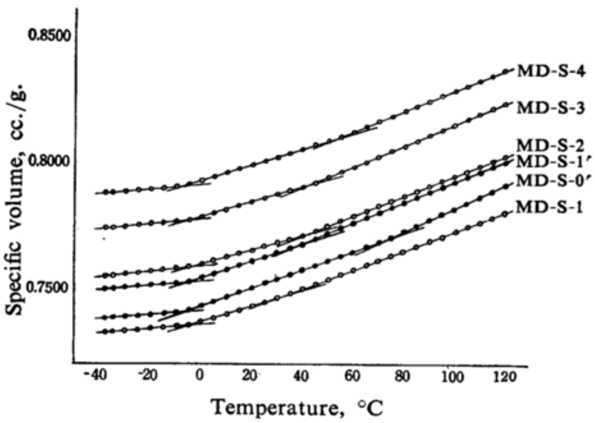

Fig. 3. The volume-temperature curves for the samples of MD series.

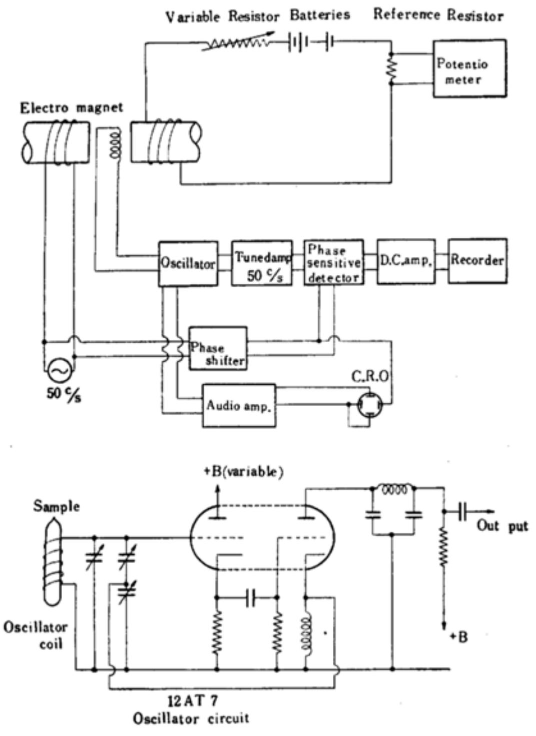

Fig. 2. The constitution of the apparatus for nuclear magnetic resonance absorption.

freezing point of mercury to about 120°C. The bath temperature was varied about five degrees at a time and 20 min. were taken before every measurement in order to let the sample attain equilibrium temperature.

Hydrostatic Method of Measuring Density.— Apparatus. — *Balance.* — An ordinary chemical-balance remodeled a little was used. (sensitivity 1/5 mg.)

Thermostat.—The chrome-plated vessel with stirrer and two heaters of 500 W. was used. It could accomodate two litters of liquid. Temperature control was performed by connecting the Ostwald-type mercury regulator to micro relay in the range of ±0.05 degree.

Dipping Liquid.—As a dipping liquid silicone oil was used. Its qualities were as follows; viscosity 10 c. s. at 25°C, freezing point −65°C, boiling point 200°C, flash point 163°C, and thermal conductivity 0.00032.

Procedure.—The sample was connected to the balance with terylene fiber and dipped into silicone oil, and the density was measured in the temperature range from room temperature to 120°C. The temperature was raised five degrees at a time and 15 min. were taken before every measurement.

Calculation.—The calculation of density at every temperature, d_t was performed according to the following expression,

$$d_t = \frac{W}{W - W_t} \times \rho_t$$

where W was the weight of the sample in air, W_t that in silicone oil and ρ_t the density of silicone oil at the measured temperature. The density-temperature relationship of silicone oil was determined by volume dilatometry in the temperature range from room temperature to 130°C and shown in Fig. 2.

Nuclear Magnetic Resonance Absorption Method. — The usual apparatus consisting of an autodyne oscillator, a lock-in-amplifier, and a recorder was used (Fig. 3). The field intensity was about 3000 gauss. The sample was sealed in the evacuated glass tube.

Results

Dilatometric study was perfomed for the samples of MD series. Specific volume-temperature curves obtained are shown in Fig. 4. In the figure MD-S-O′ is the sample MD-S-O gelatinized by heating at 110°C for three days and MD-S-1′ the sample MD-S-1 after-cured at 100°C for a day.

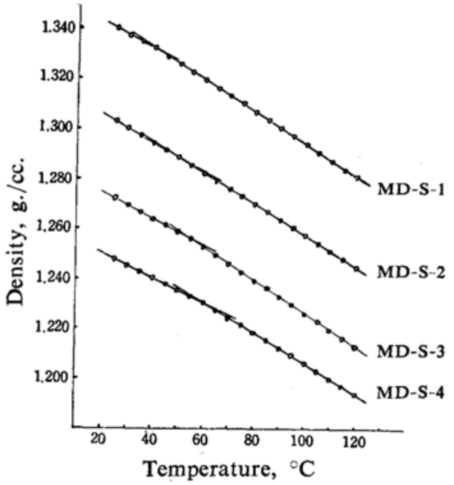

Fig. 4. The density-temperature curves for the samples of MD series.

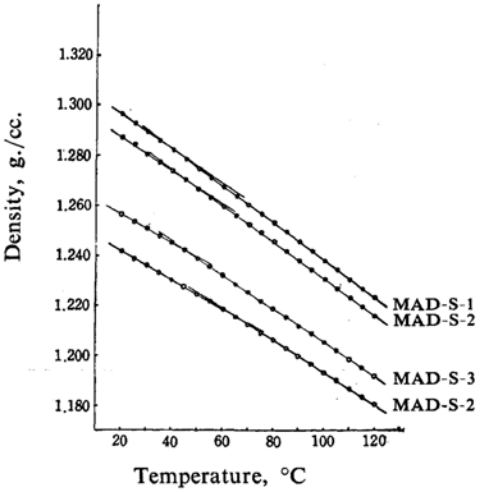

Fig. 5. The density-temperature curves for the samples of MAD series.

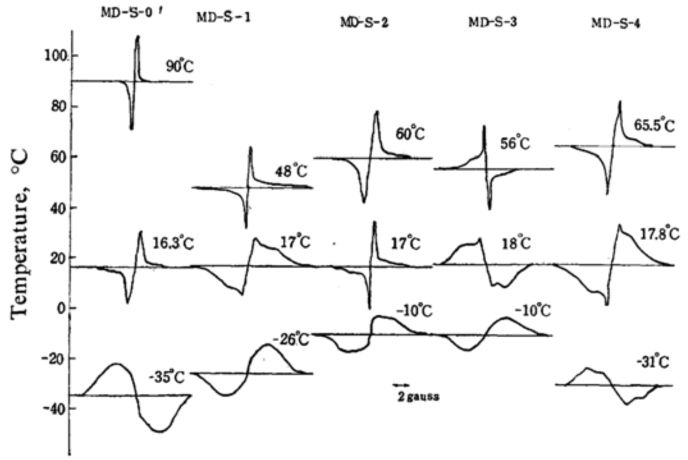

Fig. 6. The derivative absorption curves for the samples of polyester resin.

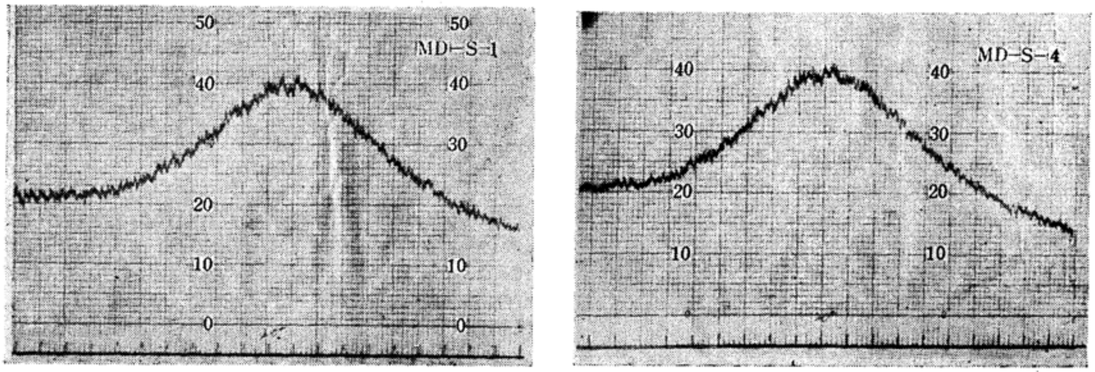

Fig. 7. The X-ray diffraction diagrams for MD-S-1 and MD-S-4.

Hydrostatic study was carried out for all the samples except MD-S-0 and MAD-S-0. Density-temperature curves obtained are illustrated in Figs. 5 and 6.

As is shown in Fig. 2, two second order transition points were observed for each sample of MD series. These temperatures are listed in Table II with the results for MD and MAD series by hydrostatic method.

In Fig. 7 are shown derivative line shapes by nuclear magnetic resonance absorption method for the samples of MD series and the values of second moment, $<\Delta H^2>$, obtained from the derivative curves above and below two second-order transition temperatures for each sample of MD series are listed in Table III.

TABLE II. THE SECOND ORDER TRANSITION TEMPERATURES OF THE SAMPLES OF POLYESTER RESIN (IN °C)

Sample	Dilatometric result		Hydrostatic results
	Lower point	Upper point	
MD-S-0′	−6.5	77.9	—
MD-S-1	−3.5	36.0	40.0
MD-S-1′	−6.0	39.7	—
MD-S-2	−3.0	40.3	50.0
MD-S-3	−4.9	46.0	55.0
MD-S-4	−5.8	57.4	60.0
MAD-S-1	—	—	39.0
MAD-S-2	—	—	42.0
MAD-S-3	—	—	45.0
MAD-S-4	—	—	60.0

TABLE III. THE SECOND MOMENT, (IN GAUSS^2) $<\Delta H^2>$, AT TEMPERATURES ABOVE AND BELOW THE TWO SECOND-ORDER TRANSITION TEMPERATURES FOR THE SAMPLES OF POLYESTER RESIN

Sample	$<\Delta H^2>$ (°C)	$<\Delta H^2>$ (°C)	$<\Delta H^2>$ (°C)	$<\Delta H^2>$ (°C)
MD-S-0′	0.25 (81.3)	5.2 (15.0)	13.7 (−10.0)	19.8 (−78.0)
MD-S-1	3.0 (84.2)	12.9 (16.8)	14.7 (−26.0)	17.3 (−48.0)
MD-S-2	3.1 (70.2)	12.2 (0.0)	14.3 (−17.0)	15.6 (−50.0)
MD-S-3	5.7 (108.0)	11.6 (18.0)	14.3 (−10.0)	16.0 (−45.0)
MD-S-4	5.7 (65.0)	13.5 (18.0)	13.7 (−31.0)	—

Discussion

As was mentioned already, the dilatometric study on the samples of MD series showed that they have two transition points of second-order, and the one was observed below 0°C and the other above room temperature. The transitions below 0°C were observed at nearly equal temperatures for all the samples, while apart from MD-S-0′ and MD-S-1′, those above room temperature were observed at the higher temperature for the sample crosslinked by the larger amount of styrene. Hydrostatic study above room temperature also showed a similar tendency for the samples of MD series and MAD series. Therefore the transition above room temperature is considered to be associated with the crosslinkng structure of the sample. The three dimensional net structure of polyester resin caused by the crosslinking with styrene will become more compact with the increasing amount of styrene until the sample is completely crosslinked. Hence, it is considered that the segmental motion of the polymer is restricted more severely and that the transiton occurs at a higher temperature with the increase of the amount of styrene. This result is well consistent with the result obtained from dielectric measurement by Nakajima and Ishikawa[4] who found two dielectric absorptions at the temperatures above room temperature and below 0°C for the samples of polyester resin. The specific volume of the samples of MD series increases with the increasing amount of styrene. Probably the reason is that the molecular interval is extended by the crosslinking by styrene. Fig. 5 also shows a similar result and the values of density are well consistent with those obtained from Fig. 4.

For MD-S-0′, the lower transition occurs at a temperature almost equal to that of other samples, but the upper transition occurs at 77.9°C, which is higher than that of any other samples. Probably the sample was crosslinked without styrene by the long-time heating and in the sample of this sort the segmental motion was restricted more severely than in the sample completely crosslinked by styrene.

For MD-S-1′, in which the crosslinkings without styrene are considered to exist in addition to those with styrene, only a slight rise of the upper transition temperature was observed. It is likely that the crosslinking without styrene was limited by the styrene contained already in the polymer.

For the samples of MAD series, it was also found that the density decreasing with the increase of the amount of styrene, though it was less affected by the amount of styrene than those of the MD series. In comparing Fig. 6 with Fig. 5, densities and the transition temperature of the sample of MAD series are always lower than those of the sample of MD series containing an equal amount of styrene. Adipic acid does not have C=C bond and is not

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4) T. Nakajima and E. Ishikawa, *Bull. Electrotech. Lab. (Japan)*, **20**, 20 (1956).

crosslinked by styrene, so it is considered that an almost constant spaces are always kept at the vicinity of this atomic group and the segmental motion is not so restricted there. For MAD-S-4, the densities are always smaller than those of others of MAD series and the transition temperature is higher. This sample contains an excess amount of styrene and it is considered that it consists of the mixture of MAD-S-3 and styrene polymer or that it is crosslinked by a dimer or trimer of styrene in addition to the crosslinking by the monomer. If the structure of this sample is of the latter type, the molecular interval will be partly wider than that of MAD-S-3, so the decrease of density is reasonable. However, if so, the lowering of the transition point must be observed because the restriction of mobility became smaller than MAD-S-3. The density of polystyrene is about 1.05 at room temperature and the second order transition temperature is around 80°C. Therefore it is considered that the decrease of density and the rise of transition temperature is due to the existence of styrene polymer.

It is considered generally that the second order transition temperature of the crystalline polymer and the non-crystalline one is the point at which the amorphous region of the polymer starts the large-scale segmental motion or at which side chains and molecular terminal groups start the motion. What is, then, the origin of these two second-order transition points of the crosslinked polymer observed ? The X-ray diffraction diagrams for the two samples of MD series are shown in Fig. 8. These diagrams did not give any peaks showing the existence of the crystalline part. Therefore the samples investigated are considered to have random network of three-dimensions.

According to Nakajima and Ishikawa[4], polar groups attributed to dielectric absorption at a lower temperature are hydroxyl groups at the molecular terminal and free water contained in the polymer, and those at a higher temperature are ester and ether groups whose mobility is affected by crosslinking by styrene. However, it is not considered that the transition at a lower temperature is attributable only to the molecular-end groups and free water, since, as is shown in Table III, the second moment obtained from the derivative curve in Fig. 7 shows the remarkable change at the vicinity of the lower second-order transition point of each sample. In addition, the amount of protons in the motional state estimated from the derivative curves at the vicinity of room temperature, each of which consists of the absorption curve of protons in the rigid state and that of protons in the motional state, is more than 30% in all the samples investigated and the value of 30% is too large to be considered as protons in the molecular terminal groups and in free water. Therefore it is considered that the second-order transition point at a lower temperature range is the one at which protons in diethyleneglycol located at a place distant from the crosslinking point in the sample of polyester resin start the motion. At the temperature above the upper second-order transition point the narrowing of the movement of protons occurs and a sharp derivative curve was obtained. Therefore the transition point is the temperature at which the Brownian motion of the whole molecule becomes violent. But unlike an amorphous polymer such as atactic polystyrene, it is interesting that the shoulders of the derivative curve are observed at the temperature range above the transition temperature till near the temperature at which thermal degradation of the sample takes place and also that the existence of protons in rigid state (which are considered to be protons at the vicinity of crosslinking points) is recognized.

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