

Characterization of Diene Polymers.¹ II. Dilatometric Measurements of Crystallization on Stretching

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ABSTRACT: The crystallization of cured natural rubber and synthetic *cis*-1,4-polyisoprene was investigated by directly following the volume change on stretching and releasing. For this purpose, a dilatometer was constructed, which contained a stretching device in the sealed apparatus. The specimen was stretched and released in a stepwise manner at a constant temperature and the volume change was read out. At higher elongations the volume of the specimen showed a large decrease by increasing the extension ratio, and this was confirmed to be due to crystallization by X-ray measurements. When the crystallization occurred, the volume decreased slowly after stretching and reached a constant value within an hour. Such a time dependence of the volume change was not found in the releasing process. The relationship between the extension ratio and the volume change gave straight lines inflected at the extension ratio α_c on the stretching steps, and α_m on the releasing steps, and α_c was always higher than α_m . The value α_c indicated the extension ratio at which crystallization begins on stretching, while the value α_m indicated the extension ratio at which the last traces of crystallinity disappear on releasing. These two values of synthetic *cis*-1,4-polyisoprene are higher than those of natural rubber. The rate of crystallization of synthetic *cis*-1,4-polyisoprene on stretching is essentially the same as that of natural rubber.

KEY WORDS Characterization / Diene Polymers / Dilatometric Measurements / Crystallization / Stretching / Melting Temperature / Natural Rubber / *cis*-1,4-Polyisoprene / Crystallizability /

Natural rubber is almost pure *cis*-1,4-polyisoprene and does not contain any detectable amounts of other isomeric-structural units,² while synthetic *cis*-1,4-polyisoprene prepared with a Ziegler type catalyst or a lithium catalyst was estimated to contain 99%³ or 92%⁴ of the *cis*-1,4 unit, respectively. Small changes in the structural purity of these polymers must strongly affect their thermal and mechanical properties. Bruzzone, *et al.*,⁵ investigated the mechanical properties of cured natural rubber and synthetic *cis*-1,4-polyisoprenes and suggested that the difference in mechanical properties is due to the crystallizability of the samples.

Although the thermodynamic properties of natural rubber crystallized either by lowering

the temperature or stretching have been studied extensively, those of synthetic polyisoprene have not yet been investigated in detail. So far the results of differential thermal analyses have been reported by Cooper and Smith,⁶ showing that the synthetic *cis*-1,4-polyisoprenes have lower melting transitions than those of natural rubber.

The present investigation was undertaken in order to elucidate the crystallization and the melting behavior of stretched polyisoprene and to evaluate quantitatively the influence of the *cis*-1,4 content on elastomeric properties. In the work reported here an attempt has been made to study the crystallization process by directly following the change of volume on stretching and releasing.

EXPERIMENTAL

Dilatometer

The apparatus for measuring the change of volume is illustrated in Figure 1. It consists of a stretching apparatus (1) connected by a side arm to a glass capillary tube (2) and a glass tube (3) sealed with two rubber O-ring packings (4) and two polytetrafluoroethylene packings (5). Two ring-shaped specimens (about 0.9 g, see later section) were set between a fixed hook (6) and a movable hook (7). The metal parts of the dilatometer were made of stainless steel. The apparatus was filled with mercury up to the height of the movable hook at the maximum elongation of the specimens and was degassed under a vacuum of 10^{-2} mmHg. Then the upper part of the apparatus was filled with degassed water to the reservoir above a needle valve (8) under reduced pressure. The dilatometer was held in a water bath at a constant temperature (within $\pm 0.01^\circ\text{C}$) for the long periods

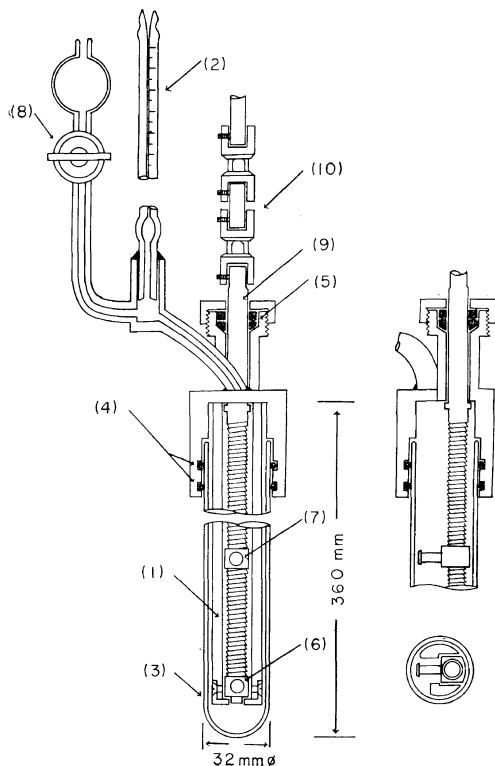


Figure 1. Dilatometer for measuring the volume change of rubber on stretching and releasing.

(usually 6–10 hr) of continuous operation. The fluctuation of the volume of the dilatometer caused by the fluctuation of temperature or a leakage of water was checked for two hours in advance of the measurements, giving an accuracy better than 2×10^{-4} ml. The specimens were stretched by rotating the shaft (9) connected through a universal joint (10) to a geared motor. The fluctuation of the volume of the dilatometer on rotation of the shaft without setting the specimens was found to be within 4×10^{-4} ml, which was accurate enough for practical measurements compared with the volume change of the specimens. The extension ratio was measured with the number of rotations of the shaft.

After the specimens were stretched to a given elongation (usually extension ratio L/L_0 of 0.27 in 20 sec), the change of volume was read out at intervals of a few minutes. When the volume reached a constant value, the next elongation was carried out. After stretching to the highest elongation, usually from 5 to 6 of the extension ratio, the specimens were released in a stepwise manner.

Samples

In the present study (A) smoked sheet natural rubber and (B) synthetic *cis*-1,4-polyisoprene (Goodyear Tire & Rubber Co., Natsyn-2200) were used. Dicumyl peroxide (1.5%) and 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) (1.0%) were used as the curing agent and antioxidant, respectively. The sample was cured for 60 min at 156°C under a pressure of 78 kg/cm^2 so as to make a sheet of 2-mm thickness. Ring-shaped specimens (26 mm of the external diameter and 20 mm of the internal) were prepared by punching the sheet. The density of the specimens was measured with a density gradient tube by using a mixture of water and ethanol as the flotation medium at 10, 20, and 30°C .

X-Ray Measurements

A $1 \text{ cm} \times 3 \text{ cm}$ rectangular strip cut from the sheet was stretched with a stretching apparatus mounted on the goniometer head. Stretching and releasing were carried out in a stepwise manner in a similar way to that in the dilatometer. After the specimen was held at the given elongation for 40 min at 20°C , X-ray

diffraction was measured with a Geiger-counter in the usual manner.

RESULTS AND DISCUSSION

In the region of the extension ratio lower than 3.55 for natural rubber (4.37 for synthetic *cis*-1,4-polyisoprene) at 15°C, the volume of the stretched rubber showed a slight increase immediately on stretching, then a decrease within five minutes. Such a volume change may be due to the heat evolution on stretching. The equilibrium value of the volume at each elongation step increases slightly with the increase of the extension ratio. At the extension ratio higher than 3.55 for natural rubber, the equilibrium value of the volume shows a large decrease after stretching as shown in Figure 2. It was confirmed by X-ray measurements that the decrease in volume in this figure corresponds to the increase of the crystallinity.

In the cases of releasing, the volume increases immediately on releasing and reaches a constant value within two minutes in the region of an extension ratio higher than 2.19 for natural rubber (2.46 for synthetic *cis*-1,4-polyisoprene), and in the region lower than this value the time dependence of the volume was not observed. The time dependence of the volume change is common to natural rubber and synthetic *cis*-

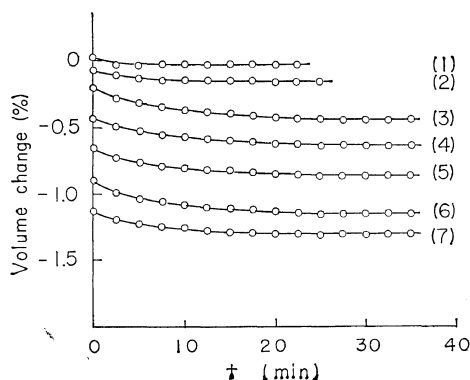


Figure 2. Time dependence of the volume change of crystallized natural rubber after stretching in a stepwise manner at 15°C: (1) on stretching from 3.55 to 3.82 of the extension ratio; (2) from 3.82 to 4.10; (3) from 4.10 to 4.37; (4) from 4.37 to 4.66; (5) from 4.66 to 4.93; (6) from 4.93 to 5.21; (7) from 5.21 to 5.49.

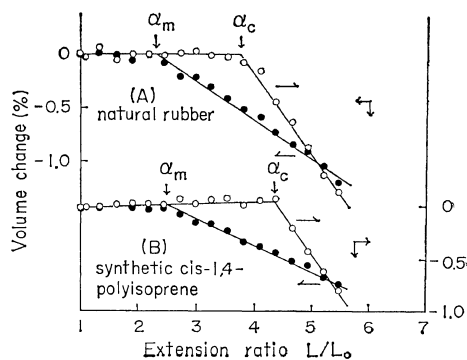


Figure 3. The volume change of rubber on stretching and releasing in a stepwise manner at 15°C: (A) natural rubber; $\alpha_c = 3.70$ and $\alpha_m = 2.30$ of the extension ratio and (B) synthetic *cis*-1,4-polyisoprene; $\alpha_c = 4.30$ and $\alpha_m = 2.50$ of the extension ratio; ○, stretching and ●, releasing.

1,4-polyisoprene. It is noteworthy that the crystallinity reaches a constant value at each of the stretching and releasing steps. These results do not coincide with the report on similar measurements for sulfur-cured natural rubber by Holt and McPherson⁷ showing that the sample does not reach the equilibrium state within the time scale of the same order. This difference may be related to the composition of rubber compounds and the degree of cross linking of the specimen.

The dependence of the change of the equilibrium volume on the extension ratio for natural rubber and synthetic *cis*-1,4-polyisoprene is shown in Figure 3. The change of volume on stretching and releasing shows similar patterns for both samples except for the positions of the inflection points. In the case of stretching, the inflection point, denoted by α_c , indicates clearly the extension ratio at which crystallization begins on stretching. The increase of the volume on releasing is attributed to the decrease of the crystallinity, and therefore the inflection point on the plots of releasing steps, denoted by α_m , indicates the extension ratio at which the last traces of the crystallinity disappear on releasing.

In the region of the extension ratio higher than α_c , the relationship between the extension ratio and the volume change on the stretching steps gives a straight line having the slope of 0.74% per extension ratio for natural rubber

and 0.73% per extension ratio for synthetic *cis*-1,4-polyisoprene. On the other hand, the slope of the volume change on the releasing steps varies depending upon the value of the extension ratio of the highest elongation from which the specimens are released. However, the inflection point α_m is constant regardless of the slope of the volume change-extension ratio relationship. These facts indicate that α_c and α_m are the characteristic values for the sample at 15°C.

These two values, α_c and α_m , of natural rubber are always lower than those of synthetic *cis*-1,4-polyisoprene. The lower value of α_c of natural rubber exhibits the higher crystallizability, while the lower value of α_m may be related to the higher melting point of natural rubber.

A similar relationship was obtained with X-ray measurements, as shown in Figure 4. The ordinate in this figure represents the ratio of the peak intensity of the crystalline reflexion at $2\theta = 21.5^\circ$ to the intensity of the amorphous halo at $2\theta = 18.0^\circ$, which may be regarded as a measure of the crystallinity. It was confirmed by the measurements of the half-intensity width ($10 \pm 1^\circ$ for all extension ratios) that the intensity of the crystalline reflexions is practically

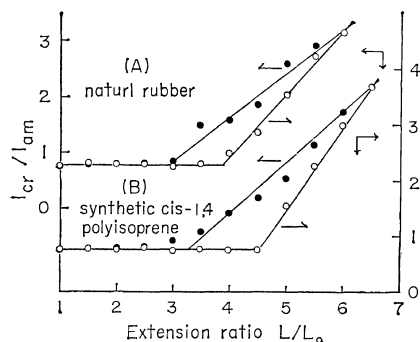


Figure 4. Correlation between I_{cr}/I_{am} and the extension ratio at 20°C: (A) natural rubber and (B) synthetic *cis*-1,4-polyisoprene; I_{cr} , X-ray intensity at $2\theta = 21.5^\circ$ and I_{am} , X-ray intensity at $2\theta = 18.0^\circ$; \circ , stretching and \bullet , releasing.

independent of the crystallite orientation. In Figure 4 two inflection points are also found for both samples. The inflection points in Figure 4 show the one-to-one correspondence with those obtained by the dilatometric measurements and moreover appear at a lower extension ratio for natural rubber than for synthetic *cis*-1,4-polyisoprene in the same way as is found in Figure 3, although the absolute values are different probably because of the difference in the temperature of the two experiments. The higher crystallizability of natural rubber on stretching is also clearly demonstrated in this X-ray measurement. As shown in Figures 3 and 4, the equilibrium crystallinities on the stretching process are lower than those on the releasing process at the same extension ratios, giving a hysteresis loop. This phenomenon may prove very interesting as a clue to the detailed study of the mechanism of crystallization of rubber-like substances.

From the facts mentioned above we can conclude that the two values, α_c and α_m , are available for characterizing the crystallization of rubber on stretching. Comparison of the results of both the dilatometric and X-ray measurements at various temperatures will be reported in a succeeding paper, which will give further elucidation of the nature of the value α_m .

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