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on surface 1 is essentially complete.[16] Under these conditions the ratio of the v_m values found will be simply θ_1, i.e. $v_{m1}/(v_{m1}+v_{m2})$.

Experimental results of this type have been frequently found, notably by Armbruster[6] who obtained values of v_s, the Langmuir[17] saturation adsorption (equivalent to $\theta_1 v_m$ or v_{m1}, if the present theory applies), corresponding to θ_1 values in the range 0.2–1 for argon, nitrogen, carbon monoxide, etc. on silver foil at 78 and 90°K, based on the assumption that v_m equals the apparent geometric area. While such figures are not unreasonable, this leaves unexplained the "coefficient of thermal expansion," $d\ln v_s/dT$, observed in that work. On the basis of the inhomogeneity hypothesis the temperature dependence of v_s would probably also be connected with the properties of surface 2, but a complete test of such an explanation must await measurements which extend throughout the range of about 0.05 to 1.5 monolayers (based on the largest v_m value obtained).

This extension of the BET equation appears to offer no explanation of the observed low roughness factors recently reported by Emmett,[18] since these occur at relative pressures of 0.1 or above.

In conclusion, the author wishes to thank Drs. P. H. Emmett and S. W. Weller for several helpful discussions of this work. Grateful acknowledgment is made to the John Simon Guggenheim Memorial Foundation, which supported this investigation.

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[16] Here we had best make again the restriction $c_2 \gg 1$, for otherwise c_0 will be low, and, correspondingly, the value of $x_m = 1/[1+(c)^{\frac{1}{2}}]$ so large that the usual deviations at large x may appear despite the approximate constancy of c as given by Eq. (6).

[17] Reference 2, pp. 60, ff.

[18] Reported at the Chicago meeting of the American Chemical Society, September 1946; See Abstracts of Papers, 110th Meeting, No. 44, p. 25E.

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Thermodynamics of Crystallization in High Polymers. I. Crystallization Induced by Stretching*

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A theory of oriented crystallization in elongated polymers having network structures (e.g., in vulcanized rubber) is developed through the application of statistical mechanical procedures similar to those employed in rubber elasticity theory. Expressions are derived which, within the limitation imposed by the simplifying assumptions, relate the incipient crystallization temperature with the elongation, the degree of crystallinity with the elongation and temperature, and the retractive force at crystallization equilibrium with the elongation at constant temperature. The reciprocal of the absolute temperature for incipient crystallization is predicted to decrease linearly with a simple function of the elongation and the average number of chain segments between cross linkages. Only moderate degrees of crystallinity are predicted at equilibrium. In conformity with requirements of the second law of thermodynamics, equilibrium crystallization decreases the tension in the stretched specimen.

Apparent discrepancies between some of these predictions and various observations are attributed to severe departure from equilibrium crystallization when the polymer undergoes crystallization *during* the stretching process. A better approach to equilibrium should be achieved by stretching under conditions which prevent crystallization (e.g., at elevated temperature), then allowing crystallization to proceed at fixed elongation. Few experiments have been performed in this manner, but such results as are available confirm qualitatively the predictions of the theory.

Reasons for the rapid increase in tension which is observed when crystallization occurs during ordinary stretching of rubber are discussed. It is pointed out that crystalline and amorphous regions preferably should not be regarded as separate phases. Likewise, the conversion of amorphous to crystalline polymer does not conform to the definition of a phase transition.

INTRODUCTION

THE tendency for a high polymer to crystallize may be greatly enhanced by deformation. This is particularly true if the polymer possesses a network structure, in which case the deformation imposes on the structure an orientation which cannot be dissipated by ordinary

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internal relaxation processes. Thus, vulcanized rubber, which does not crystallize at ordinary temperatures, becomes highly crystalline when sufficiently elongated, even at temperatures above 100°.[1] Similarly, butyl rubber develops a high degree of crystallinity when stretched at temperatures below 50°,[2] although so far as is known it does not crystallize at all when cooled without stretching.

The reasons for the effects of deformation on crystallization are fairly obvious. When the polymer having a network structure is stretched, chains between network junctions are deformed from their most probable configurations, most of them being elongated. The configurational entropies of these chains consequently are decreased. Less entropy remains to be sacrificed in passing to the crystalline state, where the configurational entropy can be taken as zero. Crystallization will occur when $T\Delta S_f < \Delta H_f$. Consequently, crystallinity may develop at a higher temperature the smaller ΔS_f becomes as a result of elongation.

Alfrey and Mark[3] attempted to give quantitative expression to this concept. Their treatment, which resembles in certain respects the one presented here, applies only to an individual chain, and cannot, therefore, be related to the composite network structure elongated by a factor, α. Recently James[4] has considered the problem in one dimension. The application of his results to actual three-dimensional network systems is of doubtful significance.

In the present paper the influence of stretching on crystallization will be treated by an extension of the statistical mechanical theory of rubber elasticity as it is applied to three-dimensional network structures.[5–10] Because of the approximations introduced for the purpose of simplification, the quantitative validity of some of the relationships which are derived is questionable. Regardless of this deficiency it is felt that the present treatment clarifies the nature of the problem and that the results deduced should at least be valuable as a guide for appropriate future experiments in this field.

THEORETICAL DEVELOPMENT

Consider a network structure composed of long polymer chains joined together at cross linkages. (A "chain" is defined[10] as that portion of the network extending from one cross linkage to the next.) The number of chains united at one "cross linkage" need not necessarily be four; if the cross linkages are trifunctional, or of higher functionality than four, the theory presented here need not be modified. In the development which follows it is considered implicitly that crystallization occurs *after* the polymer has been elongated to the final relative length, α. Experimentally this condition would be fulfilled if the sample were elongated at an elevated temperature at which crystallization would not occur, then cooled gradually. Thus, the final state is to be achieved by two separate and distinct steps, namely, stretching and crystallization, which occur in this order. If crystallization occurs simultaneously with stretching, as indeed ordinarily is the case, the present treatment cannot be expected to apply directly.

Crystallites formed in stretched network polymers (e.g., in vulcanized natural rubber) are observed to be well oriented with their fiber axes parallel to the direction of stretch. This experimental observation is one of the premises of the theory presented below.

As is customary in dealing with the properties of semiflexible chain molecules,[8–12] it is assumed that the behavior of the polymer chains can be approximated satisfactorily by a hypothetical chain composed of a large number of relatively

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[1] Unpublished results of Kirsch referred to in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, p. 67.

[2] W. O. Baker and N. R. Pape, unpublished results submitted to the Office of the Rubber Director.

[3] T. Alfrey and H. Mark, J. Phys. Chem. **46**, 112 (1942).

[4] H. M. James, unpublished work described by Guth, James, and Mark in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, pp. 279–285.

[5] W. Kuhn, Kolloid Zeits. **76**, 258 (1936); W. Kuhn and F. Grün, J. Polymer Sci. **1**, 183 (1946).

[6] F. T. Wall, J. Chem. Phys. **10**, 132 (1942); **10**, 485 (1942); **11**, 527 (1943).

[7] L. R. G. Treloar, Trans. Faraday Soc. **39**, 36 (1943).

[8] H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943); J. App. Phys. **15**, 294 (1944); E. Guth, H. M. James, and H. Mark in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, p. 253.

[9] P. J. Flory and J. Rehner, Jr., Ann. N. Y. Acad. Sci. **44**, 419 (1943); J. Chem. Phys. **11**, 512 (1943).

[10] P. J. Flory, Chem. Rev. **35**, 51 (1944).

[11] W. Kuhn, Kolloid Zeits. **87**, 3 (1939). W. Kuhn and H. Kuhn, Helv. Chim. Acta, **29**, 1095 (1946).

[12] L. R. G. Treloar, Trans. Faraday Soc. **42**, 77, 83 (1946).

small rigid segments joined together by bonds which permit a considerable latitude of freedom in the disposition of one segment relative to the preceding one in the chain. Because of thermal agitation, these segments are assumed to shift at a rapid rate from one position to another, consistent with their attachments to neighboring segments of the same chain and the availability of free space in their immediate environment. Under these circumstances the occasional transitory occurrence of σ segments of neighboring chains arranged in a close packed array in a plane perpendicular to the direction of elongation is not improbable. Such a temporary arrangement can be regarded as a potential crystallite nucleus. If successive neighboring segments of these same chains also align themselves similarly in planes parallel to the first, a crystallite is formed with its fiber axis parallel to the direction of stretch. The potential nuclei referred to may exist momentarily under any conditions, but crystallites are stable thermodynamically only when propagation of this arrangement through consecutive segments of these chains is accompanied by a decrease in free energy.

It should be noted that the formation of crystal nuclei as described above involves no significant configurational entropy change. Alignment of the segments in a planar array ordinarily will require merely that segments intersected at a given instant by the hypothetical plane be shifted by small distances, less than the dimensions of the segments themselves. The selection of chains and the selection of which segment of each of these chains shall occur in the planar array are essentially arbitrary. Any one of a large number of segments of a given chain may be assigned to the planar array, or crystal nucleus, and the σ segments from the σ chains can be permuted over the cross section without altering appreciably the macro-state.[13a] If the crystal nucleus grows, these segments become fixed in this particular array. The locations of these fixed segments generally will correspond approximately to a most probable group of configurations for their respective chains. This is essentially a "freezing in" process unaccompanied by change in entropy.

On the other hand, those potential nuclei in which the particular array of segments is most conducive to crystal growth under the conditions of deformation will be the ones which survive. Here the element of selection enters to some extent, and a corresponding entropy decrease should be considered. No means for estimating the magnitude of this entropy change is evident. In the belief that it is relatively small, it is neglected here. In effect, it is assumed, as an approximation, that the crystal nuclei are formed without change in entropy.[13b]

As the crystal nucleus grows in either direction parallel to the axis of elongation, which is taken as the z-axis, two contributions to the entropy change must be considered. A segment entering the crystallite sacrifices all freedom of orientation relative to the preceding segment of the same chain. The entropy must decrease accordingly. A further entropy change arises from the alteration of the distance traversed ("displacement length"[10]) by the remaining amorphous portions of the chain. As the crystal grows parallel to the axis of elongation (z-axis), the z-component of this distance, or displacement length, is decreased while at the same time the number of amorphous segments available to traverse the required distance is diminished. At the onset of crystal growth, the chains having had their z-components increased by stretching, this change permits the amorphous portion of the chain to assume a greater number of configurations, since the displacement length is decreased out of proportion to the decrease in number of amor-

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[13a] The latter half of this statement is not strictly true when the chains are directionally unsymmetrical, as for example is the case in natural rubber. In a bundle of parallel rubber chains, some will have their methyl groups to the right of the double bond and some to the left. The crystalline array doubtless includes the two orientations in equal numbers arranged in regular array. (Compare, C. W. Bunn, in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II, p. 113). Since the arrangement of "right" and "left" chains is systematic in the crystal, the entropy of nucleation in polymers such as natural rubber should include the term $-k\sigma \ln 2$. This term is neglected here.

[13b] It might appear necessary to consider that each chain has been separated at the crystallite into two chains. The crystallite does in fact fix the positions of segments at the ends of the crystallites, hence, computation of the number of configurations available when the crystallite is present would require consideration of two separate sub-chains with coordinates fixed by the location of the crystallite. However, the crystallite is permitted to form at *any* convenient location. In order to include all potential configurations (for the same macro-state) it is necessary, therefore, to disregard both the specific location of the crystallite and the particular sequence of ζ-segments of a given chain which occur in the crystal.

phous segments. Hence, the entropy of the amorphous portion generally is increased by crystallization. As an increasing proportion of the chain joins the crystallite, a condition may be reached where this is no longer true, or at any rate where this source of entropy gain with further crystallization is diminished. It is evident that this must be so inasmuch as the elongated z-component of the displacement length of the amorphous portion is rapidly decreased by the lengthening of the crystallite, while fewer amorphous segments are available to traverse the unaltered x and y distances. The computation of the net entropy change in the amorphous portion of the chain is the major problem to be solved.

The desired total entropy change accompanying crystallization might be obtained by computing the separate entropy changes as detailed above. Instead, calculation of an "absolute" configurational entropy of the semi-crystalline stretched polymer will be carried out, taking the hypothetical totally crystalline (single crystal) polymer as the standard state.

The dependence of the relative number of configurations (configurational probability) of an amorphous chain on the distance of separation of its ends, or chain displacement length, is assumed to be a Gaussian function of this distance $r[=(x^2+y^2+z^2)^{\frac{1}{2}}]$, i.e.,[14, 15]

$$W(xyz)=(\beta/\pi^{\frac{1}{2}})^3\exp[-\beta^2(x^2+y^2+z^2)] \quad (1)$$

where x, y and z represent the coordinates of one end of the chain with respect to the other and $1/\beta$ equals the most probable value of the chain displacement length, r. The cross linkages are introduced into the polymer while it is in its undeformed state, in which the molecules are free to assume random configurations. Hence, the above function must also represent the distribution of chain coordinates which exists before stretching.

After stretching along the z-axis by a factor, α, the volume remaining constant, the distribution of chain coordinates becomes

$$\nu(xyz)=\sigma(\beta/\pi^{\frac{1}{2}})^3\exp[-\beta^2(\alpha x^2+\alpha y^2+z^2/\alpha^2)] \quad (2)$$

where σ is the total number of chains under consideration.

We shall adopt as our hypothetical model a chain composed of rigid segments connected by bonds which permit complete freedom of orientation of one segment relative to the one preceding it in the chain.[8–12] For such chains the reciprocal most probable displacement length is given by

$$\beta=(3/2n)^{\frac{1}{2}}/l \quad (3)$$

where l is the length of each segment and n is the number of segments per chain. The product nl is taken equal to the maximum extension L of the actual chain consistent with bond angles and dimensions and with steric interferences of substituents. The quantities n and the corresponding value of $l=L/n$ are fixed by the further stipulation that the Gaussian function must give the best possible fit to the actual distribution of chain displacement lengths, except, of course, for values of r approaching the maximum extension L, where the Gaussian function necessarily is a poor approximation.

If an alternative model chain were chosen in which the segments are connected by valence bonds at fixed tetrahedral angles about which rotation is completely free, then[14–16]

$$\beta=(3/4n)^{\frac{1}{2}}/l. \quad (4)$$

In this case, in order to match the configuration distribution of the actual chain, it would be necessary to make l smaller and n correspondingly larger than in the case of the previously considered chain model. It is evident that the distribution function is preserved if n for the second model is twice that for the first, l being decreased to one-half.

When ζ of the n segments of the chain occur in a crystalline region, the relative number of configurations available to the remaining $n-\zeta$ segments becomes

$$W'(xyz')=(\beta'/\pi^{\frac{1}{2}})^3\exp[-(\beta')^2(x^2+y^2+z'^2)] \quad (5)$$

where

$$\beta'=[\mathrm{Const.}/(n-\zeta)l^2]^{\frac{1}{2}}=\beta[n/(n-\zeta)]^{\frac{1}{2}} \quad (6)$$

and z' is the algebraic sum of the z displacement lengths of the (two) amorphous sections of the chain. The x and y displacements are unaffected

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[14] W. Kuhn, Kolloid Zeits. **68**, 2 (1934).

[15] E. Guth and H. Mark, Monats. f. Chem. **65**, 93 (1934).

[16] H. Eyring, Phys. Rev. **39**, 746 (1932).

by the formation of crystallites with axes parallel to the direction of elongation, but z in general will be altered by an amount ζl. If α is sufficiently greater than unity, then in most cases the chain will traverse the crystallite in the same direction as the displacement between the ends of the chain located at cross linkages, which are assumed to be fixed at their most probable positions,[17] the coordinates of one with respect to the other being x, y, and z. As an expedient, though regrettable, approximation, it is considered here that all chains traverse the crystallite in the same direction as the z displacement of one end of the chain with respect to the other; i.e., it is assumed that

$$z'=\pm(|z|-\zeta l) \qquad (7)$$

where the plus sign is to be used for $z>0$ and the minus for $z<0$. For small values of z this approximation is a particularly poor one. However, the z' term enters the summations which follow as the square, and the contributions of these small z terms consequently are of minor importance. The consequences of this approximation will be dealt with later.

For the calculation of the configurational entropy with respect to the totally crystalline polymer, two hypothetical steps are considered: (a) melting of $n-\zeta$ of the segments of each of σ chains composed of n segments, the ends of the chains being free (i.e., not attached to cross linkages) to occupy most probable locations such that the distribution of displacement lengths x, y, and z' for the amorphous portions is given by

$$\nu'(xyz')=\sigma W'(xyz') \qquad (8)$$

and (b) assignment of the ends of the chains to the locations of the cross linkages within the elongated polymer, as prescribed by Eq. (2). The entropy change for the first of these steps is given by

$$S_a=\sigma(n-\zeta)s_f \qquad (9)$$

where s_f is the entropy of fusion per segment.[18a] According to the lattice theory[18b] of thermodynamic properties of high polymers

$$s_f=k[\ln(\gamma-1)-1] \qquad (10)$$

where k is Boltzmann's constant and γ is the coordination number of the lattice; at any rate Eq. (10) should represent that portion of the entropy of fusion arising from the randomness of arrangement of the segments in space, but not including entropy contributions from internal changes within the segments during melting, or from enhanced freedom of oscillation within a cell of the liquid lattice.

The entropy change S_b in step (b), arises from the transformation of the chain length distribution for the amorphous portion from $\nu'(xyz')$ given by Eq. (8) to $\nu(xyz)$ given by Eq. (2). Employing the Boltzmann relationship[19] $S=k\sum\nu\ln W$,

$$S_b=k\sum_{xyz}\nu(xyz)\ln W'(xyz')-k\sum_{xyz'}\nu'(xyz')\ln W'(xyz').$$

Converting to integrals and substituting the previously given expressions for the various functions

$$S_b=\sigma k(\beta/\pi^{\frac{1}{2}})^3\iiint_{-\infty}^{\infty}\exp[-\beta^2(\alpha x^2+\alpha y^2+z^2/\alpha^2)][A'-\beta'^2(x^2+y^2+z'^2)]dxdydz$$

$$-\sigma k(\beta'/\pi^{\frac{1}{2}})^3\iiint_{-\infty}^{\infty}\exp[-\beta'^2(x^2+y^2+z'^2)][A'-\beta'^2(x^2+y^2+z'^2)]dxdydz'$$

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[17] See reference 9; also H. M. James and E. Guth, J. Chem. Phys. **11**, 478 (1943).

[18a] Under the plausible assumption that cross linkages (i.e., ends of chains) are prohibited for stereochemical reasons from occurring within crystallites, a further entropy term $\sigma k\ln(n-\zeta+1)/n$ should be added to account for the limitations on the choice of the sequence of ζ crystalline segments. The effect of this term is small when n is large. Hence, it has not been considered of sufficient importance to merit incorporation in the present treatment.

[18b] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

[19] The alternate treatment of Wall[6] in which interchangeability of chain elements is taken into account leads to results insignificantly different from those deduced here by merely summing over the *a priori* probabilities for the individual chains. In this connection see also, Kuhn and Grün[5] and Kuhn and Kuhn.[27]

where $A'=\ln(\beta'/\pi^{\frac{1}{2}})^3$. The second integral expression can be integrated at once to $-\sigma k(A'-\frac{3}{2})$. In accordance with Eq. (7), the integral over z in the first expression can be separated into two parts, one from 0 to ∞, where $z'=z-\zeta l$, and the other from $-\infty$ to 0, where $z'=z+\zeta l$. With appropriate further rearrangement, there is obtained

$$S_b=8\sigma k(\beta/\pi^{\frac{1}{2}})^3\int\int_0^\infty\int \exp[-\beta^2(\alpha x^2+\alpha y^2+z^2/\alpha^2)]\{A'-\beta^2[n/(n-\zeta)][x^2+y^2+(z-\zeta l)^2]dxdydz$$
$$-\sigma k(A'-\tfrac{3}{2})\}.$$

After carrying out the integrations

$$S_b=-\sigma k[(\zeta\beta l)^2n/(n-\zeta)-2\alpha(\zeta\beta l/\pi^{\frac{1}{2}})n/(n-\zeta)+(\alpha^2/2+1/\alpha)n/(n-\zeta)-\tfrac{3}{2}]. \quad (11)$$

For small degrees of crystallinity and low elongations Eq. (11) assigns a small positive value to S_b; it is negative for all higher elongations. For example, if α is less than about 2, then for a certain range of small degrees of crystallinity S_b as computed from Eq. (11) is positive. Obviously, S_b should always be zero or negative since the final state may not have higher entropy than the most probable state. This failure of Eq. (11) at low elongations seems to arise, in large part at any rate, from the approximation introduced in Eq. (7).

The configurational entropy of the σ chains involved in the crystallite is the sum of S_a+S_b, or

$$S=\sigma k[(n-\zeta)s_f/k-(\zeta\beta l)^2n/(n-\zeta)+(2\alpha\zeta\beta l/\pi^{\frac{1}{2}})n/(n-\zeta)-(\alpha^2/2+1/\alpha)n/(n-\zeta)+\tfrac{3}{2}]. \quad (12)$$

Letting h_f represent the heat of fusion per segment of the polymer, the heat change accompanying the fusion of $n-\zeta$ of the segments per chain is $\sigma h_f(n-\zeta)$. The second step in the hypothetical procedure for forming the partially crystalline polymer may be assumed to occur without change in internal energy. Hence, the free energy of the system, taking the perfectly ordered, totally crystalline chains as the standard state, becomes

$$F=\sigma kT[\zeta(s_f/k-h_f/kT)+(\zeta\beta l)^2n/(n-\zeta)-(2\alpha\zeta\beta l/\pi^{\frac{1}{2}})n/(n-\zeta)$$
$$+(\alpha^2/2+1/\alpha)n/(n-\zeta)-\tfrac{3}{2}-n(s_f/k-h_f/kT)]. \quad (13)$$

It is convenient to employ the following substitutions:

$$\lambda=(n-\zeta)/n$$

and

$$\theta=s_f/k-h_f/kT.$$

Converting to molar quantities, for which the same symbols will be employed, and setting $h_f/s_f=T_m{}^0$, the "incipient crystallization temperature" for the undeformed polymer,

$$\theta=(h_f/R)(1/T_m{}^0-1/T).$$

The free energy function then assumes the form

$$F=\sigma RT[n\theta(1-\lambda)+(n\beta l)^2(1-\lambda)^2/\lambda-(2\alpha n\beta l/\pi^{\frac{1}{2}})(1-\lambda)/\lambda+(\alpha^2/2+1/\alpha)/\lambda-\tfrac{3}{2}-n\theta]. \quad (13')$$

The condition for equilibrium with respect to the degree of longitudinal growth of the crystallite can be stated as $(\partial F/\partial\zeta)_\alpha=0$, or $(\partial F/\partial\lambda)_\alpha=0$. Differentiating Eq. (13′) with respect to λ

$$(1/\sigma RT)(\partial F/\partial\lambda)_\alpha=-[n\theta+(n\beta l)^2(1/\lambda^2-1)-(2\alpha n\beta l/\pi^{\frac{1}{2}})/\lambda^2+(\alpha^2/2+1/\alpha)/\lambda^2] \quad (14)$$

which on equating to zero gives

$$\theta\lambda^2+n\beta^2l^2(1-\lambda^2)=\varphi(\alpha)$$

where

$$\varphi(\alpha)=2\alpha\beta l/\pi^{\frac{1}{2}}-(\alpha^2/2+1/\alpha)/n. \quad (15)$$

Solving the above equation for the equilibrium value of λ

$$\lambda=\{[n\beta^2l^2-\varphi(\alpha)]/[n\beta^2l^2-\theta]\}^{\frac{1}{2}}. \tag{16}$$

Substituting from Eq. (3) for β

$$\varphi(\alpha)=(6/\pi)^{\frac{1}{2}}\alpha/n^{\frac{1}{2}}-(\alpha^2/2+1/\alpha)/n \tag{17}$$

$$\lambda=\{[\tfrac{3}{2}-\varphi(\alpha)]/[(\tfrac{3}{2}-\theta)]\}^{\frac{1}{2}}. \tag{18}$$

Before proceeding with the interpretation and application of the relationships derived above, it may be well to recapitulate as follows the assumptions and approximations employed in their derivation:

(1) Crystallization is assumed to occur in a thermodynamically most favorable manner, i.e., a state of equilibrium is assumed.

(2) Possible small entropy changes associated with the formation of nuclei are neglected. Thus, for example, the tendency for chains having comparatively large z components in the undeformed state to crystallize selectively is disregarded.

(3) Crystallites are considered to be oriented parallel to the axis of elongation.

(4) Each chain is assumed to traverse the crystallite in the direction of the displacement of its ends with respect to the z-axis. See Eq. (7).

(5) The Gaussian distribution is employed to represent the relative number of configurations although it is known to be unsatisfactory for this purpose at high extensions of the chains.

Finally, the approximate invariance of these equations (and those deduced from them in subsequent sections of this paper) with change of model should be pointed out. If, for example, a model for the chain is adopted in which the segments are attached by tetrahedrally disposed valence bonds about which rotation is unrestricted, β will be given by Eq. (4), in place of (3). However, this chain of the same contour length nl as the chain composed of freely orienting segments necessarily will have to be made up of a greater number of smaller segments in order to conform to the actual chain. Perusal of the equation given above will show that they remain unchanged when βl is replaced by its value (see Eq. (4)) for tetrahedrally bonded segments, provided that n is doubled while l, and likewise h_f and s_f, are halved. Thus, it appears that the conclusions to be drawn are not sensitive to the type of chain model selected.

DEGREE OF CRYSTALLINITY

The quantity $1-\lambda$ represents the fractional degree of crystallinity of the σ chains under consideration. To the extent that these chains are typical of the network as a whole, $1-\lambda$ may be regarded as the degree of crystallinity in the entire system. This interpretation of λ may be reasonably satisfactory for low degrees of crystallinity, but it is beset with doubts, partly of intuitive origin, when a substantial fraction of the material becomes crystalline. A literal extension of the above description of the formation of a single crystallite to the system as a whole would imply that nucleation is restricted to the initial crystallization interval, further crystallization thereafter being restricted to *longitudinal* growth of existing crystallites. Actually nucleation doubtless occurs simultaneously with growth of existing crystalline regions, and these may grow laterally as well as longitudinally. As a result of this course of the crystallization, a given chain may pass through several crystalline regions. Fundamentally, the above treatment is also applicable to chains which pass through several crystalline regions of total length ζ. However, these several crystalline regions generally will not be co-linear, and if $1-\lambda$ is relatively large, additional "x and y" restraints consequently may be imposed. Consideration of this factor and others arising from the various assumptions previously introduced (especially assumption (4)) casts doubt on the quantitative validity of equilibrium degrees of crystallinity computed from the present theory. On the other hand, it seems likely that such calculations may represent useful approximations.

In Fig. 1, the degree of crystallinity computed from Eq. (18) is plotted against the elongation α for arbitrary values of the parameters. The number of segments n has been taken as 50. The heat of fusion h_f has been assigned a value of $600R$ and the incipient crystallization tempera-

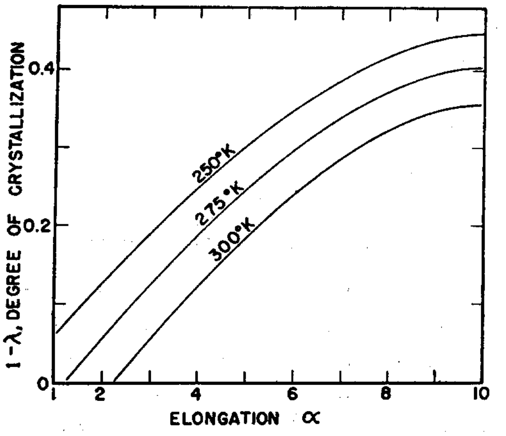

FIG. 1. Degree of crystallization $(1-\lambda)$ at equilibrium *vs.* elongation at the three temperatures indicated. Curves calculated from Eq. (18) taking $n=50$, $h_f=600R$ and $T_m{}^0=250$°K.

ture $T_m{}^0$ for the unstretched polymer has been taken as 250°K. Accordingly,

$$\theta=600(1/250-1/T).$$

These values have been chosen so as to obtain relationships which may resemble the behavior of vulcanized rubber.[20] The uppermost curve represents the calculation for $T=T_m{}^0$, corresponding to $\theta=0$; the middle and lowest curves represent crystallization at $T=275$°K and 300°K corresponding to $\theta=0.2182$ and 0.4000, respectively.

It will be observed that the $T=T_m{}^0=250$°K curve fails to fall to zero crystallinity at $\alpha=1$. This is a result of the failure of Eq. (11) at low elongations as already noted. Presumably all of the curves give values of $1-\lambda$ which, at low elongations at any rate, are somewhat too high. The maxima in the curves in Fig. 1 near $\alpha=(2n)^{\frac{1}{2}}$ are of dubious significance in view of the inadequacy of the Gaussian distribution for highly extended chains and in view also of other approximations.

According to these calculations the equilibrium degree of crystallinity induced by stretching is never large. This prediction of the theory might appear to be at variance with the established highly crystalline character of stretched vulcanized rubber.[21] However, the calculations refer to an equilibrium crystalline state which ordinarily is not reached when crystallization occurs simultaneously with elongation; under these circumstances crystallinity may exceed the equilibrium value (compare the following).

INCIPIENT CRYSTALLIZATION TEMPERATURE

In consideration of the expectation that the present theory should apply with optimum validity when the equilibrium degree of crystallinity is very small, calculation of the dependence of the incipient crystallization temperature T_m on the elongation α is particularly appropriate. Placing $\lambda=1$ in Eq. (16)

$$\theta\equiv(h_f/R)(1/T_m{}^0-1/T_m)=\varphi(\alpha)$$

from which it follows that the reciprocal of the incipient crystallization temperature should vary linearly with the function φ of the elongation α in accordance with the relationship

$$1/T_m=1/T_m{}^0-(R/h_f)\varphi(\alpha). \qquad (19)$$

Here again an incongruity arises as a result of the failure of Eq. (11) at low elongations: $\varphi(\alpha)$ retains a small positive value when α is decreased to unity and as a result T_m at $\alpha=1$ is predicted to be less than $T_m{}^0$. It may be presumed that a more accurate theory would replace $\varphi(\alpha)$ with a function which would equal zero at $\alpha=1$, thus removing the inconsistency just mentioned. The important present result is the form assumed by Eq. (19) relating incipient crystallization temperature to the heat of fusion and to a function of the elongation, although the latter admittedly is not given accurately by the present theory.

The function $\varphi(\alpha)$ as given by Eq. (17) depends on the structure of the network in a particularly simple manner. Except at quite low elongations, Eq. (17) can be written, approximately,

$$\varphi(\alpha)\cong(6/\pi)^{\frac{1}{2}}(\alpha/n^{\frac{1}{2}})-(\tfrac{1}{2})(\alpha/n^{\frac{1}{2}})^2 \qquad (17')$$

from which it is evident that the effect of increasing n, the number of segments between cross linkages, by a factor a can be compensated by increasing the elongation by $a^{\frac{1}{2}}$.

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[20] The value assigned to $T_m{}^0$ is some 50 to 60° lower than the crystallization temperature for raw rubber. (See L. A. Wood and N. Bekkedahl, J. App. Phys. **17**, 362 (1946); also, reference (24)). The incipient crystallization temperature probably is lowered somewhat, though perhaps not this much, by vulcanization or, more accurately, by the chemical changes accompanying vulcanization. Similarly, the value of h_f employed here may be rather larger than would be expected in view of the low heat of fusion of crystalline rubber. (See L. A. Wood, N. Bekkedahl and R. E. Gibson, J. Chem. Phys. **13**, 475 (1945)).

[21] J. E. Field, J. App. Phys. **12**, 23 (1941).

EFFECT OF CRYSTALLIZATION ON FORCE OF RETRACTION

Under assumptions paralleling those employed in the computation of the equilibrium degree of crystallinity, the retractive force f after the stretched rubber has been allowed to crystallize can be deduced as follows.

$$f=(\partial F/\partial \alpha)_e$$

where the subscript "e" implies a condition of equilibrium with respect to degree of crystallinity (i.e., equilibrium ζ or λ). Here f is expressed in force per unit initial cross-sectional area provided that σ represents the number of chains per unit volume. In general, recalling Eq. (13′) where F is expressed as a function of α and λ,

$$dF/d\alpha=(\partial F/\partial \alpha)_\lambda+(\partial F/\partial \lambda)_\alpha(d\lambda/d\alpha).$$

At equilibrium with respect to crystallinity, $(\partial F/\partial \lambda)_\alpha=0$ (see above). Hence,

$$\begin{aligned}f&=(\partial F/\partial \alpha)_e=(\partial F/\partial \alpha)_\lambda\\&=\sigma RT[(\alpha-1/\alpha^2)-(2n\beta l/\pi^{\frac{1}{2}})(1-\lambda)]/\lambda \qquad (20)\end{aligned}$$

where λ represents the equilibrium fraction of amorphous material calculable as a function of α and T from Eq. (16) or (18). Substituting for β from Eq. (3)

$$f=\sigma RT[(\alpha-1/\alpha^2)-(6n/\pi)^{\frac{1}{2}}(1-\lambda)]/\lambda. \qquad (21)$$

When $\lambda=1$, Eqs. (20) and (21) reduce to

$$f=\sigma RT(\alpha-1/\alpha^2) \qquad (22)$$

which is the expression ordinarily obtained for a network of Gaussian chains in the absence of crystallization.

In Fig. 2 stress-strain curves have been computed from Eq. (21) using the same values of the parameters employed for the calculations shown in Fig. 1. The uppermost curve corresponds to the non-crystalline material ($\lambda=1$); other curves correspond to the temperatures indicated. According to these calculations, crystallization subsequent to elongation (i.e., equilibrium crystallization) should markedly decrease the tension at extensions well above that for incipient crystallization. That the tension must be decreased by spontaneous isothermal crystallization at fixed elongation is an obvious consequence of the second law of thermodynamics. (A partial exception to this statement can be conceived in the case of a hypothetical elastic substance in which an increase in tension resulting from equilibrium crystallization at high elongations would be compensated by a decrease in tension at lower elongations.)

This deduction from theory is supported by observations of Meyer and Ferri[22] on the dependence of the tension in stretched vulcanized rubber on temperature. When samples stretched to fixed length were cooled gradually, an accelerated decrease in tension was observed on entering the crystallization range. Gradual decay in the tension at constant temperature in this region was similarly attributed to further slow crystallization. These observations were confirmed and extended by Wood and Roth.[23, 24]

If temperatures somewhat lower than the temperature $T_m{}^0$ for incipient crystallization in the undeformed material are employed, the equilibrium tensions calculated from Eq. (21), using λ from Eq. (18), are found to be negative. Calculations in this range may not be quantitatively significant for the following reason. As crystallization progresses in the sample at fixed elongation α, the tension decreases steadily according to Eq. (21). When the tension becomes small, indicating negligible orientation of amorphous portions of chains, additional nuclei which may form should no longer be preferentially oriented with respect to the z-axis. Crystal growth arising from these nuclei should not, therefore, decrease (algebraically) the tension in the sample, although longitudinal growth of crystals formed earlier should be expected to do so.

Smith and Saylor[25] observed increases in length when samples of stretched rubber were cooled to −25°C. This "secondary elongation" amounted

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[22] K. H. Meyer and C. Ferri, Helv. Chim. Acta **18**, 570 (1935).

[23] L. A. Wood and F. C. Roth, J. App. Phys. **15**, 781 (1944).

[24] For a thorough and comprehensive discussion of crystallization in rubber-like materials under various conditions, see "Crystallization Phenomena in Natural and Synthetic Rubbers" by L. A. Wood, in *Advances in Colloid Science* (Interscience Publishers, Inc., New York, 1946), Vol. II.

[25] W. H. Smith and C. P. Saylor, Bur. Stand. J. Research **21**, 257 (1938).

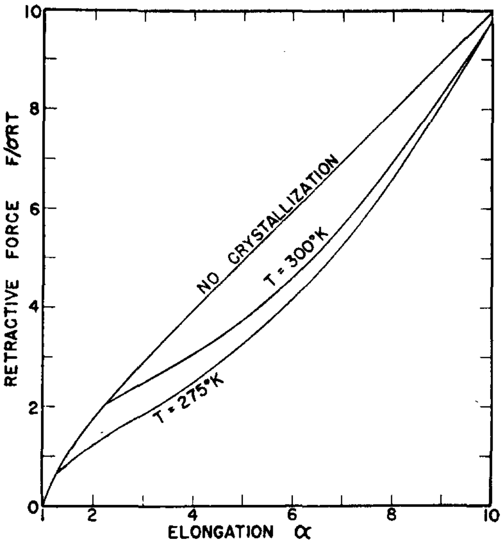

FIG. 2. Stress-strain curves, respectively, without crystallization and with equilibrium crystallization at the two temperatures indicated. Results calculated from Eq. (21) using the same parameters as those employed for computing the curves shown in Fig. 1.

to as much as 4 percent of the stretched length when the elongation was 200 to 300 percent.[24] This observation is readily explained by the present theory. It shows further that increase in crystallinity, even after the tension has been totally relieved, proceeds in part at least by longitudinal growth of existing oriented crystallites.

DISCUSSION

In attempting to characterize the effects of crystallization on elastic properties of rubber, one is faced with a superficially paradoxical situation. Abundant evidence shows that the tension in a highly elongated vulcanized rubber which has undergone crystallization during stretching is substantially greater than in another similarly vulcanized rubber (or the same rubber at higher temperature) in which no crystallization occurs at the same elongation. On the other hand, theory leads inevitably to the conclusion that crystallization should decrease the tension.[3,4] This can be deduced from a theoretical analysis such as has been set forth above, or more directly from thermodynamic (equilibrium) considerations.

As earlier remarks have indicated, the clue to the resolution of this "paradox" may be found in the limitation of thermodynamical theories to states of equilibrium. When vulcanized rubber is stretched in the customary manner, such that crystallites form during the stretching process, the equilibrium state to which the theory applies will not ordinarily be reached. This point appears to have been overlooked in previous discussions of the theory of crystallization on stretching.[3,4] For example, James[4] attributes the observed increase in tension resulting from crystallization to "filler action" of the crystallites. The following discussion attempts to show in some detail how crystallites as normally formed in stretching may markedly enhance the retractive force.

Formation of crystal nuclei at an elongation, α, occurs without significant change in entropy as pointed out above. These identical nuclei, made up of the same chain segments in the same arrangement, could not be assembled at a different elongation without decreasing the entropy. Their formation at an elongation either greater or less than α would involve assignment of the chains to configurations not in conformity with their most probable arrangement consistent with this elongation. The situation is analogous to the formation of cross linkages at an intermediate elongation; in fact, the crystal nuclei may be regarded as giant cross linkages. Random introduction of cross linkages at an elongation, α, entails no change in configurational entropy, but if the elongation is altered in either direction the entropy will be less than it would have been in the absence of these cross linkages. It becomes evident, therefore, that both the entropy S_α and $(dS/d\alpha)$ at the elongation α remain unaltered when cross linkages, or crystal nuclei (disregarding the effects of their growth to finite size), are introduced at random at the extension α. Hence, the tension at α also is unchanged. As the elongation is increased, however, the tension will be augmented by the presence of these additional cross linkages, or by the crystal nuclei.

In the ordinary "non-equilibrium" stretching of rubber, the first crystal nuclei may be presumed to form at an extension α_1 only slightly beyond the extension for incipient crystallization at equilibrium. Growth of these crystallites may actually reduce the tension somewhat at elongations not greatly exceeding α_1, in accordance with concepts set forth by Alfrey and Mark[3] and with the above theory. As the elongation is increased to α_2, these crystallites, being of sufficient permanence to resist dissolution in favor of a crystalline arrangement more stable at the higher elongation, act in the manner discussed above to increase the tension. However, further crystallization will occur at α_2 and thus counteract this effect. The portion of this further crystallization which consists of nucleation and of attachment of chains to existing crystallites (lateral, as apart from longitudinal, growth of existing crystallites) introduces restraints which increase the tension developed in passing to a higher elongation α_3; etc. In this way a state is soon reached where the tension rises rapidly with elongation.

Under the influence of these compounded internal stresses, the degree of crystallinity ultimately reached may exceed considerably its equilibrium value as calculated above. Additional deformation is borne largely by the remaining amorphous material, and when only a small fraction remains in the amorphous condition that fraction must undergo an actual deformation exceeding correspondingly the incremental macroscopic deformation of the sample.[3, 4]

Thus, we reach the conclusion that the accelerated increase in tension with elongation and the ultimate steep slope of the stress-strain curve for crystallizing rubbers are consequences of two interrelated factors: (a) sub-division of amorphous chains, or portions thereof, by attachments to crystalline regions (i.e., the "cross-linking effect"), which increases the number of elastically effective elements at all higher elongations, and (b) the small residue of easily deformable (i.e., amorphous) material at high elongations. Explanations according to which the accelerated rise in the stress-strain curve is attributed primarily to the rapid decrease in entropy as the chain approaches full extension,[3, 26] or to the combined entropy decrease and internal energy increase arising from bond deformations for chains nearing full extension,[27] crystallization being disregarded as a primary factor, are rejected here. Near the breaking point unquestionably many chain elements are stretched approximately to full extension. However, in order to arrive at an adequate interpretation of the stress-strain curve at intermediate and high extensions, consideration must be given first of all to the large increase in the number of elastic elements brought about as a result of crystallization.

The non-equilibrium character of crystallinity as it ordinarily occurs in stretched rubber is confirmed by various observations. Hystersis loops are larger when the deformation cycle extends into the region of crystallization.[23, 28] Rohde[29] and Braendle and Wiegand[30] compared the relaxation of stress or strain in vulcanized natural rubber subjected to repeated elongation with that which occurred in Buna-S, or in GR-S, under the same conditions. At low maximum elongations relaxation of the synthetic rubber was greater, but this order was reversed at higher elongations extending into the crystallizing range for natural rubber. The latter showed marked relaxation effects with repeated stretching to high elongations. These results can be attributed plausibly to recrystallization induced by the cyclic deformation. Some vestiges of crystallinity presumably survive the retraction phase of the cycle, and these may serve as nuclei for crystallization during the subsequent elongation. It is to be expected that more favorably located crystalline regions will be developed preferentially under these circumstances. In any event, a change in crystalline arrangement must necessarily proceed in the direction of the more stable state, and this change will diminish the tension. Braendle and Wiegand[30] emphasize the practical merit of this relaxation phenomenon in rubber when subjected to repeated stresses which approach the ultimate strength of the material (e.g., in cut growth in tire treads).

Throughout this paper the term "melting point" has been avoided, "crystallization temperature," or "incipient crystallization temperature," having been used instead. In the opinion of the author it is best to avoid designation of the amorphous and crystalline regions as separate phases. Neither would exist in the same state apart from the other. The configurational re-

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[26] L. R. G. Treloar, Trans. Faraday Soc. **42**, 83 (1946).

[27] W. Kuhn and H. Kuhn, Helv. Chim. Acta **29**, 1095, 1615, 1634 (1946).

[28] I. Williams and B. M. Sturgis, Ind. Eng. Chem. **31**, 1303 (1939).

[29] E. Rohde, Kautschuk **15**, 64 (1939).

[30] H. A. Braendle and W. B. Wiegand, J. App. Phys. **15**, 304 (1944).

strictions imposed on amorphous sections of chains by the crystallites to which they are attached are evident from the above discussion.[31] The partial molal free energy of the amorphous "phase," if formulation of such a function were attempted, would depend on the amount of that phase, in direct violation of the concept that such functions are intensive only.

If the amorphous and crystalline regions were considered as separate phases, the phase rule would dictate that the system be characterized by an invariant melting temperature (at fixed pressure). High polymers invariably change from amorphous to crystalline (or *vice versa*) over a range of temperature, although the onset of crystallinity may occur at a well defined temperature. Corresponding complications arise in two component systems if the semi-crystalline polymer is counted as two phases.[32]

The present theory appears to be in satisfactory qualitative agreement with observation, although, as is evident from the above discussion, few experimental measurements have been reported on the crystallization of stretched vulcanized rubbers under conditions which assure satisfactory approach to equilibrium. It is not possible at the present time, therefore, to compare quantitative aspects of the theory with experiment. In view of the desirability of minimizing complications (both theoretical and experimental) which may enter at appreciable degrees of crystallinity, a test of Eq. (19) relating elongation with incipient crystallization temperature seems most immediately appropriate. Experiments designed to furnish data suitable for this purpose are under way in this laboratory at the present time.

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[31] E. M. Frith and R. F. Tuckett, Trans. Faraday Soc. **40**, 251 (1944), have discussed the thermodynamics of crystallization in polymers in the absence of deformation. The equations (see J. Chem. Phys. **10**, 51 (1942)) which they used to express the entropy of chain elements within the amorphous region actually apply only to chains the ends of which are free to locate anywhere. The dependence of melting temperature on degree of crystallinity deduced by Frith and Tuckett originates entirely from this erroneously implied freedom of each of the amorphous chain elements with respect to the remainder of the semicrystalline structure.

[32] R. B. Richards, Trans. Faraday Soc. **42**, 10 (1946).