

THE ELASTICITY OF LONG-CHAIN COMPOUNDS AS A STATISTICAL EFFECT

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I. INTRODUCTION

All substances built up of long, flexible, main-valence chains show a *high reversible elasticity* as one common property (18, 19). The range of temperature in which this phenomenon occurs may be rather wide (polyvinyl alcohol and rubber exhibit high elasticity at normal temperature, whereas other compounds as, for example, polystyrene, sulfur, etc., require higher temperatures). However, rubber-like elasticity occurs only with substances built up of long, flexible chains, which may be linked together in a flexible network. We find typical rubber-like elasticity in polyvinyl alcohol (Vinarol), polybutadiene (Buna), polydimethylbutadiene (methyl rubber), polyacrylester as well as vinyl chloride (Mipolam), muscle fibroin, polychlorobutadiene (Neoprene, Sovprene), polyethylene sulfide (Thiokol, Baerit), polyphosphonitrilic chloride, and finally in vulcanized oils (rubber substitute) as well as in elastic sulfur. At certain temperatures all these substances exhibit a reversible elastic limit up to at least 500 per cent and show a modulus of elasticity lying between $10^{5.5}$ and 10^7 dynes per square centimeter. In the investigations of rubber, Buna, Mipolam, methyl rubber, and rubber substitute, it was found that the modulus of elasticity increases proportionally with the absolute temperature. The fact that heat is generated during elongation stands in direct contrast to the behavior of normal elastic bodies as, for example, aluminum, steel, quartz, glass, etc.

It is very remarkable that substances of such different chemical character exhibit such similar mechanical properties. One is induced to explain this behavior on the basis of their having the same principle of molecular structure. In fact, all the materials mentioned consist of long, chain-like molecules of a certain degree of flexibility, the number of the chain links varying between 100 and 1000. The flexibility is the result of the free, or nearly free, rotation of the units round the normal carbon linkage.

II. THE FREE ROTATION

This principle of free rotation, detected long ago by the organic chemists, is necessary to explain that a great number of isomers never could be

¹ Revised in proof.

isolated. This principle has been very useful in discussing racemizations and isomerizations of different kinds. Recently it received quantitative support in the experimental work of Eucken and his collaborators (4), as well as in the theoretical considerations of Eyring (5).

We know that at normal temperature the two CH_3 - groups in the molecule of ethane rotate freely, because the normal thermal movement is sufficient to overcome the energy level that separates the different stable arrangements of the molecule. Eyring, Hückel, Pauling, and Slater have shown that a quantum-mechanical treatment of the single carbon-carbon bond explains the free rotation fairly well. On the other hand, experiment and theory agree that the double carbon-carbon linkage is rigid and defines a certain plane; this is characteristic for the structure of the molecule containing the double bond.

If one introduces substituents into ethane a certain hindrance of the free rotation results, which may lead to the formation of different stable arrangements. This intramolecular steric hindrance decreases with increasing temperature, because an increase of the vibratory and rotary motion of the different parts of a molecule tends to reproduce the free rotation (15).

Many investigations concerning the form of paraffin chains in the gaseous and in the dissolved state show that unbranched and unsubstituted hydrocarbon chains show free, or nearly free, rotation at normal temperature, and that even after substitution with groups of medium size the mobility of the molecule is maintained to a certain degree. Only if many large substituents are incorporated into the chain does the free rotation decrease remarkably. This is connected with the behavior of many main-valence chains, which also have long thread-like molecules but do not exhibit rubber-like elasticity. Carothers (2), Staudinger (25), and others have shown that polystyrene, polyindene, etc., are built up of long chains without rubber-like elasticity at normal temperatures. At higher temperatures elasticity can be observed. This is due to the fact that the steric hindrance of the rather large groups decreases with increasing thermal motion. Similarly, many cellulose derivatives do not show rubber-like elasticity, although they are built up of long chains. This is due to the fact that the ring structure of the glucosidic residue and of the 1,4-glucosidic linkage as detected by W. N. Haworth does not produce enough internal mobility for these substances at room temperature. They all have a certain rubber-like elasticity at higher temperatures.

Summarizing, we may state that rubber-like elasticity will always be observed if the presence of long-chain molecules with sufficient *internal* mobility can be assumed.

III. THE ELONGATION OF NORMAL BODIES AND LONG-CHAIN SUBSTANCES

It also seems necessary to point out that substances that do not exhibit *both* of these qualities never have an appreciable range of reversible elongation. They are characterized by the normal elastic properties of solid bodies. Their elasticity differs very distinctly from that of rubber in the limit of extensibility and especially in the different thermoelastic behavior.

We are rather well informed as to the mechanism of elastic elongation of crystals. The elementary particles of the substance—atoms, ions, or molecules—are arranged in equilibrium positions and perform small, nearly elastic oscillations around the minimum points of the potential energy; the vibrations increase with rising temperature. If one stresses such a body, then the elementary particles are moved out of their equilibrium positions and vibrate around a new minimum of potential energy, the distance of which is slightly larger than before and the energy level of which is increased. The increase in distance represents the elongation of the substance; the increase of the energy level of the equilibrium position means that now a certain amount of elastic energy is contained in the sample.

When the stress ceases, then the elementary particles return to their original positions and lose their excess of energy. The normal state is reproduced entirely. According to thermodynamics the substance must cool off during rapid elongation and heat up during rapid relaxation. Experiments confirm this postulate and show that normal solid bodies—diamond, quartz, platinum, etc.—show for their elastic elongation a range lying between 10^{-2} and 1 per cent. The modulus of elasticity is of the order of magnitude of 10^{10} to 10^{12} dynes per square centimeter and decreases with increasing temperature.

Quite different behavior is exhibited by all rubber-like substances. The limit of reversible elastic extension amounts to 1000 per cent and more; the elongation curve generally starts linear from the point of origin but afterwards exhibits a very complicated behavior; the modulus of elasticity is not at all constant during elastic extension.

Figure 1 shows a characteristic elongation curve of rubber of a low degree of vulcanization, the modulus of which lies at the beginning of the elongation between 10^5 and 10^7 dynes per square centimeter. It is much lower than for crystallized substances. During rapid elongation the substance evolves heat and during rapid relaxation it cools down (7, 12, 15, 16, 18, 19, 24).

If one observes the elongation of rubber by means of x-ray analysis as first reported by Katz (14), one finds a diffused halo in the unstressed state, which shows that the substance is of amorphous character. This diffuse ring was very carefully studied by Warren; it remains up to an

elongation of about 100 per cent. Later, sharp clear crystal-interference spots occur and demonstrate that during stretching an orientation of increasing degree takes place. Hauser and Mark (10), Mark and von Susich (18), Lotmar and Meyer (16), and recently especially P. A. Thiessen (27) and G. L. Clark (3) have investigated the crystal interferences and have derived from them a model for the molecular structure of natural rubber.

Other long-chain substances show a similar behavior. Carothers (2) in the case of Neoprene and Brill (1) in the case of Oppanol succeeded in detecting remarkably sharp crystal interferences during elongation. The

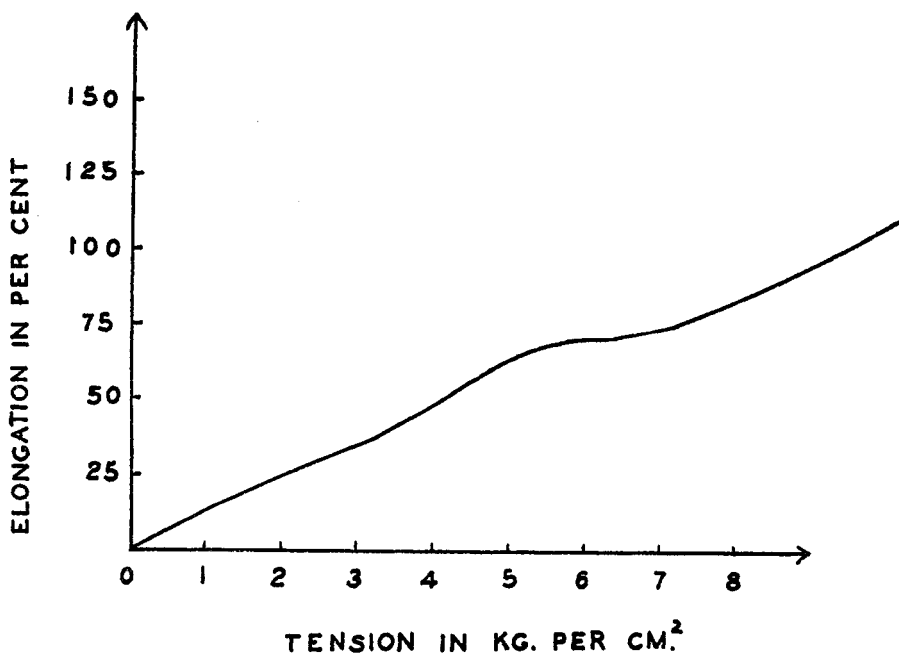


FIG. 1

modulus of elasticity and the trend of the stretching curve depend to a high degree on the temperature and on the degree of vulcanization. The typical rubber elasticity is shown only by samples that are not too highly vulcanized. If too many cross linkages are formed between the movable chains by means of sulfur bridges, the rubber-like elasticity disappears and one approaches more and more the normal behavior of crystallized solid bodies (hard rubber). The modulus of elasticity, which is calculated from the first part of the elongation curve, increases if the temperature is raised. This has been specifically demonstrated by K. H. Meyer (19) and Ornstein (21).

The enumeration of these properties shows that the molecular mechanism of the elasticity of rubber is fundamentally different from that of normal elasticity. It is very probable that the elasticity of rubber is intimately connected with the existence of flexible, long-chain molecules. Several years ago E. Wöhlisch (29) and K. H. Meyer (19), on the basis of their examination of the dependability of the modulus of elasticity on temperature, interpreted the elasticity of rubber and of proteins as a kinetic effect.

IV. THE INTRAMOLECULAR STATISTICS OF AN ISOLATED LONG-CHAIN MOLECULE

We start from a very simple example and consider first an isolated long-chain molecule, for instance, a normal hydrocarbon chain with n chain links, i.e., with $(n + 1)$ carbon atoms

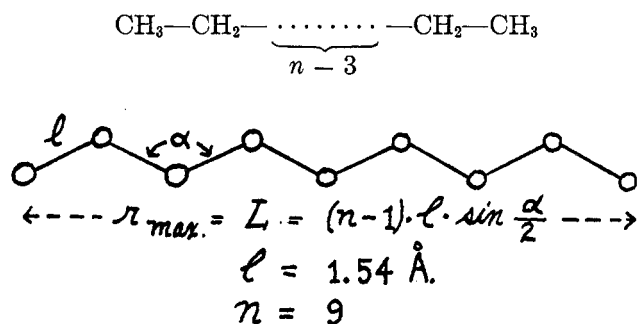


FIG. 2

the number n being of the order of magnitude between 100 and 10,000. This model is much simpler than natural rubber, because the methyl groups and the double linkages are not present, but we want to study first the behavior from the principal point of view. Later we shall have to bear in mind that there exists no real free rotation and that the different chains of a macroscopic sample mutually hinder each other.

Stereochemistry teaches that the distance x between two subsequent carbon atoms is 1.54 Å. and the angle α between two valences is about 109°. If we stretch the chain to its maximum length, as shown in figure 2, the distance between the end groups is given by

$$r_{\max.} = L = (n - 1) \cdot l \cdot \sin \frac{\alpha}{2} \quad (1)$$

One can easily see that this maximum length of the chain can be realized only in one way: namely, if all linkages lie in one plane building up the zigzag band shown in figure 2.

On the other hand, if we do not want the maximum possible distance between the first and the last carbon atom, but rather want to have a shorter distance for r ,

$$r < r_{\max.}$$

we can realize this in many different ways. Owing to the flexibility of the chain, we have ample possibilities for arrangement of its different chain links, so that the distance r between the two ends is always maintained.

For every given r a quite definite number of realizations exist, which, according to Boltzmann, can also be called the "complexions." In order to calculate these complexions as a function of r one has to make certain assumptions concerning the constitution of the chain and the mobility of its parts. When the length of one chain link is designated by l , the number by n , the angle between two subsequent links by α , and absolutely free rotation is assumed, E. Guth (8) and H. Eyring (5) have shown that the probability W that the distance between the two chain ends corresponds to r is represented by

$$W(n, l, \alpha, r)r^2 dr = 3 \sqrt{\frac{6}{\pi}} \cdot \frac{1}{n^3 l^2 \alpha} \cdot e^{-\frac{3r^2}{2nl^2 \alpha}} r^2 dr \quad (2)$$

$$l^2 d = l^2 \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha}$$

The equation shows that there exists a most probable distance, λ , between the chain ends: namely, the r by which the function W reaches its maximum value. This r is given by

$$\lambda = l \cdot \sqrt{\frac{2}{3}} \cdot \sqrt{n}$$

and is proportional to the square root of the chain links, as one would expect on the basis of the statistical character of the whole calculation.

Figure 3 shows W as function of r for $n = 30$. One sees that W is unsymmetrical compared with the well-known Maxwell-Boltzmann distribution curve. The distribution function is much broader than in normal statistics, owing to the fact that the number of members that are treated statistically is very much smaller than in the gas theory. As a consequence, in dealing with intramolecular statistics one has always to take seriously into account the phenomena of fluctuation, much more so than in the statistics of gaseous or solid bodies. All these considerations lead to the assumption that a chain that is in thermodynamical equilibrium with its surrounding matter will always tend to get into the condition that has the greatest number of possible realizations. This means noth-

ing else but the application of the Maxwell-Boltzmann statistics to one single macromolecule, and serious objections will not be raised as long as the number of independent elements for a statistical treatment is sufficiently large.

With this limitation we ascribe to an isolated main-valence chain an entropy, s , and calculate this entropy by the Boltzmann equation

$$s = k \ln W \quad (3)$$

W being taken from equation 2.

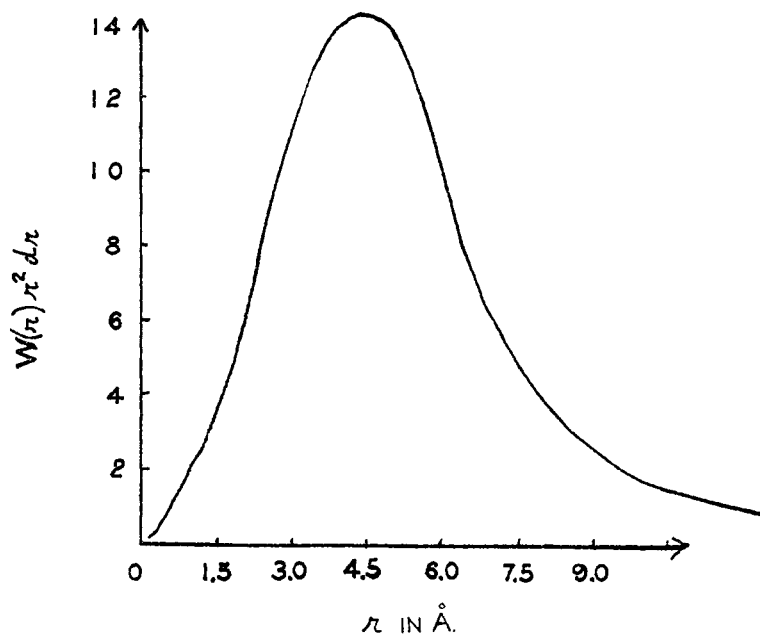


FIG. 3

First we find that such a chain will by itself always tend towards the state of greatest entropy, i.e., greatest probability. If one wants to obtain a state of smaller entropy one has to put work into the system. If we have a chain with the distance r between the end groups and want to stretch it to its maximum length, $r_{\max.} = L$, we have to put in a work A , which is equal to the difference of the entropy between the two states

$$A = S_r - S_L \quad (4)$$

During an adiabatic extension an equivalent amount of heat

$$Q = A$$

is produced. This is absolutely identical with the heating of an ideal gas during adiabatic compression. Here we obtain a loss of entropy because certain parts of the volume, which formerly were at the disposal of the gas molecules, are now blocked for them. As a consequence the number of realization possibilities and hence the probability and the entropy must decrease.

The pressure, p , of an ideal gas is exerted by the irregular motion of the molecules, which tends to increase the volume of the gas and hence to increase the number of complexions. In the same way the tension σ at the ends of a stretched main-valence chain is caused by the irregular thermal movement of the different parts, which tries to shorten the chain, because the shorter state has a greater number of possible realizations and hence a higher entropy value. In formulas:

$$p = + \left(\frac{\partial S}{\partial V} \right)_T \cdot T \quad (5)$$

$$\sigma = - \left(\frac{\partial S}{\partial(\delta l)} \right)_T \cdot T \quad (6)$$

δl = the change in the length of the chain

One can understand now why rubber-like substances show a rise in temperature during stretching and cool during relaxation, in absolute analogy to the behavior of ideal gases and in complete contradiction to normal crystal elasticity.

Ideal gases have an inner energy, U , which is independent of the volume. In the same way we can define as "ideal rubber" highly elastic substances that have an inner energy independent of elongation. Experiments carried out by E. Guth and coworkers (8, 9, 12, 22) have shown that rubber samples of a low degree of vulcanization have at about 250 per cent elongation an inner energy, which varies only very little with the stress. Real gases and rubber under other conditions show another behavior, because the forces between the different parts of a chain and the forces between different chains result in a dependence of the inner energy upon the elongation.

V. THE EQUATION OF STATE FOR THE IDEAL RUBBER

We will now, in analogy to an ideal gas, attempt to establish an equation of state for the ideal rubber. We start with equation 6. If we introduce $k \ln W$ for s and eliminate W from equation 2 we obtain:

$$\sigma = kT \cdot \frac{3}{nl^2} \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha} \cdot \delta l \quad (7)$$

δl = the elongation of a single chain, just as one gets for one molecule of an ideal gas the relation

$$p = kT \cdot \frac{1}{V}$$

Therefore we seem to be justified in interpreting equation 7 as the equation of state of the ideal rubber. It combines the tension σ with the elongation δl and represents the extension curve of a single main-valence chain.

Experimentally one always measures the elongation with a macroscopic piece of rubber, which has an original length L_0 and which reaches a certain elongation δL under the influence of the stress. Therefore we must pass from formula 7 to a macroscopic piece of material.

We consider a volume unit of rubber and assume that there are Z chains contained in it. When we put the sample under a certain macroscopic tension Σ , it undergoes an elongation δL . Now, as a first approximation we make the assumption that the entropy of the macroscopic piece of rubber is given by the sum of the entropies of the single chains. This is surely only a very rough approximation, and we shall see later what change we have to make in this preliminary hypothesis.

With such assumptions we obtain:

$$\begin{aligned} \Sigma &= Z \cdot kT \cdot \frac{3}{nl^2} \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha} \cdot \delta L \\ &= Z \cdot kT \cdot K \cdot \delta L \end{aligned} \tag{8}$$

$$\Sigma = E \cdot \delta L$$

$$E = kT \cdot K \cdot Z \tag{9}$$

From equation 9 one sees that the macroscopic modulus of elasticity E of rubber-like substances is proportional to the absolute temperature. This fact was proved in the range between -50° and $+80^\circ\text{C}$. by recent experiments of K. H. Meyer (19), Ornstein (21), and their collaborators for the first part of the elongation curve. Equation 8 further shows that there is proportionality between the tension Σ and the elongation δL , a fact which is also in very good agreement with many experimental investigations of the first part of the elongation curve of rubber of a low degree of vulcanization.

A further evaluation of relation 9 was given by W. Kuhn (15). The number of chains, Z , in the volume unit is closely connected with the

average molecular weight, M , of a single chain. If ρ designates the density of the material one finds

$$Z = \frac{\rho}{M} \cdot N$$

$$E = RT \cdot K \cdot \frac{\rho}{M} \quad (10)$$

Therefore the modulus of elasticity can be used to determine the average molecular weight (M) of the single chain. If one starts from the experimental values mentioned above (10^6 to 10^7 dynes per square centimeter), one obtains for the molecular weight of the rubber chains figures between 20,000 and 100,000, which are in good agreement with other quantitative data for this substance.

Another close analogy between ideal rubber and an ideal gas, based on the similar statistical treatment, results when one compares the conditions during very slow and very rapid elongation with the slow and rapid compression of an ideal gas. If one stretches rapidly one can realize with good approximation an adiabatic process, while an isothermal process is realized when one stretches slowly. One can combine isothermal and adiabatic processes of elongation and relaxation of rubber in a Carnot-cycle process exactly as with an ideal gas, and it is easy to show that one obtains the same results as when applying the second law of thermodynamics in the usual way. It may be of interest to add that one must distinguish between the specific heat at constant length and the specific heat at constant tension exactly as one has to consider two specific heats in the case of an ideal gas. The part of the gas constant R is represented in our case by R and K .

VI. HIGHER DEGREES OF ELONGATION; TRANSITION TO THE REAL RUBBER

Although it is possible to get fairly good qualitative agreement with the properties of rubber when applying the idea of intramolecular statistics, it must be clearly pointed out that there exists so far no quantitative treatment for the behavior of a macroscopic piece of rubber during the whole range of its elastic stretch. Relation 7 only refers to the beginning of the elongation curve, during which the tension and the elongation are proportional. If one wants to go further, one must improve the equation of state of the ideal rubber in the same way as is done with the ideal gas equation by van der Waals' theory. If one wants to do this, one must consider that two kinds of corrections must be taken into account. The first of them concerns the single isolated chain, the other the interaction of different chains.

When discussing the single chain, we have so far made certain assump-

tions which surely are not right and therefore it will be necessary to give them up gradually. On the other hand, it certainly is not correct to consider a single chain in a macroscopic piece of rubber as independent of all others. Hence the required improvements can be divided into two groups: (1) The statistics of an isolated main-valence chain, which have up to now only been evaluated as a pure statistics for different positions with equal energy, have to be improved by taking the attraction and repulsion forces between the parts of a chain into account. (2) The forces between the different chains in a macroscopic piece of the substance must be discussed in a suitable way.

(1) We must point out that in regard to the van der Waals attraction and repulsion forces not all possible arrangements of a chain have the same energy. Calculating W in equation 2 we have considered them all as statistically equivalent. This certainly is not permissible. We have to proceed in another way. Every individual position of a chain has to receive a certain statistical weight, g , i.e., we have to multiply every microscopic possibility of realization for a certain given distance r between the chain ends by a Boltzmann weight factor of the form

$$g_i = e^{-\frac{\epsilon_i}{kT}}$$

and to take all these factors in account when we calculate the probability of a given (macroscopic) distance r . This would be a very complicated and nearly impossible task, and one may be induced to try some possible abbreviation. It seems reasonable to follow the ideas of van der Waals and to divide the two possible influences into (a) repulsion forces and (b) attraction forces.

As E. Guth (8) has pointed out, the *repulsion forces* can be considered in a preliminary way by something like a volume correction, exactly as was done in the theory for a real gas. In our case this means that if we want to give to our single main-valence chain a certain individual position to produce a given distance r between its ends, we begin with one end of the chain and arrange link after link in such a way that the distance between the ends becomes r . In doing this we have to be careful not to put new links in a place which is already occupied by a former part of our chain. The molecule has a certain *own volume*, which can be introduced into the formulas by replacing l in equation 2 by another quantity, l_0 .

In analogy to the van der Waals covolume b , the quantity l_0 could be called the colength of the chain. The application of this correction increases the most probable chain length, λ , and has the consequence that the distribution function of figure 3 is shifted to higher chain lengths. The particles increase in length as compared to their dimensions without this correction.

The average and the most probable shape of a given main-valence chain is a very important problem, which can not yet be entirely solved. W. Kuhn (15) has shown in a very interesting publication that one always must expect the form of a coil. But, as Guth (8) has pointed out, the calculations cannot be regarded as being quite satisfactory from a quantitative point of view. Anyhow one finds that the chains are certainly not straight, as Staudinger (25) assumes in many of his well-known contributions. They also seem not to be so much wound as is called for by the calculations of Kuhn. Experiment and, as Guth was able to show by a very interesting calculation, theoretical considerations also lead to the result that the chains are in their free state only moderately curved and wound without showing sharp angles or curvatures (8).

The forces of attraction between the different links of a single chain have been used by Fikentscher and Mark (6) and by E. Mack (17) in formulating a theory of the elasticity of rubber. The former authors emphasized that the secondary valences between the double bonds should be responsible for the attraction between the different isoprene residues and tend to shorten an extended rubber chain. E. Mack showed that more probability seems to exist for the hypothesis that the van der Waals forces between the hydrogen atoms of the hydrocarbon are responsible for this inner tension of a rubber macromolecule. In these two theories only the inner van der Waals forces of the thread-like molecules have been considered, but so far no reference has been made to the entropy of such a chain. This seems to be not justified, but one certainly has to use these forces as a correction in the same sense as the van der Waals force constant enables the treatment of a real gas.

(2) Considering the mutual interaction between the different chains it is very striking that rubber, after elongation to 100 per cent, exhibits the well-known crystal structure that was first reported by Katz and further investigated by different authors during recent years. Also, synthetic long-chain products as, for example, Neoprene and Oppanol, show similar effects. Especially in the former case W. Carothers (2), as previously mentioned, was able to observe very sharp and intensive interference spots, while R. Brill (1) obtained with samples of Oppanol at least an orientation parallel to the direction of the stress. These facts show that at higher stretches the chains arrange themselves more and more in the extended form and aggregate under the influence of the mutual attraction forces to more or less oriented bundles, which give rise to the crystal interferences, the size of which can be estimated by following the procedure of Hengstenberg and Mark (11).

The relatively short hydrocarbon chains of normal paraffins crystallize spontaneously (20). They have a small number (n) of links in every individual chain and hence (cf. equation 2) the probability of the extended or

nearly extended form, which fits in the crystal lattice, is only somewhat smaller than the one which results as most probable from statistical considerations. The natural energy and entropy fluctuations of the system are sufficient to produce straight chains to such an extent that the material crystallizes rather quickly. Therefore such substances crystallize spontaneously from solution or from the liquid phase. It fits well into this picture that the power to crystallize decreases rapidly with increasing chain length.

Truly high-polymer substances have chains which are built up of much more independent parts and their distribution function is therefore much steeper. In such cases the normal fluctuations are not sufficient to realize a frequent formation of straight or nearly straight chains. Hence the velocity of crystallization decreases more and more, and finally there is no orientation of the macromolecules at all. Only if one stretches the single chains by applying additional tension from outside and thereby increases the number of straight (less probable) individuals, does the number of these chains, which alone fit into the lattice and hence alone can undergo crystallization, become large enough and the well-known crystal interference patterns appear.

Very interesting measurements of G. von Susich (26), P. A. Thiessen and Wittstadt (27, 28), and Hauck and Neumann (9) show that at a given temperature the amount of crystallization increases with increasing tension and that at a given tension the crystals can be destroyed by increasing the temperature. As Thiessen has clearly pointed out, we have the case of an equilibrium between two phases—liquid and crystalline—which largely depends on the tension (as in other cases on the pressure).

It has been observed that when a stretched rubber band, which exhibits very distinct interference patterns, is heated, the intensity of these spots decreases with increasing temperature and at last completely vanishes. The temperature at which the x-ray interference spots disappear depends primarily on the degree of extension. However, if one has a stretched rubber band at a temperature at which interference spots are just not yet detectable and one increases the tension, then the x-ray diagram appears. This means that the intensity of the interference lines, i.e., the amount of crystallized rubber present, depends on two variables, namely, the tension σ and the temperature T . The melting point, T_m , depends on the tension, and the crystallization tension, σ_c , depends on the temperature.

These facts induce one to apply (8) the Clausius-Clapeyron equation for equilibrium between liquid and crystallized rubber depending on temperature and stress. This well-known thermodynamic law relates to the dependence of the melting point upon the tension $dT/d\sigma$, with the difference in length during the extension ΔL and the heat of crystallization r .

One can now test whether the application of this equation gives the same order of magnitude for the heat of melting as was previously measured by L. Hock (13).

For phase transformations of the first order the Clausius-Clapeyron equation has in our case the form

$$\frac{d\sigma}{dT} = -\frac{n}{T} \cdot \frac{1}{\Delta L} \quad (11)$$

When we assume that r is nearly independent of temperature we get by integration

$$\sigma = -\frac{r}{\Delta L} \ln T + \text{const.} \quad (12)$$

For the dependence of the melting point upon the temperature we have to take the quantities that have been determined by Rosbaud and Schmid (23), van Rossem (24), G. von Susich (26) and especially by P. A. Thiessen and Wittstadt (27). If one does that, one obtains for an elongation of 200 per cent and for a temperature of 40°C. the heat of crystallization per gram of rubber to be about 1 cal. This is the same order of magnitude as observed by L. Hock (13).

Therefore it seems reasonable to assume that with increasing tension gradually more and more chains are brought into the extended state and hence can crystallize. If one increases the temperature, the crystallization is hindered by the increased contraction of the chains. When one increases the tension, it is favored. This stands in absolute analogy to a real gas, where temperature increase shifts the equilibrium in the direction of the gaseous state, while an increase in pressure shifts it towards the liquid state.

It may be that in the case of rubber also something like a critical temperature exists, i.e., a temperature above which one cannot obtain interference spots even if one stretches the rubber to its highest degree. Experiments in this direction have demonstrated that it is in fact difficult to obtain interference spots above a certain temperature.

All comparisons of the ideas based on intramolecular statistics with experiment show a perfect qualitative agreement with the observed facts. This might assist in improving the formulas that have been derived to date and in working out some quantitative tests for this new theory of the elasticity of rubber and of rubber-like substances. It is of course evident that the statistical elasticity of rubber only constitutes one side of the total elastic behavior of this material and that its total elasticity is a composed effect, including the action of forces as well as the action of the kinetic movements of the molecules.

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