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Stress-Temperature Coefficients of Polymer Networks and the Conformational Energy of Polymer Chains¹

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Stress-temperature coefficients have been determined for cross-linked networks of polyethylene and polyisobutylene elongated in the amorphous state. The ratio of the energy contribution $f_e = (\partial E/\partial L)_{v,T}$ to the total tension f determined according to the relation $f_e/f = 1 - (\partial \ln f/\partial \ln T)_{v,L}$ was found to be independent of the extension ratio α from 1.25 to 3, of the degree of cross-linking, of the state of orientation and crystallization prevailing during cross-linking and of dilution of the network. According to the theory of rubber elasticity, this ratio may be identified with the temperature coefficient $d \ln \langle r^2 \rangle_0 / d \ln T$ of the mean-square length $\langle r^2 \rangle_0$ of the unperturbed polymer chain. Values of f_e/f and temperature ranges covered were: polyethylene, -0.42 ± 0.05 (137 to 200°); polyisobutylene, -0.03 ± 0.02 (20 to 100°). Values deduced from data in the literature show that natural rubber is not an ideal rubber; $f_e/f = 0.13 \pm 0.02$ (0 to 70°). Insensitivity of f_e/f to the variations noted supports the premise of the theory of rubber elasticity whereby the elastic free energy is expressed as the sum of the elastic free energies of the individual chains of the network. Insensitivity of this quantity to dilution of the network constitutes evidence against pseudo-ordering of the polymer chains in the amorphous state. Interpretation of the indicated temperature coefficient of $\langle r^2 \rangle_0$ for polyethylene according to the three-fold potential model for rotation around the C-C bonds is consistent with an energy difference of 500 cal./mole between *gauche* and *trans* states. The small temperature coefficient for polyisobutylene is subject to account in terms of the steric interactions affecting bond rotations.

Introduction

In the classic paper appearing in 1932 Meyer, von Susich and Valkó³ postulated that the elastic retractive force in stretched rubber-like materials arises from the strain-induced orientations of the component molecular chains. They developed the foundations of the molecular theory of rubber elasticity, in qualitative terms, on the basis of this premise. In recognition of the fact, known from the time of Joule, that the tension in stretched natural rubber is predominantly entropic in origin, the diminution of the conformational *entropy* of long-chain molecules with orientation was cited as the principal source of the elastic retractive force.

More refined experiments on the thermoelastic behavior of natural rubber and of certain synthetic rubbers were undertaken by various investigators in the succeeding era.^{4,5} The materials chosen for

investigation displayed stresses at fixed deformations which were very nearly proportional to the absolute temperature. The energy component of the force defined by

$$f_e = (\partial E/\partial L)_{v,T} = [\partial(f/T)/\partial(1/T)]_{v,L} \quad (1)$$

consequently was concluded to be negligible, or at most very small, and it became customary to assume this to be generally true for rubber-like materials. Hence, the theory of elasticity of polymer networks was developed on the basis of model polymer chains all conformations of which possess equal energy.⁶ An energy contribution to the elastic retractive force came to be regarded as beyond the theory itself. In instances where f_e appeared to be measurably different from zero, this quantity was deducted from the total force to obtain the entropic component f_s which was then compared with the theory of rubber elasticity.⁶

Experimental measurements on the mean dimensions of polymer molecules by light scattering and viscosity methods applied to dilute solutions indicate that the mean-square molecular end-to-end distance depends in general on the temperature. It follows that the energy of the chain must depend

(1) Partial support from the National Science Foundation Research Grant NSF-G6039 is gratefully acknowledged.

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(3) K. H. Meyer, G. von Susich and E. Valkó, *Kolloid Z.*, **59**, 208 (1932).

(4) See L. R. G. Treloar, "The Physics of Rubber Elasticity," 2nd Ed., Oxford Univ. Press, New York, N. Y., 1958, pp. 20-33.

(5) See P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 444-451.

(6) See ref. 4, pp. 64-79; also ref. 5, pp. 464-470.

on its conformation. The classical idealized chain model consisting of a sequence of bonds which can be arranged in various spatial conformations without affecting the energy is therefore inadequate. If the energy of the chain depends on its conformation, it is at once apparent that a network constructed of such chains should display *non-ideal* elasticity, *i.e.*, $f_e \neq 0$. The basis of rubber elasticity theory has therefore been re-examined recently from this point of view.^{7,8}

The theory of rubber elasticity ordinarily is developed for a system of Gaussian chains, that is, for polymer chains whose end-to-end distances r are distributed in the absence of constraints according to the Gaussian function.⁶ Compliance with this distribution is not vitiated by dependence of the energy on the bond conformations.⁷ The statistical distribution of end-to-end distances for *all* sufficiently long polymer chains whose bonds are such as to permit the existence of different conformations must be approximately Gaussian. Consequently, the form of the isotherm relating stress to strain is unaffected by generalization to include *non-ideal* polymer chains for which the energy depends on the conformation.

Whereas neither the *mathematical* form of the end-to-end distribution nor that of the stress-strain isotherm requires revision, the mean-square end-to-end distance for the unperturbed chain, $\langle r^2 \rangle_0$, acquires a temperature dependence if the chains are non-ideal.⁷ This parameter has, until recently, been treated as a constant in rubber elasticity theory. A form of the elastic equation of state for simple elongation which permits account to be taken of the impact of variation of $\langle r^2 \rangle_0$ with temperature (and of the alteration of volume due to swelling or deswelling as well) is the following^{7,9}

$$f = (\nu kT/L_i) (\langle r^2 \rangle_i / \langle r^2 \rangle_0) (\alpha - \alpha^{-2}) \quad (2)$$

where f is the tension, k is Boltzmann's constant, T the absolute temperature, ν is the number of chains in the network and L_i is the length of the specimen in the isotropic state to which it reverts when $f = 0$, the volume V remaining fixed; α is the linear extension ratio, *i.e.*, $\alpha = L/L_i$, L being the length of the elongated sample, and

$$\langle r^2 \rangle_i / \langle r^2 \rangle_0 = \nu^{-1} \sum_{i=1}^{\nu} \langle r_i^2 \rangle_i / \langle r_i^2 \rangle_0 = (V/V_0)^{2/3} \quad (3)$$

where $\langle r_i^2 \rangle_i$ denotes the mean-square end-to-end distance for network chain i in the isotropic state ($f = 0$) of the same volume V as the strained sample; $\langle r_i^2 \rangle_0$ is the mean-square value for the free chain at the same temperature and diluent concentration, and V_0 is the reference volume at which the ratio $\langle r_i^2 \rangle_i / \langle r_i^2 \rangle_0$ averaged over all chains is unity. According to these definitions, L_i is a function of V alone, and V_0 depends on T and possibly on the diluent.

Equation 2 in conjunction with 3 establishes a relationship between the temperature coefficient of the basic parameter $\langle r^2 \rangle_0$ characterizing the polymer chain and the non-ideal elasticity of a network

(7) P. J. Flory, C. A. J. Hoeve and A. Ciferri, *J. Polymer Sci.*, **34**, 337 (1959).

(8) O. B. Ptitsyn, *Fiz. Tverdого Tela*, **1**, 923 (1959).

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

constructed from such chains.^{7,8} According to the preceding equations

$$f_e/f = -T[\partial \ln(f/T)/\partial T]_{V,L} = T d \ln \langle r^2 \rangle_0 / dT \quad (4)$$

The condition for elastic ideality is equivalently specified by stipulating either that $f_e = 0$ or that f is directly proportional to T at fixed length L and at constant volume V . This equivalence is implicit in eq. 1 and again in 4. Acceptance of eq. 2 as the proper equation of state of elasticity, this equation having been derived by methods of statistical mechanics applied to the network model, establishes $d \langle r^2 \rangle_0 / dT = 0$ as a necessary and sufficient condition for ideality. Equation 4 relates the temperature coefficient of $\langle r^2 \rangle_0$ to the energy component of the force for a non-ideal network.

Experimental measurements at constant volume being impractical, we consider determinations of the force-temperature coefficient at constant pressure and length. According to eq. 2

$$[\partial \ln(f/T)/\partial T]_{p,L} = -d \ln \langle r^2 \rangle_0 / dT - \beta / (\alpha^3 - 1)$$

where $\beta = (\partial \ln V / \partial T)_p$ is the cubical thermal expansion coefficient in the isotropic state. Thus according to the rubber elastic equation of state 2,¹⁰

$$f_e/f = T d \ln \langle r^2 \rangle_0 / dT = -T[\partial \ln(f/T)/\partial T]_{p,L} - \beta T / (\alpha^3 - 1) \quad (5)$$

Further according to eq. 2, we have¹⁰

$$f_e/f = -T[\partial \ln(f/T)/\partial T]_{V,L} - T[\partial \ln(f/T)/\partial T]_{p,\alpha} + \beta T/3 \quad (6)$$

The widely used approximation $(\partial f / \partial T)_{V,L} \cong (\partial f / \partial T)_{p,\alpha}$ is equivalent to neglect of the term $\beta f/3$.¹⁰ This term, though small, is nevertheless significant for purposes of the present paper.

The theory of rubber elasticity rests on the premise that the elastic free energy of the network comprises the sum of contributions of its individual chains, interactions between neighboring chains being ignored. To be sure, such interactions invariably occur and may be quite large. Fulfillment of this postulate does not require however that these interactions be nil but rather that they be unaltered by deformation. Possible vitiating circumstances nevertheless may be envisioned. If, as has frequently been suggested, spatial requirements of the chains and interactions between neighboring chains impose partial order on their arrangement relative to one another, the chain conformation distribution will not correspond to that of non-interacting, free chains. The entropy and energy of the network would be affected also. To the extent that these effects are altered by deformation, the additivity postulate would be violated. In particular, $d \ln \langle r^2 \rangle_0 / dT$ calculated from the tension-temperature coefficient using eq. 5 would on this account depart from the value for the single chain in a dilute solution.

Even in absence of a semi-ordered arrangement, random entanglement of a polymer chain with neighboring chains in the bulk state necessarily imposes severe constraints on its conformation. Such considerations tend to call into question the application of free-chain statistics to network structures. It is to be noted however that the instantaneous conformation distribution for the

(10) P. J. Flory, A. Ciferri and C. A. J. Hoeve, *J. Polymer Sci.*, **45**, 235 (1960).

TABLE I
 CHARACTERIZATION OF SAMPLES

Sample	Material	Cross-linking	State of sample during cross-linking
P ₁	Polyethylene A	γ -rays, 29 · 10 ⁶ R.	Oriented, crystalline
P ₂	Polyethylene A	γ -rays, 58 · 10 ⁶ R.	Oriented, crystalline
P ₃	Polyethylene A	γ -rays, 100 · 10 ⁶ R.	Oriented, crystalline
P ₄	Polyethylene B	γ -rays, 26 · 10 ⁶ R.	Unoriented, crystalline
P ₅	Polyethylene B	γ -rays, 39 · 10 ⁶ R.	Unoriented, crystalline
P ₆	Polyethylene B	γ -rays, 90 · 10 ⁶ R. ^a	Liquid, 175°
P ₇ to P ₁₁	Polyethylene B	Electron beam, 40 · 10 ⁶ R.	Unoriented, crystalline
B ₁	Butyl rubber	Vulcanized ^b	Unoriented, amorphous

^a We are indebted to Dr. L. Mandelkern for placing this sample at our disposal. ^b Recipe in parts by weight; butyl rubber (GR-I-Y-110), 100; sulfur, 1.5; zinc oxide, 1.0; butyl zimate, 0.75; stearic acid, 1.0. Heated at 140° for 2 hr.

system of ν chains, and not the distribution of conformations which a given chain may experience in the course of time, is relevant in this connection.

The foregoing considerations place renewed emphasis on stress-temperature studies on polymer networks. Interest in this field is further stimulated by recent advances in the theory of polymer chain conformation.¹¹⁻¹³ More elaborate models which take account of effects of hindrances to rotation may be treated through application of methods recently developed. The average dimensions of polymer chains, and their temperature coefficients, are consequently amenable to more refined interpretation.

In this paper we present the results of tension-temperature measurements on amorphous networks consisting of polyethylene¹⁴ and polyisobutylene. The effect of incorporation of diluents in the networks has been examined in quest of evidence bearing on the additivity postulate discussed above. Values of $\ln \langle r^2 \rangle_0 / dT$ computed from these results are compared in the following paper¹⁵ with those deduced from temperature coefficients of intrinsic viscosities of dilute solutions of linear polyethylene.

Experimental

Materials.—The polyethylenes were of the low-pressure, "linear" variety. Samples carrying the designation A (Table I) were prepared by cross linking highly oriented crystalline fibers of "Marlex-50" obtained from the Phillips Petroleum Company. Those designated B were prepared by cross linking molded sheets of crystalline unoriented "super-Dylan" polyethylene obtained from the Koppers Company; in the case of sample P₆ (Table I) cross linking was performed on the amorphous polymer above its melting point.

Samples P₁ to P₆, inclusive, were cross linked in vacuum at room temperature using γ -radiation furnished by a cylindrical Co⁶⁰ source giving a uniform dose rate of 0.61 megarep/hr. Doses and the state of the sample during cross linking are indicated in Table I. Sample P₆ was similarly cross linked at 175°. Samples P₇ to P₁₁, inclusive, were cross linked in vacuum at room temperature using the electron beam from a van de Graaff accelerator. Although all samples of this latter group were subjected to the same nominal exposure, their degrees of cross linking differed owing to non-uniformity of the electron beam intensity over the area of irradiation. This non-uniformity was indicated by equilibrium swelling determinations and by measurements of the modulus.

(11) M. V. Volkenstein, *J. Polymer Sci.*, **29**, 441 (1958); O. B. Ptitsyn, *Uspekhi Fiz. Nauk*, **69**, 371 (1959).

(12) S. Lifson, *J. Chem. Phys.*, **29**, 80 (1958); **30**, 964 (1959).

(13) C. A. J. Hoeve, *ibid.*, **32**, 888 (1960).

(14) Preliminary results on polyethylene networks were published previously.⁷

(15) P. J. Flory, A. Ciferri and R. Chiang, *THIS JOURNAL*, **83**, 1023 (1961).

Butyl rubber, an isobutylene polymer modified by copolymerization with approximately 2% of isoprene units, was vulcanized with sulfur and an appropriate accelerator.

n-Hexadecane, C₁₆H₃₄, *n*-dotriacontane, C₃₂H₆₆, and di-2-ethylhexyl azelate were obtained from the Eastman Chemicals Co. and used without further purification. A sample of *n*-triacontane, C₃₀H₆₂, purified by fractional distillation and urea adduct formation, was obtained through the courtesy of W. T. Ridenour of the Gulf Fellowship at Mellon Institute.

Experimental Methods.—A dynamometer similar in design to that described previously^{16,17} was used to perform the stress-temperature measurements. One or the other of two strain gauges having capacities of 42 and 670 g., respectively, was used depending on the load. The linear responses were 0.52 and 0.042 mv./g. under an applied e.m.f. of 10 v. The passage of a slow stream of nitrogen of high purity through the sample chamber proved necessary in order to prevent oxidative degradation of the samples.

Samples for investigating the effects of diluents on the stress-temperature relationship were swollen by immersion of the previously cross-linked sample in the diluent until the desired quantity was absorbed. The amount incorporated was determined by weighing. The stream of nitrogen through the sample chamber was diminished during the course of the experiment in order to avoid excessive evaporation. After each experiment the sample was re-weighed. In those instances where the loss of diluent was appreciable, the results were discarded. Swollen samples proved much more susceptible to network degradation despite precautions to exclude air. Moreover, the maximum stresses which these samples would sustain without rupture were less than for unswollen samples. For these reasons, the results for swollen samples P₄ and P₅ are subject to greater error. Samples P₇–P₁₁ were swollen in solvent containing 0.05% phenyl- β -naphthylamine, an antioxidant. Network degradation was virtually eliminated by this procedure.

 TABLE II
 LINEAR EXPANSION COEFFICIENTS

Material	($\beta/3$) × 10 ⁴ , deg. ⁻¹
Polyethylene	2.3
Butyl rubber ¹⁸	1.9
Hexadecane ¹⁹	3.0
<i>n</i> -Triacontane ¹⁹	2.9
Di-2-ethylhexyl azelate	3.0
Polyethylene samples P ₁₀ –P ₁₁ in swelling equilibrium with <i>n</i> -dotriacontane	–1.1

The sample was elongated at the highest temperature to which it was to be subjected in the course of the experiment, and the length was fixed thereafter. Stress relaxation was allowed to proceed at this temperature until the force attained a sensibly constant value. Periods of time up to several hours were required for unswollen samples. Shorter periods sufficed for swollen samples. After the force attained a constant value, the temperature was lowered at intervals

(16) J. F. M. Oth and P. J. Flory, *ibid.*, **80**, 1297 (1958).

(17) A. Ciferri and P. J. Flory, *J. Applied Phys.*, **30**, 1498 (1959).

(18) N. Bekkedahl, *J. Research Natl. Bur. Standards*, **43**, 145 (1949).

(19) G. Egloff, "Physical Constants of Hydrocarbons," Vol. V, Reinhold Publishing Corporation, New York, N. Y., 1953, pp. 218–262.

TABLE III
 POLYETHYLENE, UNSWOLLEN

Sample	α^a	$(\partial\tau/\partial T)_{L,P}$ $\times 10^3$, kg. cm. ⁻² deg. ⁻¹	$\langle T/\tau \rangle^{-1}$ $\times 10^4$, kg. cm. ⁻² deg. ⁻¹	$\left[\frac{\partial \ln(f/T)}{\partial \ln T} \right]_{L,P}$	$\beta T(\alpha^2 - 1)^{-1}$	$-fe/f$	$-\frac{d \ln \langle r^2 \rangle_0}{dT}$ deg. ⁻¹ $\times 10^3$
P ₁	1.55	3.10	2.38	0.30	0.11	0.41	0.95
P ₁	1.82	3.62	2.85	.27	.06	.33	0.76
P ₁	2.09	4.61	3.28	.41	.04	.45	1.04
P ₁	2.46	5.18	3.77	.37	.02	.39	0.90
P ₁	2.96	6.20	4.34	.43	.02	.45	1.04
P ₂	1.43	5.30	4.09	.30	.16	.46	1.06
P ₂	1.70	7.73	5.75	.34	.08	.42	0.97
P ₂	2.02	9.63	7.08	.36	.04	.40	.92
P ₃	1.40	6.30	5.46	.15	.18	.33	.76
P ₃	1.54	8.60	6.51	.32	.11	.43	.99
P ₃	1.68	10.70	7.82	.37	.08	.45	1.04
P ₃	1.79	12.21	8.60	.42	.06	.48	1.11
P ₃	1.86	12.85	9.01	.43	.06	.49	1.13
P ₄ ^b	1.75	4.56	3.26	.40	.07	.47	1.08
P ₄ ^b	2.02	5.60	3.97	.41	.04	.45	1.04
P ₆ ^b	1.40	6.03	5.38	.12	.18	.30	0.69
					Av. 0.42		0.97

^a Extension ratio referred to rest length L_i for highest temperature; see Fig. 1. ^b Measurements from which these results were derived have not been included in Fig. 1.

and the value of the force was recorded at each temperature. The temperature then was raised at similar intervals until the initial temperature was reached. Stress relaxation in the course of the temperature cycle was inappreciable when this procedure was followed, and forces recorded on the ascending and descending phases of the temperature cycle were identical within experimental error. The time required for a cycle was about 90 minutes.

The liquid thermostats (containing Silicone Oil DC-550, Dow Corning Corporation) maintained temperatures constant to $\pm 0.5^\circ$. Temperatures could be altered at rates of ± 4 deg./min.; cooling was achieved with a Dowtherm heat exchanger.

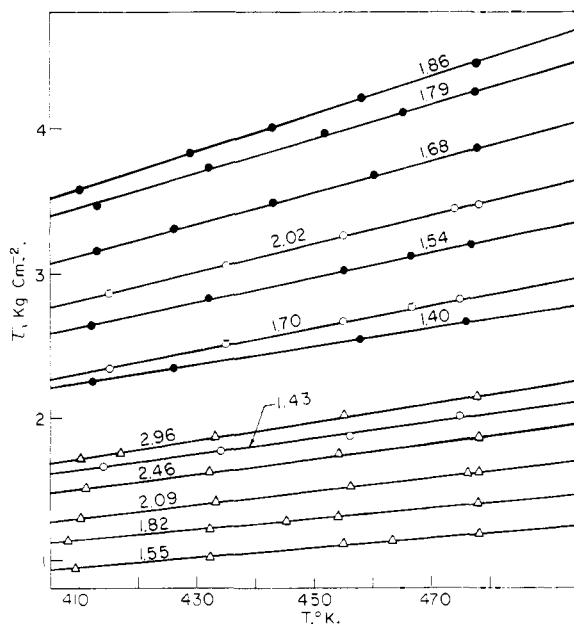


Fig. 1.—Polyethylene, unswollen; stress τ referred to the unstrained cross section vs. temperature at constant length: Δ , P₁; O, P₂; ●, P₃.

Sample cross sections in the unswollen state at the highest temperature reached in the tension-temperature measurements were determined in one of the following ways. Either the cross section was measured directly at room temperature and corrected for linear thermal expansion, or it was cal-

culated from the length and weight of the sample at room temperature, the linear thermal expansion and the density at the desired temperature. The oriented samples of polyethylene denoted by A were first melted and shrunk before determining the cross section; values obtained were approximately 10^{-3} cm.² Values for other samples were approximately 10^{-2} cm.² Sample lengths were 3 to 4 cm. in most of the experiments. Precise values of the cross sections were not required; the results of the analyses of the tension-temperature measurements are independent of them.

Linear thermal expansion coefficients, β/β , for polyethylene samples were determined by measuring the lengths of these samples with a cathetometer at various temperatures. The approximate cubical thermal expansion coefficient of di-2-ethylhexyl azelate was measured using a dilatometer. The corresponding linear expansion coefficients are given in Table II. Expansion coefficients of various swollen samples of fixed composition were computed from those given in this table for the pure components involved, additivity of volumes being assumed throughout the temperature range. The last entry in Table II represents the measured linear expansion for the open system consisting of polymer in swelling equilibrium with surrounding diluent.

Results

The results of the tension-temperature measurements at constant length are presented in Figs. 1-4; the "stress" τ , representing the observed tension divided by the unstrained cross section at the highest temperature reached in the given experiment, is plotted instead of the actual tension in order to facilitate comparison of data for samples which differ in cross section. The extension ratio α indicated with each plot is arbitrarily taken relative to L_i at the same temperature; these values of α are recorded in the second columns of Tables III-V. It is to be noted that since L is constant throughout an experiment, the value of $\alpha = L/L_i$ changes slightly with temperature owing to changes in L_i . However, corrections for this effect appeared negligible in the quantitative treatment and were therefore omitted. The results embrace elongations ranging from the lowest permitting sufficient accuracy to the highest which the samples would withstand without rupture or incidence of crystallization.

Within experimental error, the plots depicted in Figs. 1-4 are linear over the temperature ranges

TABLE IV

Sample-diluent	α^a	POLYETHYLENE SWOLLEN		$\left[\frac{\partial \ln(f/T)}{\partial \ln T} \right]_{L,P}$	$\beta T (\alpha^3 - 1)^{-1}$	$-fe/f$	$-\frac{d \ln \langle r^2 \rangle_s}{dT} \times 10^3$
		$(\partial \tau / \partial T)_{L,P} \times 10^3$, kg. cm. ⁻² deg. ⁻¹	$\langle T / \tau \rangle^{-1} \times 10^3$, kg. cm. ⁻² deg. ⁻¹				
P ₄ -DEHA, $v_2 = 0.80$	1.80	1.31	0.99	0.32	0.07	0.39	0.90
P ₄ -DEHA, $v_2 = .80$	1.85	1.32	1.00	.32	.06	.38	0.88
P ₅ -DEHA, $v_2 = .70$	1.41	2.17	1.68	.29	.18	.47	1.09
P ₇ -DEHA, $v_2 = .30$	1.42	7.07	5.15	.38	.20	.58	1.32
P ₈ -DEHA, $v_2 = .55$	1.13	3.28	4.39	-.25	.77	.52	1.20
P ₉ -DEHA, $v_2 = .53$	1.28	11.69	11.90	-.02	.32	.30	0.68
					Av.	0.44	1.01
P ₁₀ ^b -C ₃₂ H ₆₆ , $v_2 = 0.31$	1.12	9.53	5.26	0.81	-0.35	0.46	1.06
P ₁₀ -C ₃₂ H ₆₆ , $v_2 = .31$	1.14	15.00	8.91	.68	-.30	.38	0.88
P ₁₀ -C ₃₂ H ₆₆ , $v_2 = .31$	1.18	17.95	10.19	.76	-.22	.54	1.25
P ₁₁ -C ₃₂ H ₆₆ , $v_2 = .30$	1.24	23.90	14.27	.68	-.16	.52	1.20
P ₁₁ -C ₃₂ H ₆₆ , $v_2 = .30$	1.33	27.90	17.55	.59	-.11	.48	1.11
P ₁ -C ₃₀ H ₆₂ , $v_2 = .50$	1.77	0.71	0.45	.58	.06	.64	1.48
					Av.	0.50	1.16

^a Extension ratio referred to rest length L_1 for highest temperature; see Figs. 2 and 3. ^b Measurements from which these results were derived have not been included in Fig. 3.

investigated. Values of the slopes $(\partial \tau / \partial T)_{P,L}$ are recorded in the third columns of Tables III-V. Values of $[\partial \ln(\tau/T) / \partial \ln T]_{P,L}$ given in the fifth columns of the tables have been calculated from these slopes and the values of τ/T averaged over the temperature range of the experiments; reciprocals of these averages are recorded in the fourth columns of Tables III-V.

tane in which it was immersed. Full consideration of swelling equilibrium as a function of deformation and temperature according to expressions given previously,⁹ in conjunction with the necessarily

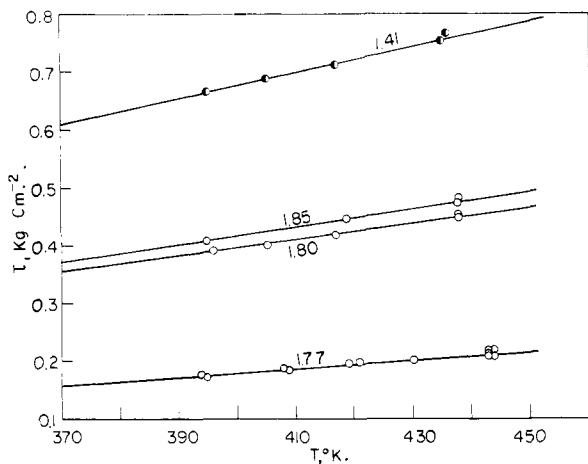


Fig. 2.—Polyethylene, swollen; stress τ referred to the unstrained cross section vs. temperature at constant length: O, $\alpha = 1.80$: P₄, di-2-ethylhexyl azelate, $v_2 = 0.80$; O, $\alpha = 1.85$: P₄, di-2-ethylhexyl azelate, $v_2 = 0.80$; O, $\alpha = 1.77$: P₄, *n*-triacontane, $v_2 = 0.50$; ●, $\alpha = 1.41$: P₅, di-2-ethylhexyl azelate, $v_2 = 0.70$.

Equations 1 and 4 stipulate constancy of the volume and length. Inasmuch as the experiments were carried out at constant pressure and length, the values of $[\partial \ln(\tau/T) / \partial \ln T]_{P,L}$ require correction. Values of the correction term, expressed by $\beta T (\alpha^3 - 1)^{-1}$ according to eq. 4 and 5, are given in the sixth columns. It is to be noted that tension-temperature measurements on samples P₁₀ and P₁₁ were conducted while the specimen was maintained in swelling equilibrium with the solvent *n*-dotriacon-

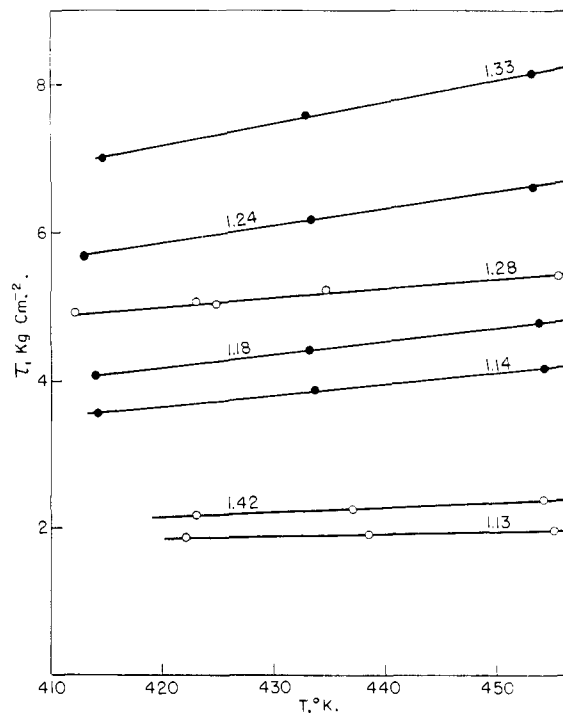


Fig. 3.—Polyethylene, swollen; stress τ referred to the unstrained cross section vs. temperature at constant length. O: samples swollen with di-2-ethylhexyl azelate; $\alpha = 1.42$: P₇, $v_2 = 0.30$; $\alpha = 1.13$: P₈, $v_2 = 0.55$; $\alpha = 1.28$: P₆, $v_2 = 0.53$. ●: samples in swelling equilibrium with *n*-dotriacontane; $\alpha = 1.14$: P₁₀, $v_2 = 0.31$; $\alpha = 1.18$: P₁₀, $v_2 = 0.31$; $\alpha = 1.24$: P₁₁, $v_2 = 0.30$; $\alpha = 1.33$: P₁₁, $v_2 = 0.30$.

small values of the interaction parameter χ_1 at all temperatures, yields the result that the correction term is given by $\beta T (\alpha^3 - 1)^{-1}$ within experimental

TABLE V
BUTYL RUBBER

Sample-diluent	α^a	$(\partial\tau/\partial T)_{L,P}$ $\times 10^3$ kg. cm. ⁻² deg. ⁻¹	$\langle T/\tau \rangle^{-1}$ $\times 10^4$ kg. cm. ⁻² deg. ⁻¹	$\left[\frac{\partial \ln(f/T)}{\partial \ln T} \right]_{L,P}$	$\beta T / (\alpha^3 - 1)^{-1}$	$-fe/ff$	$-\frac{d \ln \langle r^2 \rangle_0}{dT} \times 10^4$
B ₁ -none	1.73	4.98	5.04	-0.01	0.04	0.03	0.09
B ₁ -none	1.78	4.58	4.34	.06	.04	.10	.31
B ₁ -none	2.07	5.92	6.11	-.03	.02	-.01	-.03
B ₁ -none	2.32	5.44	5.34	.02	.02	.04	.12
B ₁ -none	2.38	5.64	5.60	.01	.01	.02	.06
B ₁ -none	2.52	7.28	7.32	-.01	.01	.00	.00
B ₁ -none	3.24	8.96	8.89	.01	.01	.02	.06
B ₁ -none	3.75	10.10	9.95	.02	.00	.02	.06
Av.						0.03	0.08
B ₁ -C ₁₆ H ₃₄ , $v_2 = 0.54$	1.67	4.66	4.74	-0.02	0.07	0.05	0.15
B ₁ -C ₁₆ H ₃₄ , $v_2 = .54$	2.28	6.66	6.68	.00	.02	.02	.06
B ₁ -C ₁₆ H ₃₄ , $v_2 = .54$	3.19	8.60	8.66	-.01	.01	.00	.00
B ₁ -C ₁₆ H ₃₄ , $v_2 = .41$	1.85	6.18	6.04	.03	.03	.06	.18
B ₁ -C ₁₆ H ₃₄ , $v_2 = .41$	2.33	7.20	6.99	.03	.02	.05	.15
B ₁ -C ₁₆ H ₃₄ , $v_2 = .41$	2.84	8.14	8.21	-.01	.01	.00	.00
Av.						0.03	0.09

^a Extension ratio referred to rest length L_1 for highest temperature; see Fig. 4.

error; in this case $\beta = (\partial \ln V / \partial T)_p$ denotes the cubical thermal expansion coefficient of the network in swelling equilibrium with the solvent.

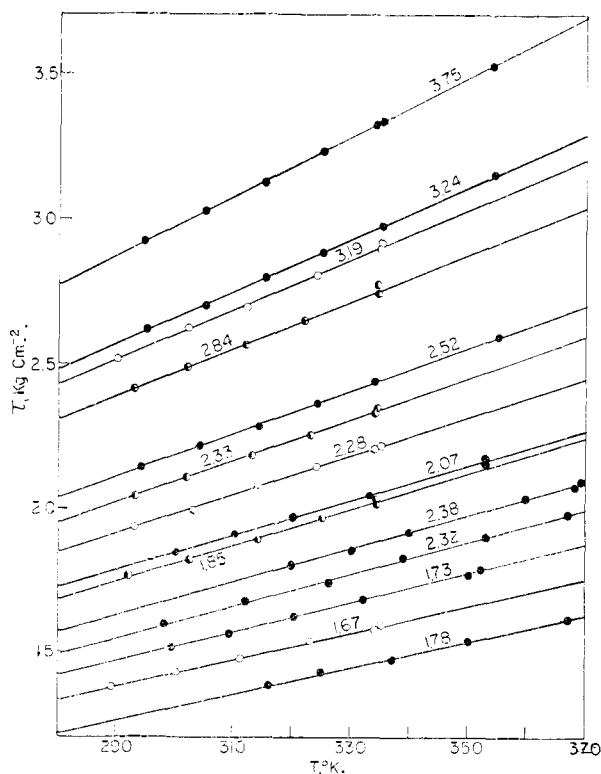


Fig. 4.—Butyl rubber, swollen and unswollen; stress τ referred to the unstrained cross section vs. temperature at constant length: ●, unswollen; ○, *n*-hexadecane, $v_2 = 0.54$; ○, *n*-hexadecane, $v_2 = 0.41$.

The degree of cross linking by γ -radiation in the case of polyethylene was varied several-fold by altering the radiation dose (see Table I). As is apparent from Fig. 1 and values of τ/T in Table

III, the stress at a given elongation is approximately proportional to the radiation dose and presumably therefore to the degree of cross linking. This proportionality is only approximate; it is subject to aberration arising from failure to achieve equilibrium with respect to the given strain. These departures from equilibrium probably depend on the degree of cross-linking; they are inconsequential insofar as the stress-temperature coefficient is concerned.

At the highest temperature investigated, the stress for vulcanized butyl rubber decreased slowly with time. This "chemical" stress relaxation is presumed to have occurred as a result of the susceptibility of the cross linkages of the butyl rubber network to rupture at elevated temperatures. Because of the varying degrees of stress relaxation in different experiments, the plots of Fig. 4 do not occur in exact order of the stated elongations. In those experiments involving higher maximum temperatures, the degree of cross-linking appears to have been reduced materially relative to other experiments in which the maximum temperatures were lower. The temperature cycles were nevertheless reversible in all cases; it was necessary however to avoid exceeding the temperature at which stress relaxation had been allowed to occur at the outset of the experiment (see Experimental).

Whereas the extension ratios α quoted for swollen samples (Figs. 2, 3 and 4 and Tables IV and V) are taken relative to the isotropic swollen length, the "stresses" are referred to the unswollen cross section. With the results expressed in this manner, at a given temperature the quantity $v_2^{1/3}\tau$ should be invariant to dilution according to the theory of rubber elasticity (eqs. 2 and 3), constancy of $\langle r^2 \rangle_0$ with dilution being assumed. We have not corrected the stresses through multiplication by the cube-root of the volume fraction v_2 of polymer inasmuch as this correction is not required for the analysis of the tension-temperature coefficients. Moreover, the factors $v_2^{1/3}$ do not differ greatly from unity. The

magnitudes of the stresses for swollen butyl rubber specimens (Fig. 4), with due allowance for the factor $v_2^{1/2}$, compare favorably with those for unswollen samples at similar extension ratios; discrepancies are no more marked than those occurring among the results for unswollen samples and attributed above to "chemical" stress relaxation.

The swollen polyethylene samples P_4 and P_6 (Fig. 2 and Table IV), on the other hand, display stresses which bear little relation to the extension ratios and which are generally much lower than for comparable experiments on unswollen samples (compare results for P_4 swollen and unswollen). Excessive network degradation was responsible for these anomalies. It is natural to attribute the degradation to oxygen, which may have been introduced in greater amount during exposure of these samples to elevated temperatures in the course of introducing the diluent and which was less effectively excluded from the sample chamber by the diminished stream of inert gas permissible in the course of an experiment. Whatever the cause of the large reduction in the network connectivity, the stress-temperature cycles were satisfactorily reversible once the tension had approached constancy at the highest temperature. The results therefore meet the requirements of the present analysis. Degradation in samples P_7 - P_{11} was suppressed by incorporation of antioxidant. We attribute lack of correlation between stresses and extension ratios (Fig. 3 and Table IV) for these samples, all of which were subjected to the same nominal dosages (Table I), to differences in degrees of cross linking as a result of the non-uniform intensity of the electron beam (see Experimental) used to cross-link this group of samples.

The results presented in Tables III-V yield values for f_e/f (seventh columns) which are consistently independent of the extension ratio. Although results for diluted samples are somewhat less accurate, the ratio f_e/f appears to be independent of dilution within experimental error. Results on butyl rubber (Table V) are especially convincing on this point. For polyethylene f_e/f is independent also of the degree of cross-linking. These observations are in full accord with rubber elasticity theory as embodied in eq. 2.

TABLE VI
SUMMARY OF RESULTS

Sample-diluent	Average value of f_e/f	Average value of $\frac{d \ln \langle r^2 \rangle_0 / dT}{\text{deg.}^{-1} \times 10^3}$
Polyethylene-none	-0.42 ± 0.05	-0.97 ± 0.10
Polyethylene- $C_{30}H_{62}$ and $C_{32}H_{64}$	$-.50 \pm .06$	$-1.16 \pm .10$
Polyethylene-di-2-ethylhexyl azelate	$-.44 \pm .10$	$-1.01 \pm .20$
Polyisobutylene-none	$-.03 \pm .02$	$-0.08 \pm .06$
Polyisobutylene- $C_{16}H_{34}$	$-.03 \pm .02$	$-.09 \pm .07$
Natural rubber ^a -none	$+.13 \pm .02$	$+.41 \pm .04$

^a Values calculated from experimental results, given by Wood and Roth.²⁰

To be noted also is the demonstration that the state of the polyethylene when cross-linked has no discernible effect on f_e/f . Thus, samples P_4 and P_6 , cross-linked in the unoriented crystalline state

and in the molten state, respectively, yield results which are indistinguishable from those for samples (e.g., P_1 and P_3) subjected to similar radiation doses in the highly oriented, crystalline condition.

Principal results are summarized in Table VI. The energy component in the case of polyethylene amounts to nearly half of the total tension $f = f_e + f_s$, f_e and f being of opposite sign. Obviously, the observed tension in a polyethylene network cannot be identified with the entropy contribution $f_s = -T(\partial S/\partial L)_{T,v}$. For polyisobutylene f_e/f is slightly negative.

The coefficient $d \ln \langle r^2 \rangle_0 / dT$ calculated from f_e/f according to eq. 5 (final column, Table VI) may be evaluated independently from appropriate viscosity measurements on dilute solutions. The intrinsic viscosities measured at the θ -points in different solvents should be proportional to $(\langle r^2 \rangle_0)^{3/2}$ in each case.²⁰ In the absence of specific solvent effects $\langle r^2 \rangle_0$ should depend only on the temperature. Hence

$$d \ln \langle r^2 \rangle_0 / dT = (2/3) (d \ln [\eta]_0 / dT) \quad (6)$$

which may, in principle, be used to deduce the temperature coefficient of $\langle r^2 \rangle_0$. For polyisobutylene, the value thus found from the results of Fox and Flory²¹ is $-10^3 d \ln \langle r^2 \rangle_0 / dT = 1.1 \pm 0.5$. This result derived from past investigations on the properties of the separate molecules in dilute solution is regrettably of much lower accuracy than that obtained from tension-temperature coefficients for networks. Relevant dilute solution viscosity measurements on polyethylene are reported in the following paper.¹⁵

Discussion

Absence of a discernible dependence of the temperature coefficient $(\partial \ln f / \partial T)_{v,L}$ on elongation, on the degree of cross-linking and on dilution, as evidenced by the constancy of f_e/f values (see eq. 4), supports the additivity postulate underlying the theory of rubber elasticity from which is derived the elastic equation of state, eq. 2. If interactions between chains contributed appreciably to f_e (i.e., if the change in these interactions with length were important) in violation of this postulate, then we might expect the contribution of these interactions to change with extension, with degree of cross-linking and especially with dilution. Such effects have not been observed in the present investigation.

Although the experimental errors in f_e/f are unfortunately large for diluted polyethylene, the values appear to be independent of dilution with such diverse diluents as *n*-triacontane and *n*-dotriacontane on the one hand and di-2-ethylhexyl azelate on the other. These results are at variance with the often postulated pseudo-ordering of chains in molten polymers such as polyethylene. The molecular shape of the latter diluent must surely be quite incompatible with any conceivable ordered arrangement of the chains of this polymer. Hence, if such order occurs, it should be markedly diminished by incorporation of the azelate ester. Yet, f_e/f found for

(20) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); P. J. Flory and T. G. Fox, Jr., *THIS JOURNAL*, **73**, 1906 (1951); see ref. 5, Chapter XIV.

(21) T. G. Fox, Jr., and P. J. Flory, *THIS JOURNAL*, **73**, 1909 (1951).

samples containing this diluent does not differ significantly from that for either the undiluted polymer or for samples diluted with *n*-triacontane and *n*-dotriacontane. The insensitivity of f_e/f , and therefore of the calculated value of $\text{dln}\langle r^2 \rangle_0/dT$, to dilution and to the nature of the diluent would be exceedingly difficult to reconcile with the occurrence of appreciable chain ordering in the amorphous state.

The potential energy associated with bond rotations in the polyethylene chain is sufficiently simple to permit an interpretation of $\langle r^2 \rangle_0$ and its temperature dependence. Three states of minimum energy²² associated with each bond have to be considered, these states being the *trans* form and the symmetrically disposed *gauche* forms differing from the *trans* by rotations of 120° in the positive and negative sense. The energy of the *trans* minimum is known to be appreciably less than that of the *gauche*. Only nearest neighbor interactions along the chain were taken into account in our earlier report,⁷ wherein equation (7),²³ valid for tetrahedral angles, was used.

$$\langle r^2 \rangle_0 = 2nl^2 (1 + \langle \cos \phi \rangle)(1 - \langle \cos \phi \rangle)^{-1} \quad (7)$$

Here n is the number of bonds in the chain, l is the length of the C-C bond, taken to be 1.54 Å., and ϕ is the angle of rotation measured from the *trans* state; $\langle \cos \phi \rangle$ denotes the average of $\cos \phi$ over *gauche* and *trans* states. The energy difference between the *gauche* and *trans* states, calculated from measured values of $\text{dln}\langle r^2 \rangle_0/dT$, was previously reported⁷ to be 540 cal./mole. However, values of $\langle r^2 \rangle_0$ deduced from dilute solution measurements are considerably higher than values calculated according to eq. 7 with the above parameter for the energy difference. The following consideration offers an explanation for this discrepancy. According to Pitzer²⁴ and Taylor²² two consecutive *gauche* states with opposite senses of rotation place a pair of methylene groups separated by three intervening backbone carbon atoms in severe steric conflict. In first approximation, therefore, such combinations of *gauche* pairs are excluded. The assumption underlying eq. 7, namely, that the rotational states of consecutive bonds are independent of one another, is thus invalidated and more elaborate methods which take account of interactions between consecutive rotations¹¹⁻¹³ are required. Detailed calculations²⁵ show that excellent agreement may be obtained between calculated and measured values of $\langle r^2 \rangle_0$ and $\text{dln}\langle r^2 \rangle_0/dT$ through use of an energy difference of 500 cal./mole between *gauche* and *trans* states and a considerably higher energy for two consecutive *gauche* states with opposite angles of rotation.

Repulsions between the methyl groups occurring on alternate carbon atoms of the polyisobutylene chain dominate all other factors in influencing the conformation. The severity of these steric interactions is such as to justify disregard of all conformations except those related to the helix characteristic of the crystalline polymer. Assuming all

(22) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).

(23) H. Benoit, *J. Chim. Phys.*, **44**, 18 (1947); H. Kuhn, *J. Chem. Phys.*, **15**, 843 (1947); W. J. Taylor, *ibid.*, **16**, 257 (1948).

(24) K. S. Pitzer, *ibid.*, **8**, 711 (1940).

(25) C. A. J. Hoeve, to be published.

valence angles θ of the main chain to be equal, the results²⁶ of X-ray diffraction yield $\theta = 114^\circ$, and a rotation angle $\phi = 82^\circ$ measured from the *trans* state. Symmetry demands equal *a priori* probabilities for $+82^\circ$ and -82° rotations. In the crystalline state a given chain must, of course, adopt one or the other direction of rotation throughout the crystal. In the amorphous state, however, both forms may be expected to occur simultaneously within the same chain.

Further examination of the polyisobutylene model reveals that the pair of bonds connecting a $-\text{CH}_2-$ group with the adjoining substituted chain atoms must adopt rotations of the same sign. The succeeding pair of bonds connecting the next $-\text{CH}_2-$ with its neighbors should be little influenced by the sign of the rotation of the aforementioned pair. Accordingly, Ptitsyn and Sharanov²⁷ have assumed that positive ($++$) and negative ($--$) dyads occur at random along the chain. It follows at once from this assumption that $\langle r^2 \rangle_0$ should be independent of temperature, contrary to observation.

Theoretical treatments which take account of correlations between the rotational directions of successive bond dyads recently have been published.^{13,28} An energy difference of 20 cal./mole²⁹ between the $++$, $--$ compared with the $+-$, $-+$ conformation is sufficient to account for the observed temperature coefficient of $\langle r^2 \rangle_0$, as given in Table VI. Moreover, the absolute value calculated for $\langle r^2 \rangle_0$ is in good agreement with experiment.

The stress-temperature coefficients at constant elongation carefully determined for vulcanized natural rubber by Wood and Roth,³⁰ and for vulcanized GR-S synthetic rubber (a butadiene-styrene copolymer) by Roth and Wood,³¹ bear reexamination in light of the theoretical relation set forth in the Introduction to this paper. Their observation that f/T is virtually independent of T for natural rubber at constant elongation α has been interpreted to denote elastic ideality, *i.e.*, that $f_e/f = 0$. According to eq. 6, however, the term $\beta T/3$ must be included. Application of this equation to their data yields $f_e/f = 0.13 \pm 0.02$ and $10^3 \text{dln}\langle r^2 \rangle_0/dT = 0.41 \pm 0.04 \text{ deg.}^{-1}$ for natural rubber, and $f_e/f = -0.13 \pm 0.06$ and $10^3 \text{dln}\langle r^2 \rangle_0/dT = -0.42 \pm 0.20 \text{ deg.}^{-1}$ for GR-S. The results of Anthony, Caston and Guth³² appear to be in accord with those of Wood and Roth³⁰ for natural rubber. Contrary to prevailing opinion, natural rubber is not an ideal elastomeric body. It alone among the polymers considered here is characterized by a positive energy contribution f_e to the total tension f .

(26) A. M. Liquori, *Acta Cryst.*, **8**, 345 (1955).

(27) O. B. Ptitsyn and I. A. Sharanov, *Zhur. Tekh. Fiz.*, **27**, 2744 and 2762 (1957).

(28) Yu. Ya. Gotlib, *ibid.*, **29**, 523 (1959); T. M. Birshtein and O. B. Ptitsyn, *ibid.*, **29**, 1048 (1959).

(29) The preliminary value¹³ -0.06 used previously for $f_e/f = d \ln \langle r^2 \rangle_0/dT$ yielded an energy difference of 40 cal./mole. However, according to Table VI $f_e/f = -0.03$. The calculated value for $\langle r^2 \rangle_0$ is not appreciably affected by this change.

(30) L. A. Wood and F. L. Roth, *J. Applied Phys.*, **15**, 781 (1944).

(31) F. L. Roth and L. A. Wood, *ibid.*, **15**, 749 (1944).

(32) R. L. Anthony, R. H. Caston and E. Guth, *J. Phys. Chem.*, **46**, 826 (1942).