are cross-linked no change occurs in the configurational entropy of the individual chains since the units which are paired together are selected at random. Thus the contribution of the configurational entropy in the liquid state to the total entropy of fusion will remain unaltered. However, as Flory[3] has pointed out, the situation is quite different when axially oriented chains are cross-linked. In this case a cross-link must join two adjacent molecules together. Thus if a unit of a given molecule is to be cross-linked to another unit, this latter unit must be in an adjacent position on a neighboring molecule. Even though the cross-links are distributed at random in space, the cross-linking process does not involve the random selection of pairs of units. The specification of adjacent units of neighboring molecules imposes an order on the system, which will persist in the liquid state because of the permanence of the cross-links. The configurational entropy of the chains in the liquid state is decreased by this process, and the entropy of fusion will be altered in a corresponding manner. The melting temperature of this type network would then be expected to be larger than that for the non-cross-linked system from which it is formed and also should be greater than the corresponding network formed from random chains. However, this expected increase in $T_m{}^i$ on cross-linking oriented chains may be offset by the non-configurational effects of the cross-links which cause a major depression of the melting point. These considerations are in accord with the observed values of $T_m{}^i$ for both types of networks.

An exact quantitative comparison between experiment and theory must await a more detailed explanation of the large melting point depression caused by the cross-linking of the random chains as well as the determination of melting temperatures under conditions more closely approaching those of equilibrium. Preliminary calculations utilizing the data of Fig. 3 indicate very good accord between the difference in melting temperature of the two types of networks and the theoretical equations.[3]

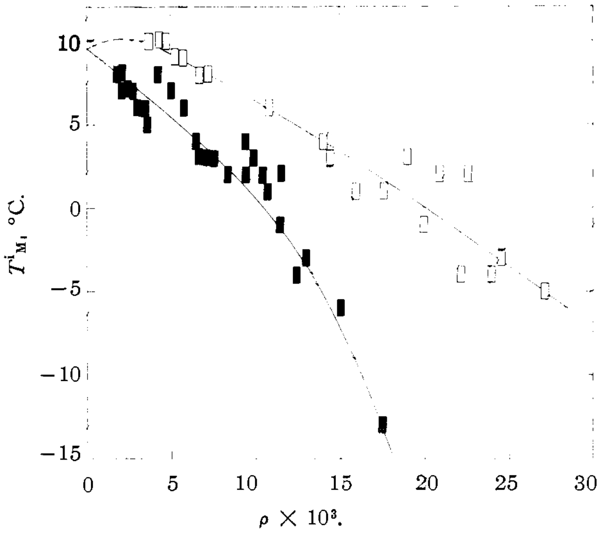

Fig. 3.—Isotropic melting temperature, T^i_M, *versus* fraction of units cross-linked, ρ: results for networks formed from random chains, ■; results for networks formed from oriented chains, □.

Acknowledgments.—The authors wish to thank Dr. P. J. Flory for an advance copy of his manuscript[3] and the many helpful and stimulating discussions. The assistance of Mr. D. W. Brown in irradiating the samples is gratefully acknowledged.

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Thermodynamics of Shrinkage of Fibrous (Racked) Rubber[1]

BY J. F. M. OTH[2] AND P. J. FLORY

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Highly oriented natural rubber samples of Roberts and Mandelkern, prepared by racking and subsequently cross-linked using γ-radiation, undergo a spontaneous shrinkage upon melting which closely resembles the shrinkage of collagen. If the transformation is arrested by application of a tensile force, a state of equilibrium may be established between two distinct zones, or phases, one being totally amorphous (shrunken) and the other unchanged (*i.e.*, racked). Determination of the stress τ_{eq} required for phase equilibrium at various temperatures is described. Extrapolation to $\tau_{eq} = 0$ gives equilibrium melting temperatures $T_m{}^i$, which are about 8° below the temperatures $T_s{}^i$ for spontaneous shrinkage. The heat of transformation of racked to amorphous rubber calculated from the dependence of τ_{eq} on T is 4.5 cal. g.$^{-1}$. Since the degree of crystallinity is only 0.24, the heat of fusion calculated for 1 g. of crystalline rubber is *ca.* 19 cal., which agrees satisfactorily with the value 15.3 cal., deduced by Roberts and Mandelkern through use of the melting point depression method. The shrinkage of racked rubber displays all of the important features associated with the similar contraction of fibrous proteins.

Highly oriented, crystalline fibrous proteins display marked contractions when subjected to conditions which induce melting. The dimensional change is particularly striking in the case of native collagen fibers which melt with reduction in length by a factor of about one-fifth. Moreover, the transformation is macroscopically discontinuous, a partially shrunken fiber comprising two distinct regions meeting at a rather well-defined boundary transverse to the fiber axis.[3] One of these regions consists of native fiber, highly birefringent and relatively inextensible under tension; the other

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(3) J. F. M. Oth, E. T. Dumitru, O. K. Spurr and P. J. Flory, THIS JOURNAL, **79**, 3288 (1957). Also J. F. M. Oth and O. K. Spurr, unpublished.

region is completely amorphous, non-birefringent (nearly) and rubber-like. The latter zone is most easily distinguished by its greater width.

In connection with a current series of investigations on the shrinkage and elastic deformation of collagen and related fibrous proteins,[3,4] it seemed desirable to prepare a model system from a random-coiling, long-chain polymer capable of crystallizing when stretched. Inasmuch as collagen becomes rubber-like upon shrinking and natural rubber can be rendered fibrous by severe stretching (racking), natural rubber seemed an appropriate choice. Preliminary samples of racked rubber made available to us by Roberts and Mandelkern[5,6] of the Bureau of Standards revealed a capacity for shrinkage upon heating which is similar in all respects to the shrinkage of collagen, except that a swelling agent (*e.g.*, water in the case of collagen) is not required. Upon heating above the shrinkage temperature (*ca.* 35° in the absence of tension) nodular regions of amorphous rubber appear between adjoining untransformed zones of racked rubber; the transformation at a given temperature can be arrested by application of tension. The introduction of cross-linkages by γ-radiation in the racked state[5] serves to suppress plastic flow upon melting, as is essential for establishment of states of equilibrium. Cross-linking in this manner is analogous to "tanning" of native collagen fibers, which likewise introduces cross linkages in the highly oriented state.

If we regard the co-existing "racked" and amorphous zones as phases, then the tensile force f_{eq} required to maintain equilibrium between these phases must be related to the temperature according to the analog of the Clapeyron equation[7,8]

$$(\partial f_{\text{eq}}/\partial T)_P = -\Delta S/\Delta L \qquad (1)$$

where ΔS and ΔL are the latent changes in entropy and length associated with the transformation of the fiber under the conditions specified by T and P. Since at equilibrium between the phases

$$\Delta H - T\Delta S - f\Delta L = 0 \qquad (2)$$

it follows that eq. 1 may be replaced by

$$[\partial(f_{\text{eq}}/T)/\partial(1/T)]_P = \Delta H/\Delta L \qquad (3)$$

where ΔH is the latent enthalpy change. Thus, determination of f_{eq} as a function of T offers a means for evaluating ΔH.

The investigation herein reported was concerned with processes of dimensional change in natural rubber samples cross-linked by exposure in the racked state to γ-radiation. The relationship of stress to strain is examined for both the racked and the totally amorphous (shrunken) states. Principal attention, however, focuses on the equilibrium between co-existing racked and amorphous portions of the sample in the partially shrunken state. A method is described for determining the force f_{eq} required for equilibrium between these phases, and the thermodynamic relation expressed in alternative forms by eq. 1 and 3 is applied to samples of racked rubber cross-linked to different extents as described in the preceding paper.[5]

Experimental

Samples.—Natural rubber specimens prepared from cast latex films were supplied by Roberts and Mandelkern,[5] whose assistance is gratefully acknowledged. The procedure used to impart high orientation (*i.e.*, racking) is described in the preceding paper.[5] A high degree of orientation was indicated both by the X-ray diffraction pattern and by the approximately eleven-fold shrinkage in length upon melting the crystalline racked sample by warming.

Cross-linking was carried out in the racked state by the action of γ-radiation, as described by Roberts and Mandelkern. Three samples irradiated for the same time (600 hr.) *in vacuo* but at different distances from the 50 curie Co^{60} source. These are designated b-2, f-1 and l-1 in decreasing order of cross-linking. The range in degree of cross-linking is about twofold; see Table III.

The cross-sections of the amorphous, *i.e.*, shrunken, samples were determined under a microscope equipped with a micrometer eyepiece. The cross-section in conjunction with the length (under zero force) between the clamps yielded the sample volume. Lengths of the racked samples were 5 to 10 cm.; the lengths of the amorphous (shrunken) samples under no force were 1 to 2 cm. Cross-sections in the amorphous state were *ca.* 7×10^{-3} cm.^{2}.

Determination of Densities and Degrees of Crystallinity.—The densities of samples in the racked and in the amorphous states were determined by comparing the weight *in vacuo* and in methanol at 25°. The quartz spring used for the weighings had a sensitivity of *ca.* 0.5 mm./mg.; the length of the spring was measured with a cathetometer to an accuracy of 5×10^{-3} mm., corresponding to 10^{-2} mg. Using samples of *ca.* 15 mg., the densities could be determined with an accuracy of *ca.* ±0.0005 g. cc.$^{-1}$. Vacuum was applied for the purpose of eliminating gas bubbles from the surface of the sample immersed in methanol prior to weighing.

The densities of the three samples investigated are recorded in Table I. The close agreement between the densities of these samples in the racked state, as well as in the amorphous state, is not unexpected inasmuch as the same racking procedure was applied to each. The X-ray density of crystalline rubber according to Bunn[9] is 1.009 (±0.010) g. cc.$^{-1}$ at 25°. Assuming that the density increases linearly with the degree of crystallinity, we obtain the results given in the last row of Table I. The values found for the per cent. crystallinity are somewhat lower than the 35% figure obtained by Roberts and Mandelkern[5] for racked samples prior to cross-linking. The difference, if real, suggests a decrease in crystallinity during the cross-linking process.

TABLE I

SAMPLE DENSITIES (GR. CC.$^{-1}$ AT 25°) AND DEGREE OF CRYSTALLINITY

	b-2	f-1	l-1	Av.
Amorphous density	0.9100	0.9102	0.911	0.910
Racked density	0.9346	0.9342	0.934	0.934
% Crystalline	25	24	24	24 ± 2

Tension Measurements.—A diagram of the dynamometer is shown in Fig. 1. The crystalline, racked sample, 5 to 10 cm. in length and *ca.* 2×10^{-3} cm.^{2} in cross-section, is suspended between two small metal clamps, C_1 and C_2. The vertical position of the lower clamp C_1 is fixed by attachment to the base B fitting inside the inner Pyrex tube J_1 and suspended from the main column A of the apparatus by two small stainless-steel rods as shown. The upper clamp C_2 is attached to the lower end of a 1.0 mm. nichrome rod, its upper end connecting with a strain gauge G. The inner Pyrex tube is filled with sufficient water to surround sample and clamps. Pure nitrogen is bubbled very slowly through the water in order to suppress oxidation of the sample.

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(4) R. R. Garrett and P. J. Flory, *Nature*, **177**, 176 (1956). Also, R. R. Garrett, Ph.D. Dissertation, Cornell University, 1957.

(5) D. E. Roberts and L. Mandelkern, THIS JOURNAL, **80**, 1289 (1958).

(6) Also, D. E. Roberts, L. Mandelkern and P. J. Flory, *ibid.*, **79**, 1515 (1957).

(7) G. Gee, *Quart. Rev.*, **1**, 265 (1947).

(8) P. J. Flory, THIS JOURNAL, **78**, 5222 (1956).

(9) C. W. Bunn, *Proc. Roy. Soc.* (*London*), **A180**, 40 (1942). Also O. Kratky and G. Porod in "Die Physik der Hochpolymeren," Vol. III, Ed. by H. A. Stuart, Berlin, 1955, p. 132.

The temperature of the sample and suspension system is controlled by circulation of water from a thermostat through the outer jacket J_2 as shown.

The strain gauge is attached to a brass block which slides on the main column, its position being controlled as shown in Fig. 1 by the screw S of low pitch. The screw is driven by a low-speed, reversible d.c. motor; the length may be varied at any constant rate from 0.02 to 0.5 cm. min.$^{-1}$. The lower rate, corresponding to an extension of 0.1 to 0.2% per min., was used in the experiments reported here. The strain gauge (Statham Instrument Company, Transducer Model G-1) has a capacity of 120 g. and a linear response of 0.16 mv. per g. under an applied e.m.f. of 9 v. The deflection of the strain gauge is negligible, being only 0.02 mm. at full load. The output of the strain gauge is connected to a Honeywell recorder giving full scale deflection at 10 mv. A deflection of 1 mm. corresponds to a load of *ca.* 0.2 g. The instrument was calibrated directly by addition of known weights before each run; in experiments of long duration calibration was repeated in the course of the run, the sample being temporarily cooled and the tension relaxed. Stress-strain curves were obtained by recording the force while the sample was elongated at the aforementioned rate. An electrical pulse at each turn of the screw (S in Fig. 1) was recorded simultaneously with the output of the gauge, thus permitting determination of the length from the record. Stress-strain curves for both crystalline (racked) and amorphous (shrunken) fibers were determined in this manner. Upon reversing the motor driving the screw S, the stress-strain curve was in each case found to deviate inappreciably from the curve established during elongation. Hysteresis is therefore negligible over the range of elongation examined (7% for racked samples, 150% for amorphous).

Results

Dependence of Length of Racked Samples on Temperature and Force.—The relation of stress to strain was determined for limited extensions of the samples in the comparatively inextensible racked state for several temperatures from 0 to 30° but not exceeding the shrinkage temperatues (*ca.* 35°, see below). Results are shown in Fig. 2 for sample f-1 at several temperatures. It will be observed that the length L^c for a force of zero, established by extrapolation, decreases by several per cent. with rise in temperature. Simultaneously, the *initial* modulus decreases from 1.7×10^9 dynes cm.$^{-2}$ at 0° to 0.4×10^9 dynes cm.$^{-2}$ at 30°.[10] Both changes are doubtless due to a slight decrease in the degree of crystallinity (*i.e.*, partial melting) as the shrinkage temperature T_s^i (see below) is approached. Up to 30° the changes with temperature are essentially reversible.

Values of L^c, established as in Fig. 2 for temperatures below 35°, are plotted against the temperature in the upper portion of Fig. 3. Irreversible shrinkage occurs at 35° (T_s^i) and above. The lower points represent lengths of the fully shrunken (amorphous) samples, those below 35° having been obtained by shrinking above 35° and then lowering the temperature.

Shrinkage Temperatures.—Upon raising the temperature shrinkage occurs abruptly at a temperature easily defined within narrow limits under given conditions. Shrinkage temperatures T_s^i under no force were determined by heating at a rate of 2°/hr., the temperature at which an amorphous "bulb" substantially larger in cross-section than the semi-crystalline sample made its appearance being taken as T_s^i. The results were reproducible within ±1°. They are recorded in the second column of Table IV for comparison with the equilibrium melting temperatures T_m^i, determined in the manner described below, for a tensile force f of zero.

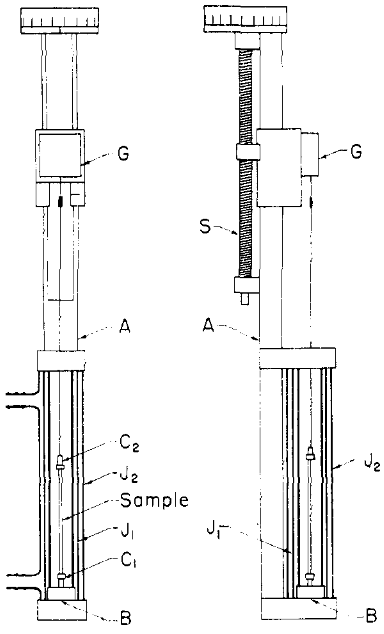

Fig. 1—The dynamometer.

As is evident from Fig. 3, sample f-1 shrinks to about one-fourth of its initial length. Similar shrinkages are exhibited by the other samples according to results presented in Table III. The degree of shrinkage approximates that exhibited by tendon collagen. Non-cross-linked samples of racked rubber shrink by a much larger factor of about eleven.[6] The degree of shrinkage diminishes with the degree of cross-linking in the manner required by theory,[8] as was shown previously.

The transformation of these racked rubber samples upon heating bears a striking resemblance to the familiar shrinkage of collagen and other fibrous proteins including keratin, epidermin, myosin and fibrin. The phenomenon of thermal shrinkage of proteins, or supercontraction as it has sometimes been called, appears to be characteristic of the melting of crystalline polymers having high axial orientation. Melting and simultaneous shrinkage is sometimes followed (upon cooling) by recrystallization to the same or to a different crystalline form. The native α-crystalline proteins, for example, may be converted to the β-form in the retracted state. There appears to be no justification for the assumption, often implied, that the subsequently formed crystalline state conduces the shrinkage. Rather, melting of the initial anisotropic state is essential, subsequent recrystallization being only incidental.

Most important is the fact established by these experiments, that the phenomenon of shrinkage is by no means restricted to polypeptides or other specific polymeric structures. It may be presumed to occur in any suitably oriented crystalline polymer comprising long molecular chains.

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(10) The modulus of elasticity of native collagen in water at room temperature is approximately an order of magnitude greater, *i.e.*, *ca.* 1 to 3×10^{10} dynes cm.$^{-2}$. The difference may be indicative of a considerably higher percentage of crystallinity in collagen.

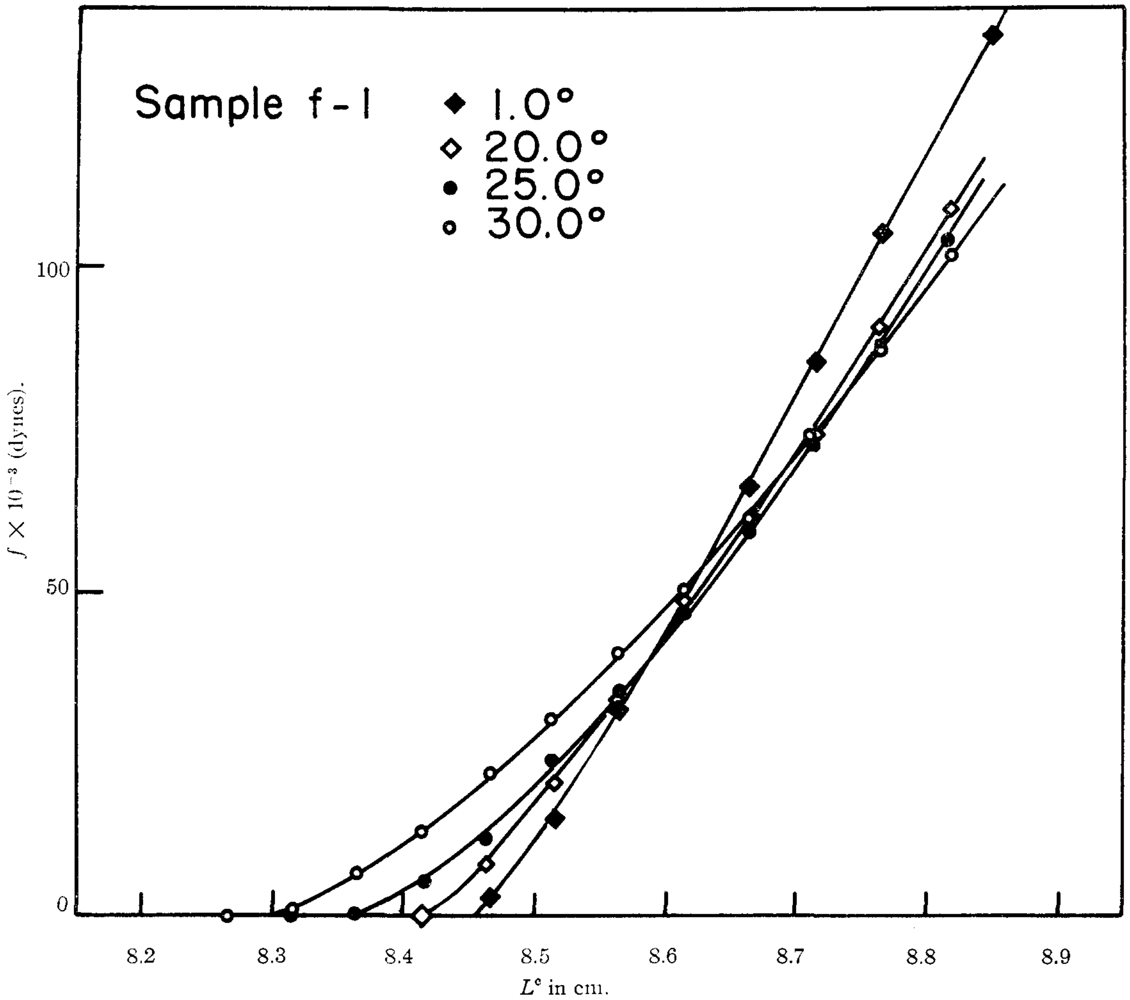

Fig. 2.—Force-length curves for racked sample f-1 prior to shrinkage.

The Stress-Strain Relation for Amorphous Samples.—The curve relating force to length for sample f-1 at 35° is shown in Fig. 4. Points obtained during retraction are virtually coincident with those for extension and therefore are not distinguished on the graph. In Fig. 5 the stress

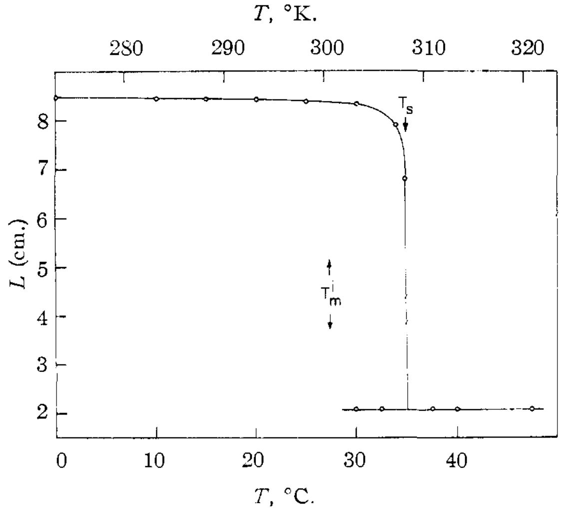

Fig. 3.—Length under zero force for sample f-1 plotted against temperature. Results obtained by extrapolation to $f = 0$.

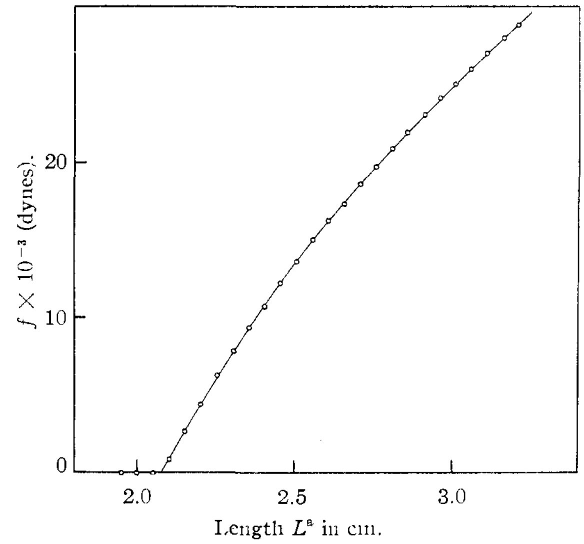

Fig. 4.—Force-length curve for sample f-1 in the amorphous state at 35°.

τ referred to the amorphous cross-section in the undeformed state is plotted according to the equation of state given by rubber elasticity theory[8]

$$\tau/T = (R\rho <\alpha>_0{}^2/M_0\bar{v})(\alpha - 1/\alpha^2) \qquad (4)$$

where ρ is the effective fraction of isoprene units which are cross-linked, M_0 is the molecular weight of an isoprene unit, $\bar{v}$ is the specific volume, R is the gas constant, $\alpha = L/L_i{}^a$ is the elongation ratio, $L_i{}^a$ being the "isotropic" length for $f = 0$ in the amorphous state at the temperature T, and $<\alpha>_0$ is the mean dilation factor.[5,8] The experimental points are well represented, over the limited range of extension of concern in the present investigation, by the straight line drawn through Fig. 5. It has been unnecessary therefore to include in the equation of state the additional term in $(1 - 1/\alpha^3)$ which ordinarily is required.[11-13]

From the slope of the line in Fig. 5 we deduce the value of the product $\rho<\alpha>^2{}_0$ according to eq. 4. Results for the various samples recorded in the second column of Table II were obtained in this manner from the observed stress–strain relationship. The cross-linking densities ρ given in the third column are based on the radiation dosages and the cross-linking efficiency established by Roberts and Mandelkern[5] for racked samples. Values for the dilation factor given in column four follow directly from columns two and three. These values, deduced from the stress–strain relationship, compare favorably with those derived by Roberts and Mandelkern[5] from swelling measurements. Thus, in common with numerous previous observations on systems cross-linked in the isotropic state, swelling and elasticity measurements on networks imposed on the racked state yield concordant results.

TABLE II

SUMMARY OF RESULTS FROM STRESS–STRAIN MEASUREMENTS ON AMORPHOUS SAMPLES

Sample	$\rho<\alpha>_0{}^2 \times 10^2$	$\rho \times 10^2$	$<\alpha>_0$
b-2	1.30	2.17	0.78
f-1	0.98	1.56	.79
l-1	0.62	1.04	.77

Equilibrium between Racked and Amorphous States.—Just as in the case of collagen,[3] it is essential to recognize the non-identity of the shrinkage temperature T_s with the "melting" temperature T_m at which equilibrium prevails between coexisting racked (semi-crystalline) and amorphous phases, or regions, at given pressure P and tensile force f.[14] If the sample is maintained at $T \geq T_s$, a shrunken zone(s) appears and, if the force is maintained constant, it spreads throughout the length of the fiber. In order to arrest the transformation once it is initiated, the force must be increased substantially or the temperature lowered. In order to achieve stable coexistence of crystalline and amorphous regions, the temperature must be lowered 5 to 10° below T_s, the force remaining constant. The equilibrium melting temperature T_m is therefore substantially lower than T_s, and the difference between them represents the superheating required for the formation of a macroscopic amorphous region.

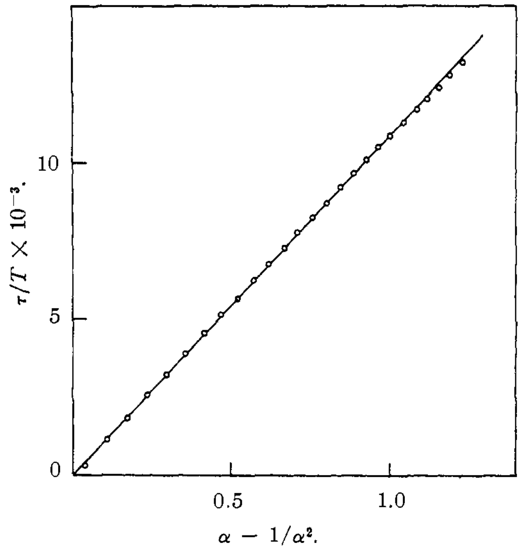

Fig. 5.—Stress-strain relation for sample f-1 at 35° plotted according to eq. 4.

In the experiments to be described, the following procedure was adopted. After mounting the sample in the dynamometer, the clamps are fixed at a distance apart somewhat less than the initial sample length L^c. The temperature is then raised to an arbitrarily chosen temperature T a few degrees above the shrinkage temperature $T_s{}^i$ for $f = 0$, and thereafter the temperature is maintained constant. Melting proceeds in one or more sections of the sample with the development of amorphous zones across the sample section. Inasmuch as the total length is fixed, the sample exerts a retractive force which increases as melting progresses. The force approaches a constant value after *ca.* 15 minutes. If the length is now increased slightly, the concomitant increase in force initially developed is observed to decay toward the former value; the initial decrease in force brought about by a small decrease in length is followed similarly by an increase in force. An example is shown in Fig. 6. Evidently, recrystallization or melting at the interface(s) between semi-crystalline (racked) and amorphous zone(s) occurs to the extent required for re-establishment of phase equilibrium. A too-drastic increase in length cannot, however, be accommodated with restoration of the initial equilibrium force.

In accordance with the observations cited, the equilibrium force f_{eq} at a given temperature may be bracketed within reasonably narrow limits by manipulating the length of the partially shrunken sample until the force remains constant with time for at least 1 hr. The equilibrium force is independent of the sample length, provided merely that semi-crystalline and amorphous regions co-

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(11) G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946).

(12) P. J. Flory, N. Rabjohn and M. C. Shaffer, *J. Polymer Sci.*, **4**, 225 (1949).

(13) S. M. Gumbrell, L. Mullins and R. S. Rivlin, *Trans. Faraday Soc.*, **49**, 1495 (1953).

(14) When $f = 0$, we employ the symbols $T_s{}^i$ and $T_m{}^1$ signifying an *isotropic* amorphous phase. Also, a subscript "m" is applied to the equilibrium temperature T occurring in eq. 1–3 in consideration of the fact that T, or T_m, is to be regarded as a melting point under the tensile force f_{eq}.

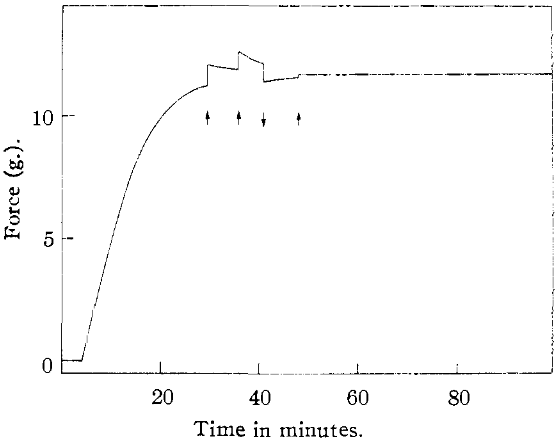

Fig. 6.—Illustrative plot of determination of equilibrium force. Points at which the length was increased or decreased are indicated by vertical arrows.

exist, *i.e.*, the equilibrium force is independent of the amount of each phase.

Having established f_{eq} at one temperature, additional points (T_m, f_{eq}) may be determined on the same sample merely by re-setting the temperature and, preferably, with simultaneous reduction of the length in order to allow advancement of the amorphous zone(s) to yield fresh interfaces. Once interfacial regions have been established through partial transformation of the sample at $T_m > T_s^i$, the equilibrium force may be determined at temperatures T_m in the range $T_m^i < T_m < T_s^i$.

Results obtained in this manner for sample f-1 are presented in columns one to three of Table III. Melting and recrystallization processes become very slow at the lower temperatures, hence it is more difficult to establish the equilibrium force. The error is therefore greatest at low forces, as is borne out by comparison of determination 8 with 6 and of 9 with 3. The results are plotted in Fig. 7.

Also included in Table III are the equilibrium stresses τ_{eq} referred to the cross-section of the amorphous sample (f-1) under a force of zero, the lengths L^c of the racked sample under the forces f given in the third column, and the lengths L^a in the amorphous state under the forces f_{eq} and at the temperatures T_m. The former lengths L^c have been taken from the 30° curve in Fig. 2, the relatively small effect of temperature being ignored. The values given for L^a have been calculated from eq. 4 for the temperatures $T = T_m$ and stresses τ_{eq}. The differences $-\Delta L = L^a - L^c$ are recorded in the next to the last column of Table III.

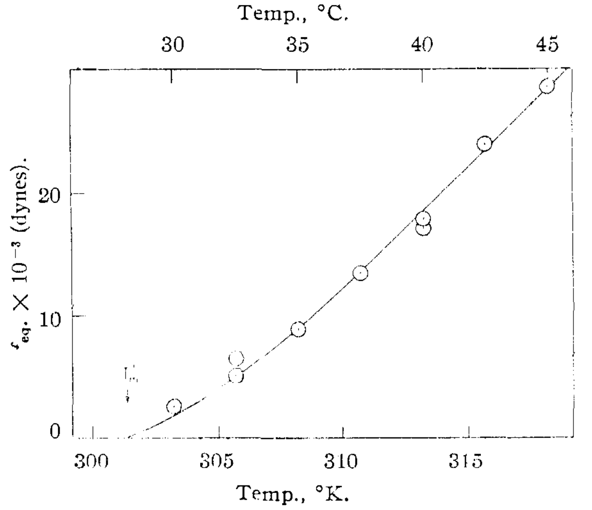

Fig. 7.—Force for phase equilibrium for sample f-1 plotted against the absolute temperature.

Table III

Phase Equilibrium Data for Sample f-1

(Dimensions in the isotropic amorphous state: cross-section = 76.3 (±0.5) × 10^{-4} cm.^{2}; L_i^a = 2.078 cm.)

T_m (°K.)	Order in sequence of detn.	f_{eq} × 10^{-3}, dynes	τ_{eq} × 10^{-5}, dyes cm.$^{-2}$	L^c, cm.	L^a, cm.	$-\Delta L$	L_i^a $J(1/T_m)$ × 10^6
303.2	7	2.7	3.5	8.335	2.145	6.190	9.2
305.7	6	5.0	6.6	8.350	2.215	6.135	18.4
	8	6.5	8.5	8.365	2.255	6.110	
308.2	5	9.0	11.8	8.390	2.335	6.055	27.3
310.7	4	13.5	17.7	8.415	2.495	5.920	36.5
313.2	3	17.5	22.9	8.445	2.665	5.780	45.5
	9	17.8	23.4	8.445	2.675	5.770	
315.7	2	24.0	31.5	8.485	2.955	5.530	55.2
318.2	1	28.9	37.8	8.510	3.195	5.315	64.6

The isotropic melting point T_m^i of sample f-1, obtained by extrapolation to $f_{eq} = 0$ in Fig. 7, is 302°K. Results for the various samples are given in Table IV. Owing to the previously mentioned difficulty of establishing equilibrium at low forces, the values of T_m^i are subject to an error of *ca.* ± 2°. An increase in the melting point with degree of cross-linking is suggested by the results. Whereas cross-linking in the isotropic state is known to lower the melting point,[15] theoretical considerations[8] suggest that the melting point should be increased by cross-linking in the highly ordered state. Roberts and Mandelkern in the preceding paper[5] report consistently higher melting points for samples cross-linked in the racked state. Although their melting temperatures, obtained by comparatively rapid heating of recrystallized samples, are admittedly some 20° below the equilibrium values, they have pointed out that, according to their Fig. 3, our sample l-1 should melt 7° higher than b-2 under the conditions employed by them. The difference is identical with that found by us and reported in our Table IV.

Table IV

Comparison of Shrinkage and Equilibrium Melting Temperatures at $f = 0$

Sample	T_s^i, °K.	T_m^i, °K.
b-2	310	299
f-1	308	302
l-1	311	306

Recrystallization.—Samples removed from the dynamometer after complete melting were nonbirefringent when viewed in the polarizing microscope. However, after standing several days at 20–25°, specimens of each sample were observed to

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(15) D. E. Roberts and L. Mandelkern, Bulletin of the American Physical Society, Series II, Vol. 1, March, 1956.

develop substantial birefringence, the direction of higher refractive index coinciding with the long axis of the sample. The birefringence vanished upon heating above 30°; the exact temperature of disappearance was not ascertained. Samples of rubber similarly cross-linked (with γ-radiation) in the amorphous state without stretching offered no evidence of either birefringence or depolarization, even after standing many days at 20 to 25°. We interpret the spontaneous generation of birefringence in the former samples as clear evidence of recrystallization with preferred orientation along the initial axis of elongation. Depolarization rather than birefringence should have been observed if the latter samples had crystallized; spontaneous development of birefringence could not have been expected from their molecularly isotropic structures. The absence of depolarization indicates absence of crystallinity.

The observations cited require that the melting point of the racked, cross-linked samples must exceed 25°, and hence offer partial confirmation for the values deduced from the stress studies. They also indicate a latent "memory" in the network structures, to the extent that recrystallization restores the original preferred axis. Finally, it is noteworthy that recrystallization in these samples requires a remarkably small degree of supercooling.[16]

Discussion

By introducing the stress τ_{eq} (referred to the amorphous isotropic cross-section $A_i = V/L_i^a$) in eq. 1 and 3 and by integrating them in the approximation that ΔS and ΔH are constant with temperature, we obtain

$$\tau_{eq} = -(\Delta S/V)L_i^a \int_{T_m^i}^{T_m} (\Delta L)^{-1}\,dT = (\Delta S/V)L_i^a I(T_m) \quad (5)$$

and

$$\tau_{eq}/T_m = (\Delta H/V)L_i^a \int_{1/T_m^i}^{1/T_m} (\Delta L)^{-1}\,d(1/T) = (\Delta H/V)L_i^a J(1/T_m) \quad (6)$$

where $\Delta S/V$ and $\Delta H/V$ represent the entropy and enthalpy changes upon melting of 1 cc. of the fiber (V being the volume of the sample in the amorphous state). The functions $I(T_m)$ and $J(1/T_m)$ defined by these equations may be evaluated by graphical integration employing results such as are given in Table III. The latent entropy and enthalpy changes associated with transformation of the sample from the racked (semi-crystalline) to the amorphous state may then be computed in accordance with eq. 5 and 6. Under the assumption of constancy of ΔH and ΔS with temperature over the small range concerned, $\Delta H = T_m^i\Delta S$; hence, evaluation of either $I(T_m)$ or $J(1/T_m)$ should suffice for the task at hand. The latter procedure, leading directly to ΔH, is presented herein; equivalent results may be deduced by the former procedure involving graphical integration according to eq. 5.

Values of L_i^a $J(1/T_m)$ for sample f-1, established by graphical integration of $(\Delta L)^{-1}$ plotted against $1/T$, are given in the last column of Table III. These results, together with those similarly obtained for the other two samples, are shown in Fig. 8 where τ_{eq}/T_m is plotted against L_i^a $J(1/T_m)$. The results for the three samples, differing in degrees of cross-linking (but not in degree of crystallinity), are in close accord. The slope of the straight line drawn through the three sets of points determines $\Delta H/V$ according to eq. 6. We thus obtain

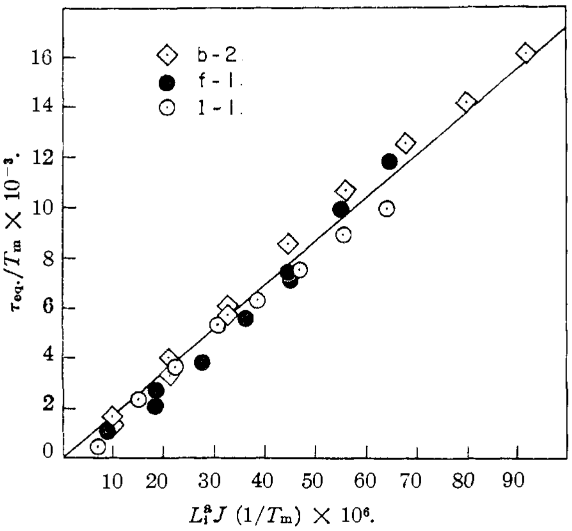

Fig. 8.—Plots of equilibrium stresses according to eq. 6.

$$\Delta H/V = 4.10 \text{ cal. cc.}^{-1}$$

where V is the volume of the sample in the amorphous state.

The quantity τ_{eq} denotes the tensile stress required for equilibrium at T_m between the adjoining (but macroscopically distinct) zones, which may be regarded as separate phases. The latent changes ΔH and ΔS computed above represent differences between the enthalpies and entropies for the two zones, or phases; that is, they refer to the process

$$\text{partially crystalline racked rubber} \longrightarrow \text{amorphous rubber}$$

The latent changes may be ascribed entirely to the melting of that fraction which is crystalline without commission of appreciable error. To be sure, molecular chains in the intervening amorphous matrix are probably in a state of strain, but in the very good approximation that amorphous rubber exhibits ideal rubber elasticity[16] (*i.e.*, that $(\partial H/\partial L)_{V,T} = 0$), the associated enthalpy change is zero. Hence, we may obtain the latent enthalpy change for the hypothetical process

$$\text{totally crystalline rubber} \longrightarrow \text{amorphous rubber}$$

merely by dividing $\Delta H/V$ given above by the fractional degree of crystallinity, which according to data given in Table I is about 0.24 ($\pm$ 0.02). Thus, with further introduction of the specific volume, 1.10 cc. g.$^{-1}$

$$\Delta H_{(c\rightarrow a)} = 18.7 \pm 2 \text{ cal. g.}^{-1}$$

The major source of error in this value arises from the uncertainty in the degree of crystallinity, which,

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(16) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter XI.

in turn, stems from the inaccuracy in the X-ray crystal density.

Under the assumption that $T_{\mathrm{m}}^{\mathrm{i}}$ represents the melting temperature of crystalline rubber when subject to no elastic deformation, the latent entropy for the latter hypothetical process may be obtained merely by dividing $\Delta H_{(c \to a)}$ by $T_{\mathrm{m}}^{\mathrm{i}}$. We thus find

$T_{\mathrm{m}}^{\mathrm{i}} = 302°\mathrm{K}.$
$\Delta H_{\mathrm{u}} = 1280 \pm 150$ cal. per mole of C_5H_8
$\Delta S_{\mathrm{u}} = 4.2 \pm 0.4$ cal. deg.$^{-1}$ per mole C_5H_8

These results compare favorably with those previously obtained by Roberts and Mandelkern[17] from the depression of the melting point of vulcanized rubber by diluents, namely

$T_{\mathrm{m}}^{\mathrm{i}} = 301°\mathrm{K}.$
$\Delta H_{\mathrm{u}} = 1040 \pm 60$ cal. mole^{-1}
$\Delta S_{\mathrm{u}} = 3.5 \pm 0.2$ cal. deg.$^{-1}$ mole^{-1}

We conclude that the transformation of highly orientated racked rubber, cross-linked by γ-radiation, to the amorphous state can be satisfactorily treated as a phase change. In particular, the dependence of the equilibrium stress on the temperature is in complete accord with the requirements of thermodynamic equilibrium between phases.

The authors are indebted to Drs. Mandelkern and Roberts for providing the samples used in this investigation and to Dr. Mandelkern for detailed suggestions and criticisms with reference to the interpretation of the results and the preparation of the manuscript.

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[17] D. E. Roberts and L. Mandelkern, THIS JOURNAL, **77**, 781 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY AND THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Vapor-phase Photochemistry of *trans*-Methyl Propenyl Ketone[1,2]

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The vapor-phase photolysis of pure *trans*-methyl propenyl ketone (*trans*-3-penten-2-one) was studied over a wide range of temperatures, pressures and wave lengths. This α,β-unsaturated ketone is unusually stable toward photo-dissociation into radicals. At 25° from 3130 to 2380 Å. and at 3130 Å. and temperatures up to 275°, a photo-rearrangement of the *trans* to the *cis* isomer is the only significant reaction. At 2380 Å. and above 125°, reactions leading to non-condensable products become important. Φ_{CO} exceeds unity at 275° and pressures below 10 mm. Other non-condensable products are 2-butene, methane, propene and ethane in decreasing order of abundance. At 200 and 275°, the reciprocals of the quantum yields of CO, C_4H_8, C_3H_6 and CH_4 are directly proportional to pressure but independent of intensity. The ratios C_4H_8/CO, C_3H_6/CO and CH_4/CO are independent of pressure. Methyl isobutyl ketone is apparently a condensable product. A mechanism is proposed in which the primary process is formation of a photo-excited molecule.

The effects of structure on photochemical decompositions have been noted in ketones having successively larger alkyl substituents, with cyclic ketones and with ketones with cyclic side chains.[3,4] It seemed worthwhile to extend these studies of structure and photochemical reactivity to ketones with unsaturated aliphatic side chains and, in particular, to the conjugated system exhibited by *trans*-methyl propenyl ketone (*trans*-3-penten-2-one).

Experimental

The *trans* form of methyl propenyl ketone was prepared by the action of dimethylcadmium on crotonoyl chloride.[5-7] The product was purified by distillation through a Piros-Glover spinning band column at a reflux ratio of 20:1, and the fraction boiling at 121.1° was retained. Its refractive index was $n^{20}\mathrm{D}$ 1.4357 compared to $n^{20}\mathrm{D}$ 1.4350 in the I. C. T. The sample was distilled *in vacuo* into a reservoir where it was stored over Drierite at −80°.

Mallinckrodt "analytical grade" acetone was used as an actinometer. It was treated with Drierite, then distilled *in vacuo* into a storage reservoir. The quantum yield of carbon monoxide formation from the photolysis of acetone was assumed to be 1.00 at 125° and 50 mm. pressure.[8]

Photolyses were carried out in a cylindrical quartz reaction cell 200 mm. long and 30 mm. outside diameter. The cell volume was about 125 cc. A Hanovia "type A" Alpine Burner was mounted at the entrance slit of the quartz monochromator (Farrand Model 300 UV), and the light beam emerging from the monochromator was collimated by a 6″ focal length quartz lens. The diameter of the light beam was adjusted so that the beam just filled the reaction cell. Relative light intensities were measured with an RCA 935 phototube in conjunction with an American Instrument Company microphotometer unit No. 10-210.

The quartz reaction cell was mounted in an aluminum block furnace inside an air-thermostated chamber. A trap, mercury manometer and the tubing and stopcocks leading to the reaction cell were also enclosed in the air-thermostat. The stopcocks connected the reaction cell to the methyl propenyl ketone supply, the actinometer supply and the sample collecting system. The furnace temperature was controlled with a Brown potentiometer, while the air-thermostat temperature was maintained at about 60° with a Fenwal thermoswitch.

Ward-LeRoy stills[9] were used to control the temperature, at which the photolysis products were collected. After each run, gases volatile at −110° were collected from the stills by means of a mercury diffusion pump in series with a

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[1] Abstracted in part from the Ph.D. thesis submitted to Northwestern University by R. S. Tolberg who held an Atomic Energy Commission Pre-doctoral Fellowship, 1951–1953. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Cincinnati, Ohio, April 6, 1955.

[2] Communications should be addressed to J. N. Pitts, Jr., Division of Physical Sciences, University of California, Riverside, California.

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