Thermodynamics of Crystallization in High Polymers. VI. Incipient Crystallization in Stretched Vulcanized Rubber

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(Received December 13, 1948)

Experimental determination of the elongation at which crystallization commences in vulcanized rubber has been attempted through measurement of density changes by a hydrostatic method. The critical elongation for incipient crystallization appears to depend on the temperature in approximate accordance with theoretical prediction. Crystallization sets in at an elongation well below that at which the stress-strain curve assumes a steep slope.

FROM consideration of the statistical thermodynamics of crystallization of rubber on stretching,[1] it has been shown that the temperature (T_m) of incipient crystallization, i.e., the highest temperature above which all crystallinity must disappear, should increase with the relative length α approximately in accordance with the relationship

$$1/T_m{}^0 - 1/T_m = (R/h_f)\phi(\alpha), \qquad (1)$$

where

$$\phi(\alpha) = (6/\pi n)^{\frac{1}{2}}\alpha - \alpha^2/2n - 1/\alpha n. \qquad (2)$$

Here $T_m{}^0$ is the crystallization temperature for the unstretched polymer $(\alpha=1)$, h_f is the heat of fusion per polymer segment, R is the gas constant, and n represents the number of "statistical segments" per chain between cross linkages. With the object of establishing the dependence of T_m on α, we have measured the density of gum vulcanized rubber as a function of elongation at three temperatures, 20, 40, and 60°C, abrupt increase in density being used as the criterion for the onset of crystallization.[2] Experimental difficulties are formidable and they were not entirely overcome in the work reported here. Inasmuch as it has been necessary to abandon further work on this project, the significant results which have been obtained are set forth briefly below.

EXPERIMENTAL

Each of six molded rubber bands,[3] 0.1×1.0 cm in section and having a circumference of 10 cm, was marked at distances $L_0=3.00$ cm apart on its outer surface. The bands were evenly stretched about pairs of aluminum support rods $\frac{3}{16}''$ in diameter which were inserted through appropriately spaced holes drilled (perpendicular to the axis) through an aluminum tube 20'' long and $\frac{1}{2}''$ in diameter. The holes were so arranged as to provide relative lengths α from 1.0 to 10 in steps of 0.25. This assembly, suspended by a thin wire from one arm of an analytical balance, was immersed in water contained in a tall glass cylinder located in a water thermostat regulated to $\pm0.01°C$. Weighings were accurate to the nearest milligram.

In carrying out an experiment, the unstretched bands were weighed in air and then in water at the temperature of the experiment. After stretching at room temperature to the desired elongation, they were held in water at a high temperature (either 70° or 90°) for ten minutes to melt crystallites which may have been formed. The bands were quickly transferred to the constant temperature bath and the weight determined after thirty minutes. On removal from the bath, the distances between the marks were measured first in the stretched condition (L_s) and then unstretched (L_0''). They were again stretched at room temperature and the cycle repeated.

RESULTS

The distance L_0'' between the marks on the bands on release of tension assumed successively larger values as the measurements proceeded from one elongation to the next, etc. This residual elongation was reduced slightly by immersion of the bands in petroleum ether (and drying in vacuo) and hence was due in part to slow elastic recovery. The remaining "permanent set" has been attributed[4] to a reversible breaking and reforming of chemical bonds between chains while the rubber is under tension. Upon release of tension the bonds which were formed while the sample was stretched oppose
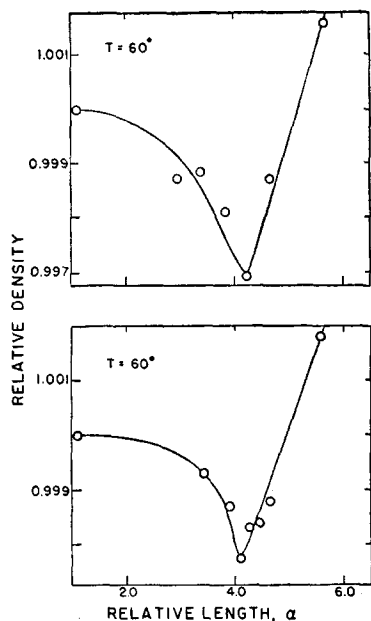
FIG. 1. Density-elongation curves obtained at 60° for two similar sets of bands.

though the major portion of the density change had occurred within thirty minutes, the time necessary to attain an apparent equilibrium varied from at least one hour at low elongation to at least ten hours at elongations above the crystallization point. In view of the occurrence of stress relaxation, such prolongation of the experiments obviously was impractical. While the equilibrium curve probably would differ from that reported here, the equilibrium elongation at which the density suddenly increases doubtless would occur near the position observed in these experiments. Hence, we believe that the present method yields a useful approximation to the equilibrium point for incipient crystallization.

The results of two experiments at 60° are shown in Fig. 1. The decrease in density with increasing α at low elongations is far greater than would be calculated from the compressibility.[6] This anomalous increase in volume may be due to the formation on stretching of vacuoles about solid vulcanization ingredients embedded in the rubber.[2,7] The elongation at the minimum point of the curve (α_c) is characteristic of the temperature and was taken as the point of incipient crystallization. The data are scattered and are not entirely reproducible for differ-

contraction of the rubber.[5] The resulting increase in L_0 appears to be characteristic of the modified network structure and must therefore be accounted for in the calculation of the elongation. As an approximate corrective measure, α has been taken equal to L_s/L_0' where L_0' represents the distance between the marks after removal of the load and relaxation by solvent treatment. In practice L_0' was obtained from the observed values of L_0'' by means of a calibration curve relating the two lengths.

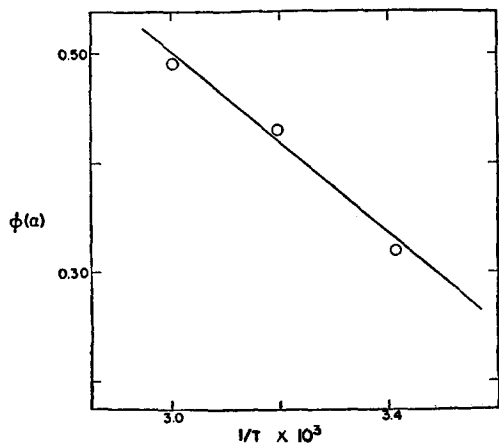Density-time studies made at 40° indicated that al-

FIG. 2. The relation between the incipient crystallization temperature and the elongation, plotted as $1/T_m$ ($°A^{-1}$) vs. $\phi(\alpha)$.

FIG. 3. The stress-strain curve for the rubber bands at room temperature.

[6] G. Gee, Trans. Faraday Soc. 42, 585 (1946).
[7] Dr. Gee and collaborators of the British Rubber Producers Research Association have independently observed a similar anomalous increase in volume, which they likewise attribute to vacuole formation. We are indebted to Dr. Gee for providing us with this unpublished information.

[5] Immersion of these bands in boiling water (a treatment speeding up both viscous relaxation and chemical rupture of bonds) reduced the ratio L_s/L_0'' from 1.3 to 1.1 in four hours, with an indication that heating for longer periods would reduce the ratio further.

TABLE I. Incipient crystallization in vulcanized rubber.

T_m	$1/T_m, °A^{-1}$	α_c	$\phi(\alpha)$
60°	3.003×10^{-3}	4.10	0.48
40	3.195	3.60	0.43
20	3.413	2.50	0.31
		1	0.12

ent sets of bands. However, the values of α_c at 20, 40, and 60° (Table I) are probably accurate to ±0.20.

Values of $\phi(\alpha)$ (Table I) were calculated from these data by Eq. (2) assuming $n=100$. From the straight line drawn through the plot in Fig. 2 of $1/T_m$ vs. $\phi(\alpha)$, h_f and T_m^0 according to Eq. (1) were found to be 400 R cal. and $-17°C$, respectively. This value of h_f compares favorably with the estimate of 600 (±300) R suggested previously by one of the authors,[1] and with the value of 465 R recently deduced in a similar manner by Goppel[8] using incipient crystallization temperatures determined by Wildschut. While the true value of T_m^0 is probably above 0°C, the figure obtained here is similar to that ($-20°C$) employed by Goppel. The discrepancy may be due in part at least to the admitted failure of the theory at low elongations.[1]

The choice of n above is somewhat arbitrary. Fortunately the values of h_f and $1/T_m^0$ are rather insensitive

[8] J. M. Goppel, Paper presented at the Rubber Technology Conference, London, June 23–25, 1948. The authors are indebted to Dr. Goppel for providing them with a copy of this paper.

to the choice of n. The equilibrium force of retraction at 100 percent elongation, 78 lbs./in.², is comparable to that obtained for a rubber vulcanizate known to contain on the average of 100 isoprene units between cross-linkages.[9] Hence, we conclude that the chains in this particular vulcanizate are about 100 *units* long. The configurational segment will not necessarily be identical with the structural unit, however.

From these data it is concluded that the theory predicts correctly the order of magnitude for the change in the incipient crystallization temperature with elongation. The experimental accuracy is not sufficient to determine the exact form of the relationship. Results of significantly greater accuracy are not to be expected from the present method.

A point of additional interest occurs in the relationship between the elongation for incipient crystallization and the shape of the stress-strain curve. Although under approximate equilibrium conditions at room temperature incipient crystallization occurs at $\alpha \cong 3$, the stress-strain curve (Fig. 3) does not exhibit a sharp "break" until a relative length α of at least 5 has been reached. Obviously the "break" in this curve must not be identified with the elongation necessary for incipient crystallization. The "break" in the curve presumably represents the region in which the degree of crystallinity becomes large.

[9] P. J. Flory, N. Rabjohn, and M. C. Shaffer, forthcoming publication in J. Polymer Sci.

Punched Card Calculation of Resonance Energies

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(Received December 21, 1948)

The calculation of resonance energies can be greatly simplified by using punched card machines. Two methods are developed. The first is easy to apply and works well for 8-, 10-, and 12-electron problems. This is used for naphthalene. The results lend themselves well to a bond probability calculation from which bond distances in good agreement with other methods are obtained. The second procedure is longer, but makes possible the calculation of anthracene and phenanthrene resonance energies. These are $-2.95_1\alpha$ and $-3.01_9\alpha$, respectively. Bond probabilities and lengths were also calculated from these data.

INTRODUCTION

AROMATIC hydrocarbons are more stable than would be predicted for any single method of drawing valence bonds by the rule of additive bond energies. This lowering of the energy, or resonance energy, is due to the freedom of the double bond electrons to move throughout the molecule instead of being localized in fixed double bonds. The magnitude of the resonance energy and the wave function of the electrons can be found by using quantum mechanics.

The valence electrons of each carbon atom are assumed to occupy one $2s$ and three $2p$ orbitals. The $2s$ and two of the $2p$ orbitals are used in forming single bonds to the adjacent hydrogen and carbon atoms. The remaining $2p$ function or π-orbital, which projects at right angles to the plane of the ring and is antisymmetric with regard to reflection in the plane of the ring, combines only with the corresponding functions on the other carbon atoms.

Two methods of attack which differ in the nature of further approximations have been devised.

Hückel[1] has proposed a molecular orbital method.

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[1] E. Hückel, Zeits. f. Physik **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).