

CHAPTER 2

STRESS RELAXATION STUDIES OF THE VISCOELASTIC PROPERTIES OF POLYMERS

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An ideally elastic substance subjected to simple tension obeys Hooke's law in the region of small strains:

$$\text{Stress} = E \times \text{Strain}$$

The quantity E is a constant known as the Young's modulus. It is a very important property of the material in question, being a measure of stiffness or resistance to deformation. For many metallic substances the value of E is of the order of 10^{11} dynes/cm.². For soft vulcanized rubbers the value of E is of the order of 10^7 dynes/cm.². The Young's modulus of a substance generally varies with the temperature.

The concept of modulus can be generalized to nonideally elastic substances by recognizing that the modulus is a function of time and also to some extent a function of the method of measurement. For example, experiments may be conducted in which the substance is subjected to a fixed extension, and the stress is measured as a function of time. The stress per unit strain necessary to maintain the sample at constant extension will be defined as the stress relaxation modulus $E_r(t)$. Similarly, the substance may be subjected to a constant tensile load, and the extension measured as a function of time—a so-called creep experiment. The stress per unit strain measured by this kind of experiment will be denoted by $E_c(t)$, the creep modulus. Furthermore vibrational experiments may be carried out

in which the substance is subjected to vibrations of angular frequency ω . From these experiments a complex dynamic modulus $E'(\omega) + iE''(\omega)$ may be determined. (In actual fact the vibrations used are generally shear vibrations so that the quantity really determined is $G'(\omega) + iG''(\omega)$, where the symbol G denotes shear modulus).

In most cases the moduli $E_r(t)$, $E_c(t)$ and $E'(1/\omega)$ —where ω corresponds to $1/t$ —are approximately equal. For substances which obey the laws of classical linear viscoelasticity, a determination of any one of these quantities over the entire time scale can be used to calculate the other two time-dependent moduli, or indeed can be used in principle to predict the results of any viscoelastic experiment.

During the past several years extensive data have been accumulated in our laboratory concerning the stress relaxation modulus $E_r(t)$ of a wide variety of polymers over a wide temperature range. The practical experimental methods for measuring stress at constant extension vary with the magnitude of the stiffness modulus and are described in the original papers. The following pages present a brief summary and generalization of some of the experimental and theoretical findings arising from this work.

Polymers divide very sharply into two categories so far as their physical properties are concerned: on one hand there are the amorphous polymers whose X-ray scattering is very similar to the scattering of liquids; on the other hand there are the polycrystalline polymers. The viscoelastic properties of amorphous polymers are relatively simpler than those of polycrystalline polymers. In the first place amorphous polymers obey the classical laws of linear viscoelasticity (at small deformations) whereas crystalline polymers frequently do not. Secondly amorphous polymers obey a time-temperature superposition principle which permits the use of data obtained at different temperatures to extend the time scale at any temperature. This is not generally true for crystalline polymers. Finally, the amorphous polymers show many features of similarity to one another in their viscoelastic behavior. For these reasons I shall discuss them first.

1. Four Regions of Viscoelastic Behavior for Amorphous Polymers

The first complete viscoelastic data for any polymers were obtained by stress-relaxation studies on polymethylmethacrylate of two different molecular weights.^{1, 2} The stress relaxation data at various temperatures are plotted in the form $\log E_r(t)$ vs $\log t$ for the entire temperature range in Fig. 1. In Fig. 2 are shown similar results for polyisobutylene of molecular weight 1.35×10^6 for average viscosity. The pattern of behavior for these polymers as shown in these figures is very much the same, and this is also

¹ J. R. McLoughlin and A. V. Tobolsky, *J. Colloid Sci.* **7**, 555 (1952).

² A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.* **8**, 543 (1952).

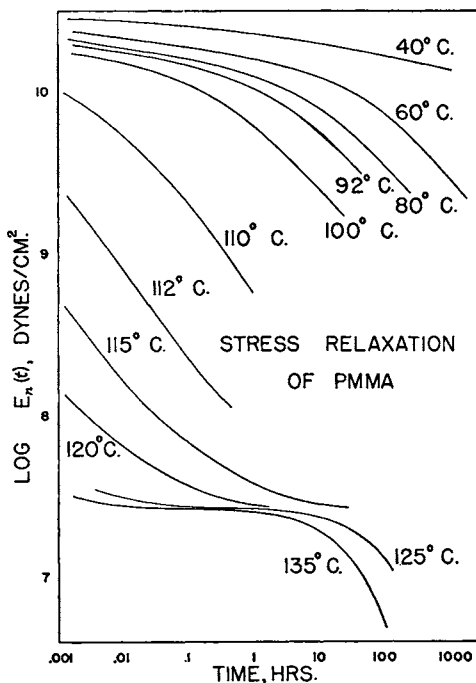


FIG. 1. $\log E_r(t)$ vs. $\log(t)$ for polymethylmethacrylate¹

true of other amorphous polymers. As was first pointed out by Tobolsky and McLoughlin² and as can be clearly seen from the figures, there are four well-defined regions of viscoelastic behavior:

1. A low-temperature *glassy region* in which the modulus $E_r(t)$ is of the order of magnitude of $10^{10 \times 5}$ dynes/cm.². The time effects are not very pronounced in this region so that we may speak of a quasi-static glassy modulus E_1 . $E_r(t)$ is fairly independent of molecular weight in this region but depends very markedly on the rate at which the sample is annealed.³

2. A *transition region* of viscoelastic behavior in which $E_r(t)$ changes very rapidly with time and temperature, the values of $E_r(t)$ ranging between 10^{10} dynes/cm.² and 10^7 dynes/cm.². The polymers feel "leathery" to the touch in this region. The values of $E_r(t)$ are independent of molecular weight in this region for polymers of sufficiently high molecular weights.⁴ The time effects in the transition region are produced by short-range motions of relatively small segments of the polymer molecules.

3. A quasi-static "rubbery plateau" region in which the modulus $E_r(t)$ is of the order of magnitude of 10^7 dynes/cm.² and changes quite slowly with

³ J. R. McLoughlin and A. V. Tobolsky, *J. Polymer Sci.* **7**, 658 (1951).

⁴ G. M. Brown and A. V. Tobolsky, *J. Polymer Sci.* **6**, 165 (1951).

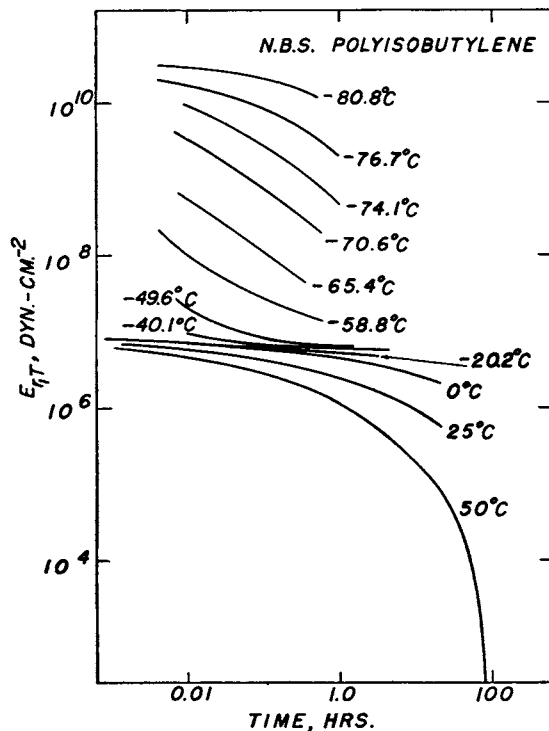


FIG. 2. Log $E_r(t)$ vs. log (t) for polyisobutylene of molecular weight $\bar{M}_v = 1.35 \times 10^6$.^{25, 26}

time. The stress in this region appears to be maintained by "entanglements" between the long chain molecules as was first pointed out in these researches.⁵ From the rubbery plateau region a quasi-static rubbery modulus E_2 can be defined, and the molecular weight between "entanglements" can be calculated.⁵ The presence of chemical cross-links will of course increase the value of the rubbery modulus E_2 .

4. A flow region in which $E_r(t)$ changes very rapidly with time from values of 10^7 dynes/cm.² to values of zero. The $E_r(t)$ curves in this region are very markedly dependent on the molecular weight and the molecular-weight distribution. For samples of the same molecular-weight distribution but different average molecular weight \bar{M}_v , the $E_r(t)$ curves appear to be shifted horizontally along the log-time axis, the shifting factor being $3.3 \log \bar{M}_v$.⁶ For samples of different molecular-weight distribution, but

⁵ H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Chapter X, p. 344. Interscience New York, 1950.

⁶ R. D. Andrews, N. Hofman Bang, and A. V. Tobolsky, *J. Polymer Sci.* **3**, 669 (1948).

the same value of \bar{M}_v , the shape of the $E_r(t)$ curve vs. $\log t$ curve appears to change, but the relative position along the log-time axis remains the same.^{5, 7}

The time effects in the rubbery flow region are due to motions of the molecules as a whole or to very large molecular segments.

When the chemical cross-linking between the linear chains is sufficient to form a continuous three-dimensional structure, the flow region is completely suppressed, to be replaced at higher temperatures by a region of chemical flow produced by the breaking of primary valence bonds by oxygen, by ionic interchanges, or by other means.

In the original publication,² the rubbery plateau region and the flow region were considered together as the "rubbery flow" region. It seems desirable to separate these into two regions for purposes of greater clarity.

II. The Time-Temperature Superposition Principle

The time-temperature superposition principle whereby viscoelastic data at one temperature are transformed to another temperature by a simple multiplicative transformation of the time scale^{6, 8, 9, 10} was independently proposed by Tobolsky and Andrews³ and by Leaderman.⁹ In its simplest form this principle means that curves of $E_r(t)$ or $\log E_r(t)$ vs. $\log t$ that are obtained at different temperatures can be superimposed by means of a horizontal shift along the $\log t$ axis. Refinements on this procedure are treated elsewhere.¹¹

By means of this principle it is possible to extend the values of $E_r(t)$ obtained at any temperature to both shorter and longer times than can be obtained experimentally. Master curves of $\log E_r(t)$ vs. $\log t$ can be constructed that are applicable for all temperatures and all times. Figure 3 shows a somewhat schematized master curve for unfractionated polyisobutylene of three different average molecular weights. The graph as it stands is valid for 25° C. because the log time origin ($\log t = 0$) is directly under the indicated mark for 25° C. The master curve for any temperature shown on the graph can easily be obtained by sliding the log time axis to the new indicated origin. The number of decades of time comprised in this master curve is truly staggering. The validity of the time-temperature

⁷ R. D. Andrews, F. H. Holmes, and A. V. Tobolsky, unpublished results.

⁸ A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **11**, 125 (1943); *J. Polymer Sci.* **3**, 669 (1948).

⁹ H. Leaderman, "Elastic and Creep Properties of Filamentous Materials." Textile Foundation, Washington D. C. 1943.

¹⁰ J. D. Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).

¹¹ J. D. Ferry and E. R. Fitzgerald, *J. Colloid Sci.* **8**, 224 (1953); see also E. Catsiff and A. V. Tobolsky, *J. Colloid Sci.* **10**, 375 (1955).

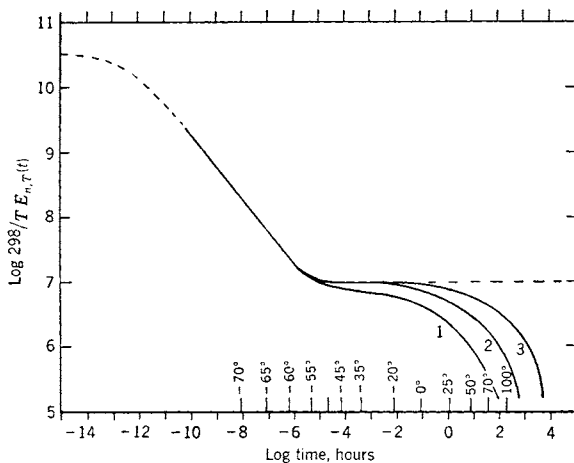


FIG. 3. Idealized master relaxation curve $\log E_r(t)$ vs. $\log(t)$ for polyisobutylene of three different average molecular weights (1) $\bar{M}_v = 1.36 \times 10^6$; (2) $\bar{M}_v = 2.80 \times 10^6$; (3) $\bar{M}_v = 6.60 \times 10^6$.¹

superposition principle will be proved later when relaxation modulus and dynamic modulus are compared.

III. Parameters Defined by the Relaxation Master Curves

Stress-relaxation data, such as are embodied in Figs. 1, 2, and 3 can be used to define certain parameters that are characteristic of the polymers being studied.¹² In the first place we have E_1 and E_2 , the quasi-static glassy modulus and the quasi-static rubbery modulus. At any temperature T the time required for the logarithm $E_r(t)$ to reach the value $(\log E_1 + \log E_2)/2$ was called the characteristic relaxation time K .¹² K is obviously a function of temperature $K(T)$. An attempt was also made to define a distinctive temperature T_d from the $E_r(t)$ curves alone which would correspond in some way to the glass transition temperature T_g obtained from volume-temperature curves. As is well known, evidence exists which indicates that the T_g value obtained from V - T curves depends on the rate at which specimen is cooled (or heated). It was hoped that the $\log E_r(t)$ vs. $\log t$ curves would provide a value of T_d that did not depend upon time effects. T_d was defined as the temperature at which $K(T)$ had a maximum value of apparent activation energy. The apparent activation energy is defined as $Rd \ln K/d(1/T)$. A difficulty that arises with this definition is that the time-temperature superposition principle very probably becomes only partially valid at temperatures close to T_g and lower. The horizontal shifts along the log time scale which produce superposition of the $\log E_r(t)$ curves

¹² J. Bischoff, E. Catsiff, and A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 3378 (1952).

for temperatures below T_g may well be valid only for the time scale of the relaxation experiments. Nevertheless, the values of T_d obtained by the method described above seems to be very close to the T_g values obtained from V - T curves, at least for the polymers we have studied thus far. The determination of T_d appears to have experimental-operational validity.

The value of T_g or T_d is perhaps the most important characteristic of the polymer. Should our experimental-operational definition of T_d fail for certain polymers, our discussion of these polymers could be couched in terms of T_g rather than of T_d .

The characteristic relaxation time K at the temperature T_d is denoted by K_d .

Another important parameter which characterizes the master relaxation curves is the quantity n , which is the negative slope of the master curve $\log E_r(t)$ vs. $\log t$ at the point at which $\log E_r(t) = (\log E_1 + \log E_2)/2$. Another characteristic parameter is the quantity h , related to n , whose quantitative definition will be discussed subsequently.

Table I contains a compilation of the parameters E_1 , E_2 , h , n , T_d , and K_d for the polymers whose viscoelastic properties have been studied by stress relaxation.

It is, of course, of great interest to inquire how these parameters depend on the molecular structure of the polymers. Among the polymers studied there does not appear to be a tremendous variation in the values of E_1 and E_2 . The glassy modulus E_1 may well depend upon the strength of the secondary valence forces between atomic groups and upon the amount of "free volume" in the glass. Nevertheless the value of E_1 obtained thus far for various polymers appears to lie in the range 10^{10} to $10^{10 \times 5}$ dynes/cm.². E_2 will depend on the chain stiffness in the case of linear polymers and upon

TABLE I
PARAMETERS CHARACTERIZING STRESS RELAXATION OF AMORPHOUS POLYMERS

<i>Polymer</i>	T_d , °K	$\log E_1$	$\log E_2$	n	h	$\log K_d$
Polymethyl methacrylate	384	10.35	7.35	0.52 ₅	0.31	-1.5
Paracril 26	241.0	10.10	7.40	0.63	0.41 ₅	-1.54
GR-S	220	10.24	7.44	0.71	0.45	-1.50
60/40 buta/sty	237.1	10.27	8.03	0.50 ₅	0.40	-1.94
50/50 buta/sty	250.8	10.212	7.558	0.545	0.364	-1.12
30/70 buta/sty	285.1	9.955	7.255	0.55	0.36	-1.13
Polyisobutylene	197.0	10.48	6.88	0.745	0.367	+1.04
(Dynamic)	—	10.52	6.88	0.723	0.352	—

the amount of cross linkage in the case of cross-linked polymers. The quantity n and the related quantity h may depend upon such factors as chain configuration and the heterogeneity of composition along the chain. Thus far the variation in these quantities as between different polymers has not proved to be very great, although larger variations have been found in the case of other polymers now under study.

The parameter which is of greatest importance in determining the properties of amorphous polymers is T_d (or T_g). To a very crude approximation one can state that the viscoelastic properties of most amorphous polymers are roughly similar for the same values of T/T_d ¹³ or $T - T_d$. The qualitative validity of this principle may be verified by inspecting Figs. 1 and 2. The value of T_d (or T_g) for any given polymer is determined by the cohesive energy density of the polymer (measured by swelling or solubility) and the stiffness of the chains (which can be measured by light scattering in polymer solutions). The higher the cohesive energy density, the higher is the value of T_d ; the stiffer the chain, the higher the value of T_d . The latter point is nicely demonstrated by the fact that polyacenaphthalene has a much higher T_g value than polystyrene.

Although all amorphous homopolymers and homogeneous copolymers studied thus far show the qualitative features of viscoelastic behavior described above, polymer alloys or polyblends, which are finely dispersed mechanical mixtures of two polymers just barely on the borderline of compatibility, show a splitting of the transition region into two discrete parts,¹⁴ as if the polyblend had preserved the two T_d values of each individual component.

IV. Stress Birefringence Ratio and the Mechanism of Viscoelastic Deformation

For an ideal cross-linked rubber (in the rubbery plateau region of viscoelastic behavior), the stress at constant extension is proportional to the absolute temperature. This means that the entropy of the rubber sample is decreased when the rubber is stretched isothermally, and the stress in the stretched rubber sample actually arises from this decrease in entropy.

The decrease in entropy occurring when a rubber sample is stretched is, in turn, due to a decrease in the long-range configurational possibilities of the chain molecules. Since birefringence is also a measure of the long-range chain configurations, it is not surprising that the following relation can be derived.¹⁵

$$\frac{\text{Stress}}{\text{Temperature} \times \text{Birefringence}} = \text{constant}$$

¹³ A. V. Tobolsky and E. Catsiff, *J. Am. Chem. Soc.* **76**, 4204 (1954).

¹⁴ R. Buchdahl and L. E. Nielsen, *J. Polymer Sci.* **15**, 1 (1955).

The value of the constant in the above equation can be used to determine the size of the "freely rotating segment" of the polymer chains.^{15, 16}

It was further shown that the quantity stress/(temperature \times birefringence) is a constant independent of temperature and *time* during stress-relaxation experiments, provided that the experiments were carried out in the rubbery flow region, the rubbery plateau region, or the low modulus portion of the transition region.^{17, 18} This indicates that in these regions of viscoelastic behavior even during a stress-relaxation experiment, where stress is changing rapidly with time, the stress must be considered as an "entropy stress," arising from long-range configurational changes. On the other hand, as one enters the high modulus portion of the transition region and the glassy region, the ratio stress/(temperature \times birefringence) changes its magnitude and often changes its sign.^{17, 19} This indicates that the molecular mechanism of stretching in the glassy region must be different from that operating in the rubbery region. Very probably the stress in the glassy region arises from internal energy changes corresponding to distortion of van der Waals' bonds and bending of valence angles, rather than from configurational entropy changes.

This fundamental change in the mechanism giving rise to stress should be taken as an indication that the time-temperature superposition principle may become invalid (or only partially valid) at temperatures close to and below the glass transition temperature.

1. MATHEMATICAL FUNCTIONS DESCRIBING $E_r(t)$

The function $E_r(t)$ has been fitted quite well by empirical functions in both the transition region and the rubbery flow region. In the transition region the following empirical function holds very well:^{12, 20}

$$\log E_r(t/K) = \frac{\log E_1 + \log E_2}{2} - \left(\frac{\log E_1 - \log E_2}{2} \right) \operatorname{erf} [h \log (t/K)]$$

where

$$\operatorname{erf} x = 2\pi^{-1/2} \int_0^x e^{-u^2} du.$$

Erf is an abbreviation of the term error function, and h is the adjustable parameter of the Gauss error curve). The quantity h , related to n , has

¹⁵ W. Kuhn and F. Grun, *Kolloid-Z.* **101**, 248 (1942); L. R. G. Treloar, *Trans. Faraday Soc.* **43**, 277, 289 (1947).

¹⁶ R. S. Stein and A. V. Tobolsky, *J. Polymer Sci.* **11**, 285 (1953).

¹⁷ R. S. Stein, S. Krimm, and A. V. Tobolsky, *Textile Research J.* **19**, 8 (1949).

¹⁸ R. S. Stein and A. V. Tobolsky, *J. Polymer Sci.* **14**, 443 (1954).

¹⁹ J. R. McLoughlin, Ph.D. thesis, Princeton University (1950).

²⁰ E. Catsiff and A. V. Tobolsky, *J. Appl. Phys.* **25**, 1092 (1954).

already been considered as one of the characteristic parameters of the master relaxation curve $E_r(t)$.

In the region of rubbery flow the relaxation curve $E_r(t)$ for polyisobutylene at 298° K. is fitted quite well by the following empirical function:^{6, 21, 22} $E_r(t) = E_0[E_i(-t/\tau_3) - E_i(-t/\tau_m)]$ where $E_i(-x)$ is the exponential integral function, τ_3 and τ_m are parameters that depend on the 3.3 power of the average molecular weight and E_0 is a parameter that appears to depend upon the molecular-weight distribution (see ref. 5, p. 343).

For a class of amorphous polymers, notably the butadiene-styrene copolymers, the empirical relation $hT_d = 100$ appears to be valid. When this is true, expressions for $E_r(t)$, which are essentially universal functions of T/T_d , can be derived.¹³ This reduced equation of state for viscoelastic behavior is not valid for polymers like polyisobutylene where $hT_d \neq 100$.

V. Distribution of Relaxation Times, Flow Viscosity, and Dynamic Modulus

A distribution function of relaxation times $H(\log \tau)$ can be defined in terms of $E_r(t)$ by means of the following integral equation:

$$E_r(t) = \int_{-\infty}^{\infty} H(\log \tau) e^{-t/\tau} d(\log \tau)$$

The distribution function $H(\log \tau)$ is very useful since other viscoelastic properties such as the flow viscosity and the real and imaginary components of the dynamic modulus can be calculated therefrom.

$$\eta = \int_{-\infty}^{\infty} \tau H(\log \tau) d(\log \tau)$$

$$E' = \int_{-\infty}^{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} H(\log \tau) d(\log \tau)$$

$$E'' = \int_{-\infty}^{\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} H(\log \tau) d(\log \tau)$$

Formulas relating E' and E'' to the distribution of relaxation times were first presented by Tobolsky and Eyring.^{22, 23} All of these formulas presuppose the validity of the laws of linear viscoelastic behavior. Then laws have been proved valid for amorphous polymers but are invalid for crystalline polymers under certain conditions.

An idealized distribution of relaxation times at 298° K. had previously been presented (in ref. 22) which had the simple graphical aspects of a "box" for the rubbery flow region and a "wedge" for the transition region.

²¹ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **6**, 221 (1951).

²² A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 3786 (1952).

²³ A. V. Tobolsky and H. Eyring, *J. Chem. Phys.* **11**, 125 (1943).

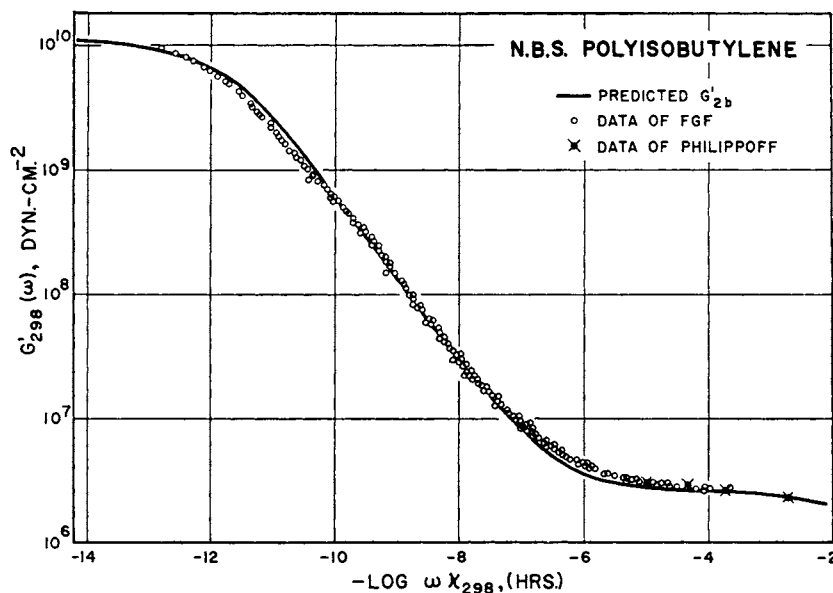


FIG. 4. Dynamic shear modulus G' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results.^{25, 26}

The “wedge” is unaffected by the molecular weight of the sample (for sufficiently high molecular weights), whereas the “box” is shifted along the log time axis with a shift factor $3.3 \log \bar{M}_v$. Although this idealized function is only an approximation of the true values of $H(\log \tau)$, it has the virtue that exact mathematical expressions for $E_r(t)$ and for E' and E'' can be derived from it, so that no mathematical approximations are necessary for converting relaxation modulus to dynamic modulus in this case.

A very accurate determination of $H(\log \tau)$ can be obtained from the experimental value of $E_r(t)$ by the use of first- and second-order approximations.^{24, 25, 26} The values of $H(\log \tau)$ at 298° K. as a function of $\log \tau$ are tabulated in ref. 26.

From the distribution function $H(\log \tau)$, obtained entirely from stress-relaxation data and the stress-relaxation data master curve $E_r(t)$, one can compute and predict the values of $E'(\omega)$ and $E''(\omega)$. Such computations (and tabulations) have been made in refs. 25 and 26. Figures 4 and 5 show the comparison between predicted values and the experimental values

²⁴ J. D. Ferry, E. R. Fitzgerald, L. D. Grandine, Jr., and M. L. Williams, *Ind. Eng. Chem.* **44**, 703 (1952).

²⁵ E. Catsiff and A. V. Tobolsky, *J. Colloid Sci.* **10**, 375 (1955). See also *J. Appl. Phys.* **25**, 145 (1954).

²⁶ A. V. Tobolsky and E. Catsiff, *J. Polymer Sci.* **19**, 111 (1956).

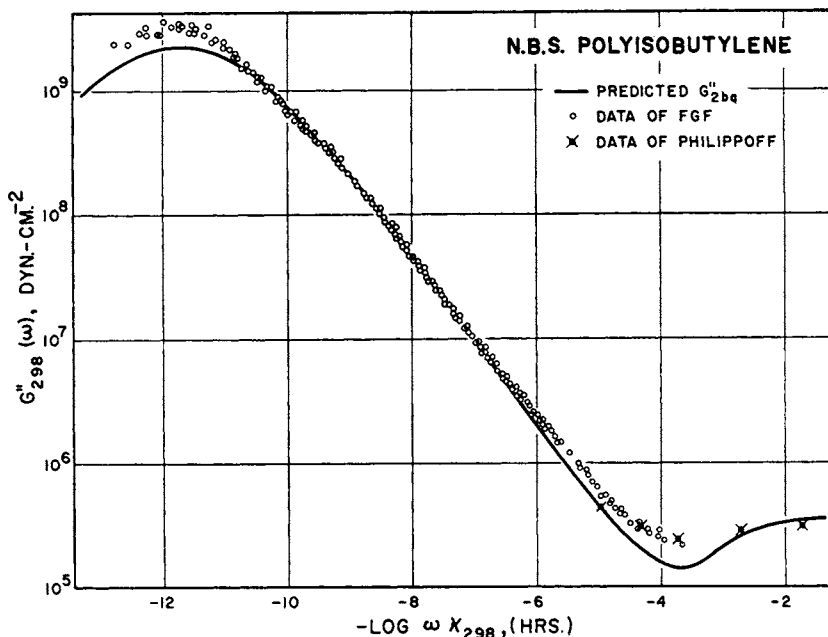


FIG. 5. Complex dynamic shear modulus G'' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results.^{25, 26}

obtained elsewhere.²⁷ The extremely good agreement provides another verification of the validity of the theory of linear viscoelastic behavior in the case of polyisobutylene. It also provides a verification of the time-temperature superposition principle, because stress-relaxation data and dynamic-modulus data are obtained in very different time intervals. Figure 6 shows stress-relaxation data and dynamic data for polyisobutylene obtained at -44° C. The solid curve represents the master curve $E_r(t)$ obtained from stress-relaxation data at various temperatures by the time-temperature superposition principle. The agreement between the two types of data is striking.

The relaxation curves of polyisobutylene in the rubbery flow region have been used to predict the bulk viscosity, using the "box" distribution as the approximation for the relaxation time distribution in that region.²⁸ Very satisfactory agreement was obtained between predicted values and experimental values of viscosity.

²⁷ J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.* **24**, 911 (1953).

²⁸ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951).

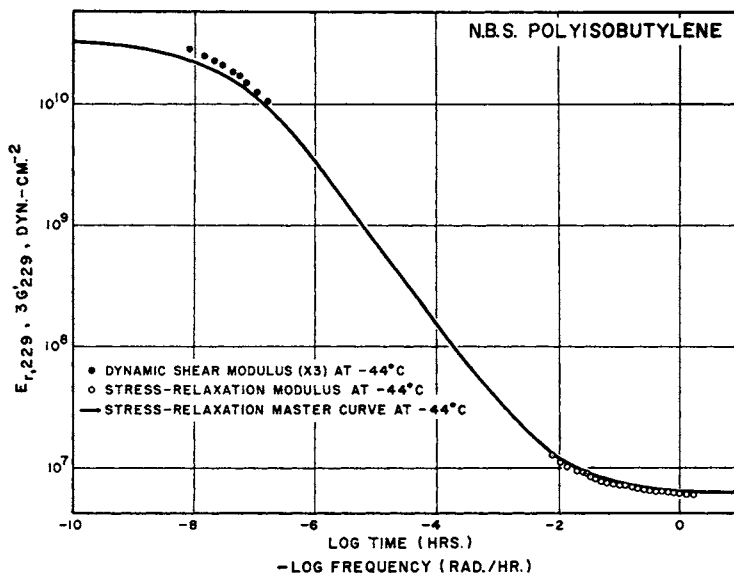


FIG. 6. Dynamic shear modulus (times three) vs. negative log frequency and stress relaxation modulus vs. log time for polyisobutylene at 44°C . Solid curve represents the stress relaxation master curve. Shear modulus G' multiplied by three to convert to a tension modulus.

VI. The Characteristic Relaxation Time $K(T)$ as a Function of Temperature

It is clearly very desirable to express the temperature variation of $K(T)$ in a manner that would be applicable to all linear polymers. Catsiff and Tobolsky had suggested that $h \log K(T)/(K_d)$ vs. T/T_d should be the same for all amorphous polymers.^{13, 12} Recently Williams²⁹ has proposed that $\log A_{\tau}$ vs. $T - T_s$ is a universal function for all polymers, where T_s is a reference temperature selected for each polymer. The function A_{τ} is linearly proportional to $K(T)$. The two theories discussed above are in agreement over the limited temperature interval over which they were commonly tested. Williams, Landel, and Ferry have ascribed a functional form for the variation of $\log A_{\tau}$ with $T - T_s$.³⁰ Expressed in terms of the notation and the parameters used in this article this new theory has the following form:

$$\log \frac{K(T)}{K_d} = -16.14 \frac{T - T_d}{56 + T - T_d}$$

All of our values for $K(T)$ for the polymers studied by stress relaxation fit this formula very well.^{25, 26} The agreement obtained with this formula and the experimental data is shown in Fig. 7.

²⁹ M. L. Williams, *J. Phys. Chem.* **59**, 95 (1955).

³⁰ M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).

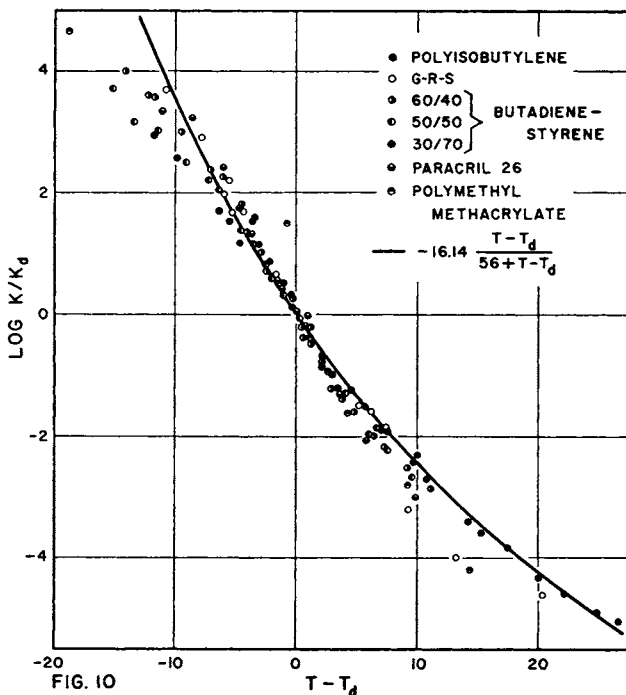


FIG. 7. $\log K(T)/K_d$ vs. $T - T_d$ for several polymers^{25, 26}

VII. Stress Relaxation of Polycrystalline Polymers

In the previous discussion of the viscoelastic properties of linear amorphous polymers it was shown that certain features are common to the behavior of all of these polymers. In particular it was shown that there are four characteristic regions of viscoelastic behavior: a glassy region, a transition region, a rubbery plateau region, and a rubbery flow region. In Fig. 2 which presents $\log E_r(t)$ vs. $\log t$ for polyisobutylene the behavior in the transition region is to be especially noticed. In the time scale of the relaxation experiments (.01 to 10 hr.) the transition region occurs in the temperature interval between -80°C. and -40°C. , a matter of 40 degrees. In this interval the modulus changes very rapidly with time and temperature between values of 10^{10} dynes/cm.² and 10^7 dynes/cm.² The behavior of partially crystalline polymers is rather different and shall be discussed, using polytrifluorochloroethylene as a well studied example.

Polytrifluorochloroethylene

Polytrifluorochloroethylene is a polycrystalline polymer whose melting temperature T_m is 215°C. Its glass transition temperature has not been

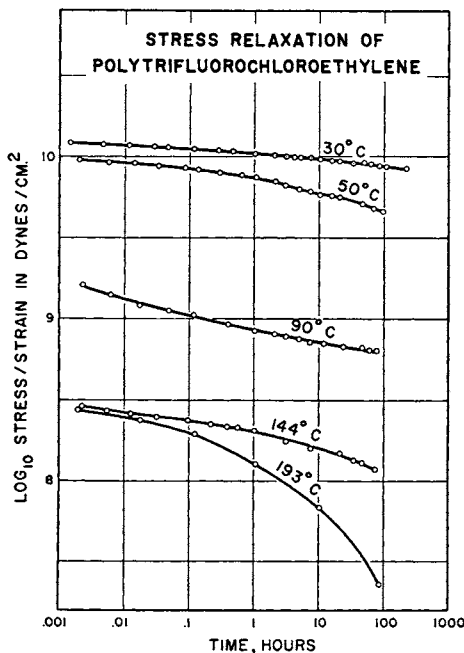


FIG. 8. $\log E_r(t)$ vs. $\log t$ for polytrifluorochloroethylene³¹

accurately determined but should be somewhere in the neighborhood of room temperature if the approximate relation $T_g = \frac{2}{3} T_m$ is valid. Figure 8 shows stress relaxation data³¹ for polytrifluorochloroethylene in the temperature range between 30 and 193° C. In this interval the modulus varies from $10^{10.1}$ to $10^{7.2}$ dynes/cm.² It is particularly interesting to contrast Figs. 2 and 8. In Fig. 8 the $\log E_r(t)$ vs. $\log t$ curves between 30° and 144° C. are relatively flat, i.e., the modulus change with time in the "transition region" polymer is much smaller for the polycrystalline polymer as compared to the amorphous polymers. Also in Fig. 8 the value of $\log E_r(t)$ at $t = 0.01$ hr. changes from a value of $10^{10.1}$ dynes/cm.² at 30° to a value of $10^{8.35}$ at 144° C., a very gradual change. The transition region, if such it can be called, for a polycrystalline polymer extends over a much wider temperature range than for an amorphous polymer. The "transition region" blends into a high-modulus "rubbery region" at high temperatures, crystallites playing the same role in the polycrystalline polymer that entanglements or cross links do in the amorphous polymers.

Because there are changes with temperature in the microcrystalline structure and in the stress-bearing mechanisms, it is certain that the simple time-temperature superposition that is valid for amorphous polymers in the tran-

³¹ A. V. Tobolsky and J. R. McLoughlin, *J. Chem. Phys.* **59**, 989 (1955).

sition region is not valid for polycrystalline polymers. There is not only a horizontal displacement along the log-time axis due to changing rate of molecular motions with temperature, but also an even more important vertical shift along the log $E_r(t)$ axis resulting from the changing structure and other factors.

It is interesting to note that the polycrystallinity of plasticized polyvinyl chloride was first discovered by Tobolsky and Stein from an examination of the $E_r(t)$ curves.³² These rubbery samples behaved like cross-linked rubbers in that $E_r(t)$ was relatively independent of time. At progressively higher temperatures the values of $E_r(t)$ became smaller, although the time dependence of $E_r(t)$ always was slight. It was inferred that crystallites were acting as temperature-sensitive but not time-sensitive cross links. The presence of crystallites was also proved by X-ray, birefringence, and other techniques.³²

1. DECAY OF STRESS AT CONSTANT EXTENSION RESULTING FROM THE GROWTH OF ORIENTED CRYSTALLITES

The first observations on the decay of stress at constant extension due to the growth of oriented crystalline material was made in this laboratory in 1946.^{33, 34, 35} It was found that vulcanized Neoprene showed very little relaxation of stress after 100 hr. at 35° C. and 50% extension. However, a complete decay of stress at zero stress was observed after only 50 hr. at 0° C. and 50% extension—a rude shock to any simple-minded belief that rate of stress relaxation should follow the Arrhenius law in all cases. Actually the Neoprene sample, after decaying to zero stress, began to increase in length beyond the original 50% stretched value, a phenomenon known as spontaneous elongation. This phenomenon was attributed by us to crystallization of the Neoprene. Observations of spontaneous elongation, but no stress decay measurements, were previously reported for natural rubber and for ether polysulfide rubber.^{36, 37}

An extensive study was made^{34, 35} on the effect of temperature and elongation on the stress decay curves of unvulcanized natural rubber (cast latex sheet) in the temperature region of crystallization. In Fig. 9 stress decay curves are shown for samples maintained at 50% elongation at temperatures of 0, -10, -20, -25, -30, -40, and -50° C. Taking the time required to attain zero stress as an index of the rate of crystallization, it is clear that the results of Figure 9 are in accord with the results of Bekkedahl, who

³² R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 302 (1948).

³³ R. D. Andrews, Ph.D. thesis, Princeton University (1948).

³⁴ G. M. Brown, Ph.D. thesis, Princeton University (1948).

³⁵ A. V. Tobolsky and G. M. Brown, *J. Polymer Sci.* **17**, 547 (1955).

³⁶ C. Park, *Rubber Chem. Technol.* **12**, 778 (1939).

³⁷ W. H. Smith and C. P. Saylor, *Rubber Chem. Technol.* **12**, 18 (1939).

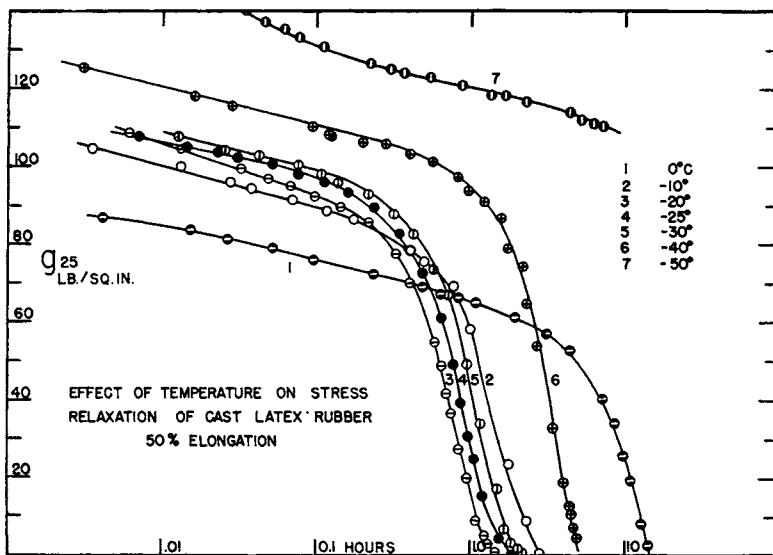


FIG. 9. Effect of temperature on stress relaxation of unvulcanized natural rubber in the crystallizing region.³⁶

studied the rates of crystallization in unvulcanized natural rubber by a dilatometric procedure.³⁸ The stress-relaxation data show a maximum rate of stress decay at -20°C . At -50°C . the rate of crystallization is very slow.

In many crystalline polymers for which no phenomenon of spontaneous elongation was observed, the decay of stress was nevertheless accompanied by an increase of birefringence, indicating that even in these cases stress decay may be caused in the part by a growth of oriented crystalline material, probably around pre-existing crystal nuclei.³⁹

VIII. Chemical Stress Relaxation (Chemorheology)

It might be expected that for chemically cross-linked rubbers, in the region of the rubbery plateau, the stress-relaxation curves $E_r(t)$ should remain constant with time, inasmuch as thermoplastic flow is suppressed by the cross links. In actual fact it was discovered that all rubbers show $E_r(t)$ curves that decay to zero stress at sufficiently high temperatures, and we attributed this stress decay to chemical reactions such as chain scission by oxidative cleavage or reorganization of the network structure by ionic interchanges.^{40, 41}

³⁸ N. Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934).

³⁹ R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 201, 302 (1948).

⁴⁰ A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.* **15**, 309 (1944).

⁴¹ M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.* **14**, 93 (1946).

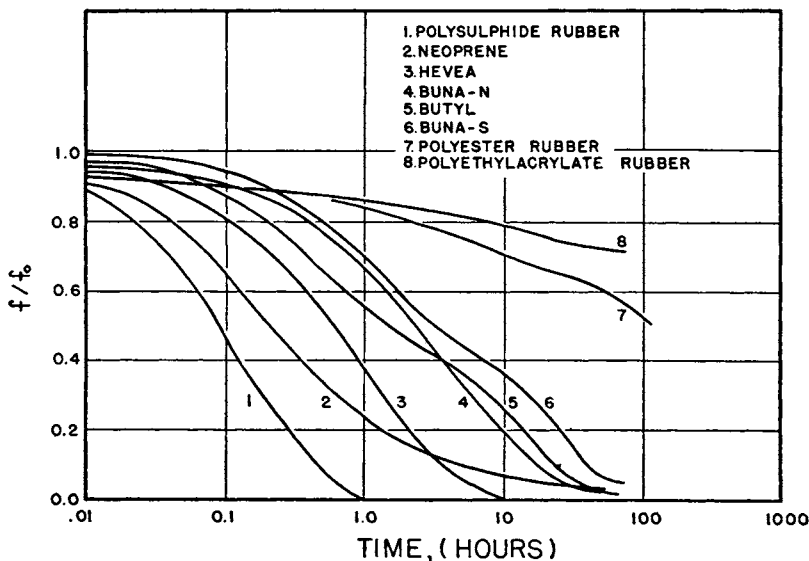


FIG. 10. Chemical stress relaxation for various vulcanized rubbers at 130° C⁵

In many cases the decay curves produced by chemical stress relaxation follow the decay law $\exp(-k^1 t)$ where k^1 is a rate constant that obeys the Arrhenius law for temperature dependence. The number of chain scissions per gram of rubber occurring per unit time can be calculated from the stress relaxation curves.⁴²

In many of the hydrocarbon rubbers (natural rubber, GR-S, Butyl, and so on) the chemical stress relaxation is brought about by a cleavage induced by molecular oxygen. At the same time there are simultaneously occurring cross-linking reactions. Fortunately these two reactions can be both examined by physical techniques. Decay of stress at constant extension measures the scission reaction alone, even though cross linking is occurring simultaneously. On the other hand, if the sample is kept in a relaxed condition at the elevated temperature and the modulus measured "intermittently," the net effect of cross linking and scission is measured. In rubbers for which cross linking predominates over scission, the "intermittent" modulus increases with time, in rubbers in which scission predominates the intermittent modulus decreases with time.^{8, 40} The concept of simultaneous scission and cross-linking originally introduced in these studies to explain the physical changes produced by high temperatures and oxygen now plays a vital role in the interpretation of the changes produced in polymers by high energy radiation.

Thin samples of rubber maintained in a stretched condition at elevated

⁴² A. V. Tobolsky, D. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.* **72**, 1942 (1950).

temperatures develop an irrecoverable permanent set because of the simultaneous cross linking and scission reactions. The permanent set can be predicted from the "continuous" relaxation curves and the "intermittent" measurements of the modulus.⁴³

The polysulfide- or Thiokol-type rubbers show a chemical stress relaxation resulting from catalyzed interchanges involving the disulfide linkage.^{41, 44} In this case the "intermittently" measured modulus shows no change with time, inasmuch as the interchanges leave the over-all structure of the network unaffected. Various types of ionic reagents catalyze the interchange.⁴⁴ In 1947 our studies on the stress relaxation of vulcanized silicone rubbers convinced us that the relaxation process was due to an ionic interchange of S; O linkages catalyzed by some unknown reagent.³⁴ In 1950 we prepared cross-linked silicone rubbers in a special way which unavoidably contained traces of H_2SO_4 as a residual catalyst.^{19, 45} These rubbers showed complete decay to zero stress at room temperature in a matter of several minutes unless the residual catalyst was stabilized by water or pyridine. Once stabilized, these specially prepared silicone rubbers showed practically no stress decay even at elevated temperatures.

A recent paper has identified the trace catalysts that cause stress relaxation in commercially prepared silicones.⁴⁶

In Fig. 10 chemical stress relaxation is shown for a number of synthetic crossed linked rubbers at 130° C. The date is plotted in the form stress/initial stress vs. log time. The tremendous variation that can be obtained in the rate of chemical stress relaxation as between several different synthetic rubbers is clearly seen from the graph. Although the stability to reactions at high temperatures is partly inherent in the structure of the polymers, very great variations in stability can be achieved—and have been achieved—by suitable purification, incorporation of stabilizers anti-oxidants etc.

Nomenclature

$E_r(t)$	Relaxation modulus; modulus measured with sample at constant extension	E'	Real part of complex dynamic modulus
$E_c(t)$	Creep modulus; modulus measured with sample under constant stress	E''	Imaginary part of complex dynamic modulus
		ω	Angular frequency of vibration

⁴³ R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.* **17**, 352 (1946).

⁴⁴ M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.* **40**, 2155 (1948).

⁴⁵ D. H. Johnson, J. R. McLoughlin, and A. V. Tobolsky, *J. Phys. Chem.* **58**, 1073 (1954).

⁴⁶ R. C. Osthoff, A. M. Bueche, and W. T. Grubb, *J. Am. Chem. Soc.* **76**, 4659 (1954).