PROBLEMS IN THE THEORETICAL PHYSICS OF POLYMERS

M. V. VOL' KENSHTEĬN

1. INTRODUCTION

THE development of chemistry, which has created an important new area of technology, the synthetic polymer industry, and the development of biology, which has led to the physicochemical interpretation of the basic phenomena of life, have presented new problems of the highest degree of scientific interest to the science of physics.

The application of polymeric substances (in distinction from other materials produced by the chemical industry) is based on their physical properties, rather than their chemical properties. In practice the most important are the mechanical properties and also the dielectric properties. One may refer to the high elasticity of synthetic rubbers, the exceptional durability of plastics and synthetic fibers, and the valuable electrical insulating properties of a series of technical polymers. The combination of various properties in one substance is essential. Thus, for example, the polymeric material used for automobile tires must possess high elasticity (i.e., large reversible deformation with a low modulus of elasticity) over a wide temperature range and over a wide range of frequencies of mechanical action. It must also show high resistance to wear, and high toughness. It is obvious that the low density of the rubber is no less important. Only polymers possess such complex physical properties; it is just for this reason that they have attained such a great role in modern technology. Their present and future development is closely connected with the development of molecular and theoretical physics. The basic problem of the physics of polymers may be formulated as follows: the establishment of the relation between the chemical structures of polymeric substances and their physical properties.

The physics of polymers is a division of technical physics. The content of this field, however, cannot at all be reduced to the application of previously-established principles to a new field of technology. On the contrary, the specific study of the molecular structure of polymers (they are composed of long-chain molecules consisting of a large number of atoms) and of their physical properties has already required the development of essentially new theoretical concepts, and above

all, of new branches of statistical physics. In this sense, one may speak of a certain similarity of the physics of polymers to the physics of ferromagnetic materials.

The technical problems associated with ferromagnetism led to the development of a special field of theoretical physics, to the establishment of the theory of second-order phase transitions, and to the concept of domain structure of ferromagnetic materials, which is the basis of the theory of magnetization technology. The physics of polymers encounters even more complex theoretical problems since it deals with an unlimited set of diverse substances occurring either in the crystalline state or, for the most part, in the amorphous state. Here the significance of theoretical studies in the field of polymer physics is determined by three factors. First, the theoretical physics of polymers must become in the future the basis for creation of new materials with especially valuable properties, and the basis for further development of polymer technology. Second, the development of the theoretical physics of polymers means an extension in principle of molecular physics, which has previously been concerned with liquids and crystals consisting of small molecules. As has been mentioned, such an extension leads to the creation of new conceptions which are, in the last analysis, of general physical significance. And finally, it is precisely by way of polymer physics that science must approach the solution of the most important problem of natural science, the problem of life. The basic substances from which living organisms are made (proteins, nucleic acids, carbohydrates, etc) are polymeric, high-molecular-weight substances. In order to establish the physico-chemical nature of the phenomena of life — heredity, muscle action, transfer of nerve impulses, etc — a physical theory of macromolecules is necessary, in particular, the macromolecules of polymeric electrolytes, which can carry electric charges.

The macromolecular nature of living organisms is obligatory, especially in view of the peculiarities of large chain molecules. One may characterize the specific properties of macromolecules which determine their role in biological systems as follows:[1]

Macromolecules are characterized by a high

degree of individuality, and at the same time maintain their integrity and continuity of structure. This degree of individuality is determined both by the chemical and geometric distribution of links in the polymeric chain, and by the multiplicity of configurations of the chain as a whole. In a macromolecule, it is possible for essential changes in the structures of the links to occur without the destruction of the structure of the chain as a whole. The macromolecules of polyelectrolytes have the property of transforming chemical energy into mechanical energy, and vice versa. Thus they provide for the existence of mechano-chemical systems operating at constant temperature and pressure. The multiplicity of internal and external structures of macromolecules makes possible the storing of vast amounts of information within them, and the subsequent transfer of the information in associated reactions. Macromolecules possess special possibilities for participation in irreversible processes occurring in open systems. These possibilities arise from the great number of internal degrees of freedom, the configurational lability of polymeric chains. Finally, macromolecules are characterized by a significant geometric and energetic diversity of structure and properties on the supermolecular level, as in aggregates and in oriented and crystalline polymers. The inherent non-equilibrium character of the series of aggregates which are formed by macromolecules is essential to them.

We shall attempt to define the fundamental problems of the theoretical physics of polymers. This is not a simple question, since we are dealing with a unified complex of phenomena, not easily subjected to analysis.

The objects of study are two types of aggregations, the ensemble of atoms or chemical bonds joined together in the macromolecular chain, and the ensemble of such chains in the bulk polymer. The second type is important in technology. However, in order to understand the properties of the bulk polymer, it is necessary to make a preliminary study of the properties of the isolated macromolecule. Isolated macromolecules exist only in solutions in solvents of low molecular weight. These solutions were considered for a long time to be colloidal; later it was shown that they are molecular in nature, and the difference in their behavior from that of ordinary solutions is caused by the long-chain structure of macromolecules. A fundamental role was played here by the work of Staudinger (see reference 2), and especially by V. A. Kargin and his coworkers.[3]

The basis of the statistical thermodynamics of polymer solutions has already been developed.

It has been shown that the essential deviations in the properties of these solutions from those of ideal solutions are caused by the flexibility of macromolecules, which are capable of taking on many different configurations in solution. For purposes of calculation, the theory makes use of the partition function of the so-called lattice model of the liquid. The solution is considered to be in the form of a lattice characterized by a definite coordination number. Within each unit cell of the lattice there may be found either a segment of the polymer chain, which is considered to be freely jointed, or a molecule of the solvent. The statistical theory permits the interpretation of the observed values of the vapor pressure, and the heat and entropy of solution. The basic result of these studies is the conclusion that macromolecules are actually flexible ofjects having a large number of configurations. The concrete values of the parameters characterizing the flexibility of macromolecules may not, however, be determined directly from the thermodynamic behavior of the solutions. This is because the number of configurations which the chain possesses in the bulk polymer is not changed upon solution, to a first degree of approximation. The statistical thermodynamics or polymer solutions is presented in a series of monographs.[4,5,6] There are a number of unsolved problems here; the applicability of the lattice model is limited, and the theory developed from it does not permit answers to a series of questions relating, in particular, to dilute solutions. A detailed analysis of the lattice model has been carried out by Prigogine.[7] The study of polymer solutions is a fundamental method of determination of the molecular weights of polymers and their polydispersity. The viscosity of the solution, the osmotic pressure, and the intensity of light scattering depend on the number of atoms in the chains. Molecular weights are determined by the methods of diffusion and sedimentation in the ultracentrifuge.[4,6] For this reason, these methods have a great practical and theoretical significance. Their development and further refinement requires the solution of the problems of the hydrodynamics of polymer solutions, which encounter significant difficulties. The problem is that of the kinetics of the motion of the flexible macromolecule, whose links interact with one another. In spite of the series of substantial studies which have been made, no complete theory of the mentioned phenomena has ever been developed.

The same methods, to which must be added the studies of dynamic birefringence (the Maxwell phenomenon) and the asymmetry of the light-scattering indicatrix, give valuable information

about the dimensions and form of macromolecules in solution. The experimental data show that flexible macromolecular chains in the free state are wound into coils having linear dimensions much smaller than the extended chain length.

The basic physical characteristic of a flexible macromolecule is its size. A chain molecule is a statistical ensemble of links having some degree of independent motion. The configurational statistics of macromolecules requires the solution of certain specific problems in the theory of probability which are not encountered in other fields of physics. We gave a review of the status of this problem in 1953.[8] In the course of the years, the configurational statistics of polymers has been developed widely. It has dealt successfully with the dimensions of macromolecules, their dipole moments and optical anisotropy, and their behavior under tensile stresses as a function of their chemical structure. We shall return later to these questions.

Thus the problems relating to isolated macromolecules have, on the one hand, a statistical-thermodynamic character, and on the other hand, a kinetic character. The same is true of bulk polymers, with the distinction that it is much harder here to carry out the experimental determination of the equilibrium (thermodynamic) and non-equilibrium (kinetic) properties of the substance. These properties are closely connected together, and to consider them separately implies a definite simplification of the problem. However, such a simplification is necessary.

The fundamental problems in the physics of bulk polymers are associated with the study of the degree of order in their amorphous and crystalline states. This involves the study of the characteristics of the intermolecular interactions of the macromolecules which determine the cooperative character of their motions in the bulk polymer, as well as the intramolecular interactions which give rise to cooperative motions within one macromolecular chain. The study of the thermoelastic properties of rubber led to the demonstration that the elasticity of rubber is quite specifically based on entropy, and led to the development of a corresponding statistical theory. This theory, however, does not agree with experiment in a number of respects. This is explained by the failure of the theory to take into account the intermolecular interactions, that is, the "gas-like" character of the theory. We do not yet have a physical theory which would permit us to relate the highly elastic properties of rubber to its structure. The establishment of such a theory would be very valuable for tech-

nology. Some related questions will be discussed in detail below.

The problems of the kinetic relaxation behavior of bulk polymers are even more complex. It is precisely the kinetic properties which are important in technology, since there a polymeric material must function according to a definite time schedule. As the studies of S. N. Zhurkov[9] have shown, the strength of polymeric and also other materials is a kinetic characteristic. The experimental study of the kinetic properties of polymers, begun in the classic studies of A. P. Aleksandrov and Yu. S. Lazurkin[10] and of P. P. Kobeko and his coworkers,[11,12] have revealed the basic features of the phenomena. However, a deep theoretical study of these encounters significant difficulties. The most important of these is connected with the occurrence of spectra of relaxation times in polymers, as a function of the chemical structure of the macromolecules. A substantial step in this direction was made in the work of V. A. Kargin and G. L. Slonimskiĭ[13] (see also reference 14). The properties of the vitreous state of polymers are closely associated with their relaxation properties. The study of the vitreous state of polymers is of general significance in the understanding of the nature of glasses. These questions will also be discussed below.
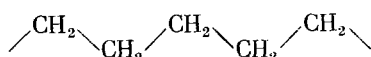
An entire series of polymers exists in the crystalline state. It is precisely this state which is inherent in strong fibrous materials, and in particular, is found in the stereospecific polymers. The crystalline state of polymers is characterized by a number of properties which distinguish it from the crystalline state of molecular compounds. The theoretical and experimental study of the crystallization and melting of polymers is of the highest degree of scientific and technical significance. The problems of the phase state of polymers and the nature of the observed thermodynamic transitions are of great interest. It must be emphasized that transformations that have all of the characteristics of thermodynamic transitions occur not only in bulk polymers, but also in isolated macromolecular chains in solution. Such transitions of the order-disorder type are observed in proteins and nucleic acids.[15] In this process, the regular helical configuration of the macromolecule is transformed into the configuration of a random coil.

The brief enumeration given here of the theoretical problems of polymer physics is provisional, and is far from encompassing the entire field being discussed. All of the mentioned problems are closely connected together; thus, for example, the physics of the elasticity of rubber utilizes both the results of the configurational statistics of macro-
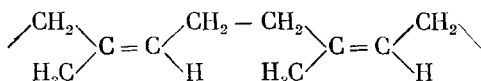
molecules and the results of the study of the crys-
talline and amorphous states of bulk polymers. The
remainder of this discussion will be an attempt to
characterize the state of the theory, as applied to
some of the most important problems of polymer
physics. This attempt will be to a certain degree
subjective, since primary attention is directed to
the problems in which the author and his associ-
ates have been interested.

2. THE CONFIGURATIONAL STATISTICS OF POLYMERIC CHAINS

The macromolecules of polymers are long chains
which, as a rule, are composed of single bonds of
the types C—C, C—O, Si—O, etc. Of this type,
for example, are the technically important poly-
mers — polyethylene

$$\diagup CH_2 \diagdown_{CH_2} \diagup CH_2 \diagdown_{CH_2} \diagup CH_2 \diagdown$$

and natural rubber

$$\diagup CH_2 \diagdown_{\substack{H_3C}} C = C \diagup_{H}^{CH_2 - CH_2} \diagdown_{\substack{H_3C}} C = C \diagup_{H}^{CH_2 \diagdown}$$

The flexibility of macromolecules, which has been
proved by the experimental study of polymer solu-
tions, is determined, in particular, by the proper-
ties of the single bonds. As is shown by many data
relating to the thermodynamic, optical, and other
properties of small molecules containing single
bonds, internal rotation of part of the molecule
about these bonds occurs, and is hindered in some
degree or another.[16,17,18] Thus, for example the
ethane molecule $H_3C—CH_3$ has the configuration
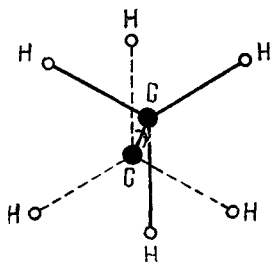shown in Fig. 1. It is obvious that the configura-

FIG. 1. Structure of ethane
molecule.

tions obtained from that shown in the diagram by
rotations of 120° and 240° about the C—C axis
are equivalent to the original configuration. How-
ever, in order to bring about such a rotation, an
energy U_0 of 2750 cal/mole is necessary. The
potential of internal rotation in ethane may be
represented by

$$U = \frac{1}{2} U_0 (1 - \cos 3\varphi), \tag{1}$$

where φ is the angle of internal rotation, as meas-

ured from the transconfiguration of the molecule
shown in Fig. 1.

The reasons for the hindrance of internal rota-
tion in molecules have not been completely eluci-
dated as yet. The hindrance is caused by the inter-
action of atoms which are not directly connected to
one another, in the given case, the hydrogen atoms
which are connected to different carbon atoms. The
interaction is not, however, simply a van der Waals
repulsion of the atoms, but has a more complex
character. A semi-empirical theory of hindered
rotation has been developed on the basis of the con-
cepts of quadrupole and octupole interactions of
chemical bonds.[18,19] The role of van der Waals re-
pulsion was studied in the papers of Mason and
Kreevoy.[20] A paper of Pauling[21] was published re-
cently, showing that the hindrance of internal rota-
tion is caused by exchange repulsion of the C—H
bonds, in which, along with the s and p states,
d and f electronic states also participate.

If a molecule in which internal rotation is pos-
sible has a symmetry lower than C_3, then the con-
figurations corresponding to the minima in the
energy of internal rotation $U(\varphi)$ are non-equiva-
lent. They are characterized by differing symme-
tries and differing energies. Such configurations
are called rotation isomers. Thus, the molecule
of n-butane $H_3C—CH_2—CH_2—CH_3$ exists in the
form of three rotation isomers (see Fig. 2). The
trans-isomer of butane shows the lowest energy,
the energy of the twisted (gauche) isomers being
larger by approximately $\Delta E = 800$ cal/mole. The
existence of rotation isomers may be demonstrated
by the method of vibration spectra, by measure-
ment of dipole moments, etc. It is obvious that on
change in temperature, a change in the relative
proportions of the rotational isomers will occur,
in agreement with the Boltzmann distribution.
Rotational isomers cannot be separated in the
gaseous or liquid states, since the rate of rota-
tional isomerization, which is determined by the
height of the potential barrier, is of the order of
10^{10} sec^{-1}. On crystallization, the molecules ac-
quire the configuration of the single most stable
isomer; thus, normal paraffins crystallize in the
form of planar zigzag trans-chains (isomer 2a
in the case of n-butane).

Internal rotation takes place also in polymer
chains containing single bonds (in particular,
C—C). Occurring in each link in the chain, the
internal rotation has the character of a micro-
Brownian movement. The macromolecule is con-
tinually fluctuating, and acquiring a multiplicity
of configurations. It is easy to show that the
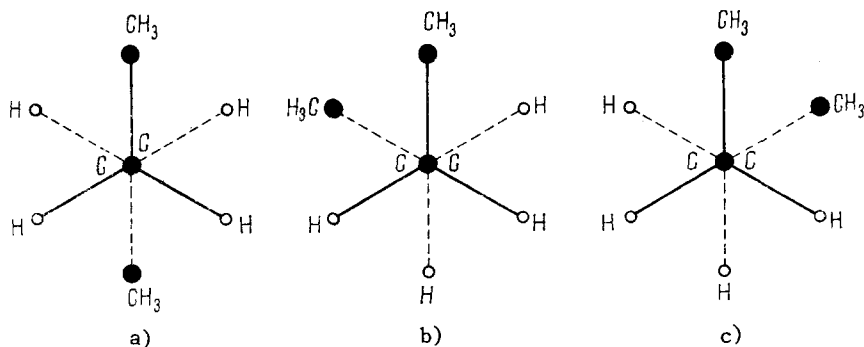most probable state of such a chain corresponds

FIG. 2. Rotation isomers of n-butane:
a — trans, b and c — twisted (gauche).

to its winding up into a random coil. If the links
have a certain freedom of rotation with respect
to one another, then the degree of correlation be-
tween the directions of these links will decline
rapidly with increasing distance between the links,
as measured along the chain. Links which are
sufficiently separated from one another are inde-
pendent in orientation. Hence it is possible to
replace the study of the real chain by the study of
a simple model, consisting of a large number Z
of freely-jointed segments of length b. The statis-
tical problem then reduces to that of finding the
distribution function of the distance between the
ends of such a chain. This problem is completely
analogous to the stochastic problem of the average
distance travelled by a particle in Brownian move-
ment.

The distribution function for the distance is the
Gaussian function[8]

$$W\,(h_x,\, h_y,\, h_z) = \left(\frac{3}{2\pi Z b^2}\right)^{\frac{3}{2}} e^{-\frac{3}{2Z b^2}(h_x^2 + h_y^2 + h_z^2)}, \tag{2}$$

and we find that

$$\bar{h} = 0, \tag{3}$$

$$\bar{h}^2 = Z b^2. \tag{4}$$

Thus, the root-mean-square length of the chain is
less than the contour length by a factor of $\sqrt{Z}$.
The Gaussian distribution (2) is valid under the
conditions, $Z \gg 1$, and $\sqrt{\bar{h}^2} \ll h_{max} = Zb$, that
is, for sufficiently long, highly coiled chains. The
distribution function in the general case was found
by Kuhn and Grun[22] (see reference 8). Formula
(4) cannot be compared with experiment, as a real
chain is not freely jointed, and the quantities Z
and b have an undefined character. From the
statistical point of view, the polymer chain is a
Markov chain, since the orientation of each link
of the chain depends in some degree on the orien-
tations of the preceding links. If the rotations
about the individual links are independent, then
the position of a given link will depend on the posi-
tions of the two preceding links. Calculation shows
that, for chains having a symmetrical potential of

internal rotation $[U(\varphi) = U(-\varphi)$, for example,
polyethylene], the mean-square length of the chain
is equal to (see reference 8)

$$\bar{h}^2 = Nl^2 \frac{1+\cos \alpha}{1-\cos \alpha} \frac{1+\eta}{1-\eta}, \tag{5}$$

where N is the number of links in the chain, l is
the length of a link, $\pi - \alpha$ is the valence angle in
the chain, and η is the mean value of the cosine
of the angle of internal rotation, that is:

$$\eta = \cos \varphi = \frac{\int_0^{2\pi} \cos \varphi e^{-\frac{U(\varphi)}{kT}} d\varphi}{\int_0^{2\pi} e^{-\frac{U(\varphi)}{kT}} d\varphi}. \tag{6}$$

The first paper in which the hindrance of internal
rotation in a polymeric chain was taken into account
was the paper of S. E. Bresler and Ya. I. Frenkel'.[23]
The topic discussed was not internal rotation, but
torsional oscillation about a single equilibrium po-
sition. From the work of Bresler and Frenkel' is
derived the formula

$$\bar{h}^2 = Nl^2 \frac{1+\cos \alpha}{1-\cos \alpha} \frac{2}{1-\eta}, \tag{7}$$

which is a special case of the more general formula
of Taylor (5), for $\eta \cong 1$, that is, for very rigid
chains.

The calculation of η in the general case is dif-
ficult, since the potential $U(\varphi)$ is not known. The
theory of rotational isomers leads to a substantial
simplification of the problem; thus, this theory has
become the basis of the modern configurational sta-
tistics of polymer chains. According to this theory,
the polymer chain must be considered as an equi-
librium mixture of rotational isomers.[24,8] In its
internal rotation, each link may not acquire any ar-
bitrary orientation, but only certain definite ones,
which are characterized by varying energy values.
In fact, it may be easily seen that in polyethylene,
for example, rotational isomers of the same types
as in n-butane (Fig. 3, cf. Fig. 2) are possible.
The existence of rotational isomerism in polyethy-
lene may be shown directly by infra-red spectro-
scopy: on change of temperature, changes occur

FIG. 3. Rotational isomers of polyethylene: ∿ — continuation of the chain.

in the relative intensities of the infra red bands belonging to the different rotational isomers.[25] Taking into account the fact that in polyethylene isomers having $\varphi = 0°$, $\pm 120°$ exist, we find, upon neglecting the entropy difference of the rotational isomers,

$$\eta = \frac{1 - e^{-\frac{\Delta E}{kT}}}{1 + 2e^{-\frac{\Delta E}{kT}}}.$$

Thus, in this case the dimensions of the chain are determined by a single energy parameter, the energy difference ΔE between the rotational isomers. The quantity η is found to depend directly on the temperature. This dependence disappears only in the case of free rotation, for which $\Delta E = 0$.

Formula (5) was derived for chains with symmetrical substituents. If the substituents are unsymmetrical, as for example, in polystyrene,

$$-\; CH_2 - C - CH_2 - C -$$
$$\underset{C_6H_5 \quad H}{\diagup\diagdown} \qquad \underset{H \quad C_6H_5}{\diagup\diagdown}$$

the potential $U(\varphi)$ will no longer satisfy the condition $U(\varphi) = U(-\varphi)$, and the expression for $\overline{h}^2$ will be different. Here, it is suitable to distinguish three cases. In the first case, the substituents (C_6C_5 in polystyrene) may all be distributed on the same side of the chain (Fig. 4). Such polymers are called isotactic. In the second case, a regular alternation of right-handed and left-handed substituents may occur (Fig. 5). Such polymers are called syndiotactic. Finally, an irregular distribution of right-handed and left-handed substituents may occur in an atactic polymer. Natta[26] was the first to synthesize stereospecific — isotactic and syndiotactic — polymers. This discovery is very important both for technology and for the theoret-

ical physics and chemistry of polymers. Stereospecific polymers were found to have new technical properties. The ordinary atactic polystyrene is a vitreous, amorphous plastic. Isotactic polystyrene is a crystalline material from which a strong fiber may be obtained. At present, new methods have been found for obtaining stereospecific polymers. It has been shown that even atactic polymers do not have a completely disordered structure. Apparently, they consist of whole blocks of isotactic and syndiotactic links. The synthesis of stereospecific polymers is an important stage on the way toward the understanding of the nature of biosynthesis. Biological polymers are always characterized by a definite stereospecificity (see reference 1).

T. M. Birshteĭn and O. B. Ptitsyn[27,28] have derived formulas for the stereospecific chains $-CH_2-CHR-$ and $-CHR-CHR-$. We shall give the expression for the isotactic chain $-CH_2-CHR-$:

$$\overline{h}^2 = Nl^2 \frac{1 + \cos\alpha}{1 - \cos\alpha} \frac{1 - \eta^2 - \varepsilon^2}{(1 - \eta)^2 + \varepsilon^2} \tag{8}$$

and for the syndiotactic chain $-CH_2-CHR-$:

$$\overline{h}^2 = Nl^2 \frac{1 + \cos\alpha}{1 - \cos\alpha} \frac{1 - (\eta^2 + \varepsilon^2)^2}{(1 - \eta)^2 + (\eta - \eta^2 - \varepsilon^2)^2}. \tag{9}$$

Here $\varepsilon = \sin\varphi$. The same method of calculation of the mean vectorial characteristics was applied to the calculation of the dipole moments of such chains.[29] The effective dipole moment of a random-coil macromolecule with polar substituents was found to depend essentially on the stereo-chemical structure of the chain and on the character of the dipole interaction.

The comparison with experiment of the formulas for $\overline{h}^2$ and the dipole moment which were derived in the cited papers does not lead to good agreement, although it permits the explanation of the observed

FIG. 4. Structure of an isotactic polymer.

FIG. 5. Structure of a syndiotactic polymer.

orders of magnitude. As has already been indicated, the cited formulas were derived under the assumption that the internal rotations of the individual links are independent. This means that only the interactions of each atom with the two atoms directly connected to it in the chain are taken into account. However, it is clear that the interaction of heavy neighboring groups which are not connected to adjacent atoms must play an essential role. When these interactions are taken into account, the problem of calculation of the dimensions of the dipole moments is no longer the Markov problem, and must be solved by another method. O. B. Ptitsyn and Yu. A. Sharonov[30] (see also reference 27) have solved this problem for the chains $-CH_2-CR_2-$ and $-CH_2-CHR-$, neglecting the interactions of the methylene groups CH_2, and taking into account only the interactions of the heavy side groups R. In other words, they took into account the correlations of the internal rotations within one monomer unit. Analogous calculations were published subsequently by Lifson.[31]

It is natural that the formulas derived by taking into account the correlation of internal rotation contain more parameters than the formulas which do not take into account this correlation. Along with η and ϵ, the expressions for $\overline{h}^2$ and μ^2 contain the quantities $\eta_1 = \overline{\cos \varphi_i \cos \varphi_{i+1}}$ and $\epsilon_1 = \overline{\sin \varphi_i \sin \varphi_{i+1}}$, where φ_i and φ_{i+1} are the rotation angles about two adjacent bonds in the chain, situated between R-groups. In order to compare the derived formulas with experiment, more detailed information about rotational isomerism in polymers is required. Such information can be obtained from the data on the structure of the polymeric links in the crystalline state, making use of symmetry properties. As has been already shown, when substances, which occur as a mixture of rotational isomers in the amorphous state are crystallized, they exist in the crystal as one single isomer. According to x-ray data, polymers crystallize either as planar trans chains (polyethylene, syndiotactic polybutadiene, etc) or in the form of helices (polyisobutylene, isotactic polystyrene, etc). If two successive links in the chain are characterized in the crystalline state by rotation angles (φ_1, φ_2), from symmetry considerations it follows that in the free chain the rotation isomer $(-\varphi_1, -\varphi_2)$ might also occur. The angles φ_1 and φ_2 are found from x-ray data. The calculations carried out by O. B. Ptitsyn and Yu. A. Sharonov were in agreement with experiment. For polyisobutylene, $-CH_2-C(CH_3)_2-$, $\varphi = 82°$ and $\pi - \alpha = 114°$, according to the x-ray data. From these values, Ptitsyn and Sharonov find a ratio of

the dimensions calculated with correlation taken into account to those calculated by formula (5), $(\overline{h}^2/\overline{h}_0^2)^{1/2} = 1.8$. The value given by experiment is 1.9 to 2.3. Agreement of the same character was obtained also for other polymers. It must be emphasized that taking correlation into account has differing effects on the dimensions and on the dipole moments. Thus, for the chain $-CH_2-CR_2-$ the formulas taking correlation into account may be written as follows (the valence angles being considered tetrahedral, $\alpha = \alpha_T$):

$$\overline{h}^2 = Nl^2 \frac{1+\cos \alpha_T}{1-\cos \alpha_T} \frac{1+\eta}{1-\eta} (1+\Delta) = \overline{h}_0^2 (1+\Delta), \qquad (10)$$

$$\mu^2 = nm_0^2 \frac{1+\eta}{1-\eta} (1-\Delta) = \mu_0^2 (1-\Delta), \qquad (11)$$

$$\Delta = \frac{\cos \alpha_T (\eta^2 - \eta_1) + \epsilon_1}{1 - \eta_1^2}. \qquad (12)$$

Here, n is the number of polar R-groups in the chain, and m_0 is the dipole moment of an R-group. We shall consider two chains with monomer units characterized respectively by rotational isomers (φ, φ) and $(\varphi, -\varphi)$. From symmetry considerations, it follows that isomers $(-\varphi, -\varphi)$ also exist in the first chain, and $(-\varphi, \varphi)$ in the second chain. In both cases, $\eta = \cos \varphi$, and consequently, the quantities $\overline{h}_0^2$ and μ_0^2 are identical for both cases. However, according to (12), $\Delta = 1$ for the first chain, while $\Delta = -1$ for the second chain. Hence, for the first chain $\overline{h}^2$ is twice as large as the value calculated by formula (5), while $\mu^2 = 0$. On the contrary, for the second chain, $\overline{h}^2 = 0$, while $\mu^2 = 2\mu_0^2$.

Thus, the theory of rotation isomerism permits the study not only of the internal rotation in the individual links, but also the correlation of internal rotations. However, it is not sufficient to take into account only the correlation within one monomer unit. Actually, the internal rotations in adjacent monomer units are also correlated, and strictly speaking, rotations are correlated along the whole chain. The rotational-isomer approximation permits one to take into account the interactions of the internal rotations in adjacent monomer units also. Yu. Ya. Gotlib[32] has developed a corresponding theory for chains with symmetrical substituents. For the chain $-CR_2-CR_2-$, the theory gives

$$\overline{h}_v^2 = q\overline{h}^2, \qquad (13)$$

where $\overline{h}^2$ is the value calculated according to formula (5), and

$$q = e^{-\frac{\Delta U}{kT}}, \qquad (14)$$

ΔU is the difference in energy between sequences of identical and differing rotational isomers. It is

obvious that this type of correlation is significant, if ΔU is not too small in comparison with kT.

Thus, modern configurational statistics permits the characterization of the dimensions and dipole moments of polymeric chains, their chemical structures being given. The theory is fully corroborated by experiment. The same is true of the calculations of the optical anisotropy of macromolecules,[33,34] as expressed in the birefringence of stretched polymers (the photoelastic effect) and in the flow birefringence of polymer solutions (the Maxwell effect). The essential fact is that all of the characteristics of macromolecules are determined by molecular constants of internal rotation and by their correlations. The specific properties of a macromolecule are basically connected with its flexibility.

It must be emphasized that the problems of configurational statistics have thus far been solved only by the approximation of the rotational-isomer theory. In all of the statistical calculations for macromolecules, the kinetic energy of internal rotation has been neglected [cf. formula (6)]. At the same time, a thorough study of the statistical problem requires consideration of this factor. It is very difficult to take into consideration even for small molecules (see, for example, reference 35). The essential point is that, in taking the kinetic energy into account, one must solve the problem not classically, but quantum-mechanically. That is, one must quantize the internal rotation in the chain, and study its interaction with the vibrations. Indeed, no one has studied these problems thus far. Nevertheless, these problems are closely connected with the kinetic behavior of macromolecules, with their relaxation spectra and the properties determined by these spectra.

All of the above discussion refers in essence to model skeleton chains. Only the interactions of neighboring portions of the flexible macromolecular filament were considered. In order to compare the theory with experiment, it is necessary to take into account the so-called volume effects — the condition that no pair of links in the polymer chain may simultaneously occupy one and the same volume element. In other words, one must take into account the repulsion forces which act between different segments of the chain which have approached one another within very small distances, and the attraction forces which act between them at larger distances. The model theory neglecting volume effects is analogous to the theory of ideal gases.

The properties of real macromolecules in solution must be studied on the basis of a theory equiv-

alent to the theory of real gases. In theoretical polymer physics, however, approximate methods have been found for taking into account the volume effects. It must be emphasized that the influence of these effects on the dimensions of chains differs in principle from the influences of fixed valence angles, hindrance of internal rotation, etc. These cited factors influence only the size of the statistical element, and do not change the general form of the distribution function for the dimensions. This function remains Gaussian, both for the freely-jointed chain and for the chain with fixed valence angles and hindered rotation. On the contrary, the distribution function for the chain with volume effects is not Gaussian. Thus, the problem of taking volume effects into account is in principle a statistical problem.

In the same degree of approximation in which higher-order interactions between segments of the polymer chain are considered, it is necessary also to take into account the interactions between segments of the chain and molecules of the solvent. In good solvents, the polymer-solvent contacts are more favorable than the polymer-polymer contacts or the solvent-solvent contacts. Since the macromolecule immobilizes a maximum quantity of solvent, its dimensions are increased. The converse situation occurs in poor solvents — the macromolecule, so to speak, repels the solvent from itself, i.e., it contracts.

Under certain definite conditions, the contraction of a macromolecule in a poor solvent is completely compensated for by the expansion caused by intramolecular volume effects. For a given polymer-solvent pair, this takes place at a characteristic temperature, which is called the θ-point or the Flory temperature, and is analogous to the Joule point in real gases. At this point an inversion takes place in the effective excluded volume of the macromolecule. The dimensions of the molecule at the θ-point are determined exclusively by the flexibility. The comparison of the statistical formulas neglecting volume effects with experimental data is possible only at the θ-point, under the conditions of an ideal solvent.

The approximate thermodynamic theory of volume effects was propounded by Flory,[36] and was developed in subsequent papers of his school.[37,38,39] The relative increase a in the linear dimensions of a macromolecule due to volume effects satisfies the approximate equation

$$a^5 - a^3 = \frac{3\sqrt{3}}{2} Z, \qquad (15)$$

where

$$Z = \left(\frac{3}{2\pi} \right)^{\frac{3}{2}} \frac{N^{\frac{1}{2}} v}{b^3},$$ (16)

N is the number of segments in the chain, b is the length, and v is the effective excluded volume of a segment. Z expresses the number of contacts per unit volume occupied by the macromolecule. A more rigorous derivation of an equation of the type of (15) has been given in reference 40 (see also reference 8). The distribution function for the length of the chain, taking volume effects into account, has been calculated by Peterlin.[41] These theoretical calculations have been very important in the interpretation of the experimental results of the study of the dimensions and forms of macromolecules by light scattering, and also in the interpretation of viscosimetric and diffusion measurements (see, for example references 42, 43, and 44). These methods, as well as flow birefringence, have been used especially effectively in studies of polymer solutions by V. N. Tsvetkov and his associates.[45,46,47] A sufficiently complete theory of volume effects has not yet been devised. The existing calculations are sufficiently rigorous only within a narrow temperature range in the neighborhood of the θ -point; in other cases up to now, the study has had to be limited to rough estimates.

We shall not deal here with the very interesting and important studies in the field of configurational statistics of polyelectrolytes, which have been carried out, for the most part, by A. Katchalsky and his associates.[48,49,50] We shall limit ourselves to mentioning the non-Gaussian character of the distribution function for a charged polymer chain, which may unfold because of the electrostatic repulsion of the links.

3. PHYSICS OF THE ELASTICITY OF RUBBER

The modern theory of the high elasticity of rubber-like polymers is based on the configurational statistics of macromolecules. Vulcanized rubber is capable of undergoing reversible deformations of several hundred percent, with a very small value of the elastic modulus, approximating that of an ideal gas. The stretching of rubber and the return to the initial state are accompanied by specific thermal effects which have no analogy in any other solid body. Rubber is heated on adiabatic stretching. A piece of rubber stretched by a constant force contracts upon heating, and hence, the stress in it increases. The internal energy of rubber depends very little on the degree of extension. In this sense, rubber is similar to an ideal gas (see reference 51).

The fundamental thermodynamic relations for the stretching of rubber are the following: the work in the isothermal deformation dL produced by the force f is

$$dA = f \, dL = dF = dE - T \, dS.$$ (17)

We have neglected the term p dV, since rubber is practically incompressible. From (17) it follows that

$$f = \left(\frac{\partial E}{\partial L} \right)_T = \left(\frac{\partial E}{\partial L} \right)_T - T \left(\frac{\partial S}{\partial L} \right)_T$$ (18)

and, since

$$\left(\frac{\partial E}{\partial L} \right)_T = - \left(\frac{\partial f}{\partial T} \right)_L,$$ (19)

we finally have

$$\left(\frac{\partial E}{\partial L} \right)_T = f - T \left(\frac{\partial f}{\partial T} \right)_{V, L}.$$ (20)

As has been shown by experiment, the following relation is valid for an entire series of different rubbers:

$$f \cong T \left(\frac{\partial f}{\partial T} \right)_{V, L} = - T \left(\frac{dS}{dL} \right)_T$$ (21)

which implies that

$$\left(\frac{\partial E}{\partial L} \right)_T \cong 0.$$ (22)

Consequently, the elasticity of rubber, like that of an ideal gas, has an entropy character, rather than an energetic character. The mentioned thermomechanical properties of rubbers arise directly from the relations which have been given here.[51]

Thus, the restoring force in rubber is caused by the decrease in entropy upon stretching, that is, by the transition of the system from a more probable state to a less probable state. The analogy between properties of rubber and those of an ideal gas makes one consider that rubber must consist of a large number of elements which change their relative positions on stretching. The physical content of the stated analogy consists only in this. It is obvious that these statistical elements are the independent segments of flexible macromolecules. It is also obvious that the decrease in entropy of rubber on stretching implies a transition from a more probable configuration of the molecules, wound into coils, to a less probable extended configuration. It is just on this basis that the molecular statistical theory of rubber elasticity has been developed in the papers of Guth and Mark[52] and Kuhn.[55] This theory has

permitted us to obtain an approximately correct description of the stress-strain relation, and gives an elastic modulus of the correct order of magnitude. This theory has been presented in a series of monographs.[51,4,54] We shall give below a brief presentation of the most highly perfected variant of the so-called network theory of high elasticity, which is due to James and Guth.[55,56]

The free energy of the system is expressed in terms of the partition function Q,

$$F = -kT \ln Q, \qquad (23)$$

and consequently,

$$f = \left(\frac{\partial F}{\partial L} \right)_{V,T} = -kT \left(\frac{\partial \ln Q}{\partial L} \right)_{V,T}. \qquad (24)$$

A sample of vulcanized rubber is considered to be a network of polymer chains, joined at certain sites by the vulcanization crosslinks. If these links are sufficiently rare, the chains distributed among them will be similar to free macromolecules, and their dimensions will be described by a Gaussian distribution function. The network is bounded by fixed points situated at the surface of the sample. Upon stretching of the sample, the mean values of the coordinates of any internal point of the network change in proportion to the corresponding dimensions of the sample. The partition function of such a Gaussian isotropic network has the form

$$Q = K_1 \exp \left\{ -\frac{K}{2} (L_x^2 + L_y^2 + L_z^2) \right\}. \qquad (25)$$

where L_x, L_y, and L_z are the dimensions of the stretched sample, which had the form of a unit cube in the unstretched state; K_1 is a constant; and K has the value

$$K = \sum_{\tau > \nu} \sum \frac{(r_{\tau\nu}^{(0)})^2}{Z_{\tau\nu} b^2}. \qquad (26)$$

Here, $r_{\tau\nu}^{(0)}$ is the vector joining the mean positions of the τ-th and ν-th points (internal or fixed) in the unstretched sample, and $Z_{\tau\nu}$ is the number of statistical segments of length b in the chain passing between these points. Neglecting the very small compressibility of rubber, for unidirectional stretching we have

$$L_x L_y L_z = L_x^2 L = V. \qquad (27)$$

Hence,

$$Q = K_1 \exp \left\{ -\frac{K}{2} (2L_x^2 + L^2) \right\}$$

$$= K_1 \exp \left\{ -\frac{K}{2} \left(L^2 + \frac{V}{L} \right) \right\} \qquad (28)$$

and according to (24)

$$f = KkT \left(L - \frac{V}{L^2} \right). \qquad (29)$$

This is the basic relation of the network theory. We see that the relation f(L) has a specific non-linear character, which is confirmed by experiment for small degrees of extension (see reference 51). Formula (29) gives an expression for the relative stress for a unit cube. The modulus of elasticity is

$$\varepsilon = \left(\frac{df}{dL} \right)_{L=1} = 3KkT. \qquad (30)$$

The linear dependence of the modulus on the temperature is generally confirmed by experiment. The quantity K has been estimated in the theory of James and Guth.[57] It is approximately half of the total number of chains in the sample being studied.

The network theory of rubber which we have briefly described was devised without taking into account the intra- and intermolecular interactions. In this sense it is similar to the theory of ideal gases. The immaterial chains of which the network is made are assumed to consist of freely-jointed links. The chains are subject to Gaussian statistics just as the free macromolecules in ideal solvents are. The connections between the chains are considered only through the condition of cross-linking. Such a view, naturally, leads to a pure entropy mechanism for the stretching of the polymer at constant volume.

The "gaseous" network theory is inadequate in two respects. First, it does not take into account the interactions of closely neighboring atoms in the polymer chain. This interaction, as has been stated, leads to the hindrance of internal rotation and to rotational isomerism. The intramolecular interactions of closely neighboring atoms must be manifest in energy changes of the polymer chain upon stretching; hence, the mechanism of stretching of polymers cannot be based solely on entropy. Taking these effects into account does not require a rejection of the network theory, and may be carried out within the framework of this theory. Here, the ordinary expression for the configurational partition function of the stretched polymer, as obtained from the network theory, takes on the meaning of an expression for the complete partition function.

Second, the network theory does not take into account the intermolecular interactions and the volume effects. These interactions must lead to a deviation from Gaussian statistics even in the region of small degrees of extension, and hence, to a change in the character of the stress-strain relation. Taking these interactions into account
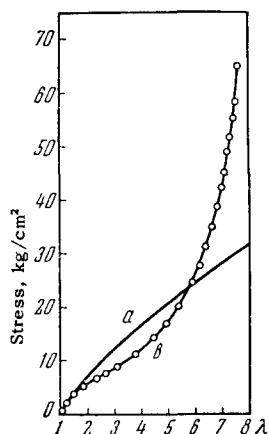
FIG. 6. Stress-strain relation in natural rubber vulcanized with 8% sulfur: a — theoretical curve; b — experimental curve.

implies an essential change in the theory of rubber elasticity — a transition from the "gas" theory to a theory of a condensed phase.

The given considerations would be of no special interest if the network theory agreed with experiment. However, substantial deviations from experiment are observed even in that range of extensions in which one would not expect deviations from Gaussian statistics associated with the finite dimensions of the chains. The theoretical curve f(L), for extensions of 100 — 200%, is markedly above the experimental curve. This is shown in Fig. 6. The theory does not in general pretend to explain the still larger deviations in the range of large deformations, which are characterized by crystallization.

Thus, in the range of moderate extensions, a smaller force is required to produce a given strain than that predicted by the theory. This deviation decreases, and may even vanish completely, upon swelling of the polymer in a solvent of low molecular weight.[58,65] The value of the elastic modulus derived from the network theory appears to depend only on the number of cross-links in the sample, that is, on the degree of vulcanization. Regardless of the lack of the necessary experimental data, one may suppose that the modulus need not be completely independent of the chemical structure of the macromolecules. Finally, the network theory cannot explain certain subtle effects associated with the thermal expansion of the sample (see reference 66).

The influence of intramolecular interactions on the stretching of rubber may be considered on the basis of the rotational-isomer theory. Considering the polymer chain to be a mixture of rotational isomers, we may arrive at the following conclusions about the mechanism of extension of the chain.[24] Two processes take place on extension. First, a redistribution of the rotational isomers along the chain takes place, such that the

length increases, but without change in the relative content of one or another of the rotational isomers. This process occurs without change in the internal energy of the chain, and the corresponding mechanism of stretching is a pure-entropy mechanism. Second, on extension of the chain, a transition occurs from the rotational isomers with more highly coiled configurations to the isomers with more extended configurations. Here the energy of rotational isomerization ΔE must be liberated or absorbed. If ΔE differs from zero, the mechanism of stretching of the polymer is not of pure entropy character, but is also energetic.

The quantitative theory of stretching of the rotational-isomeric chain is a theory of a cooperative process, since the behavior of each link of the chain in the external force field is influenced by the status of all the other links in the chain.[67] In order to solve the problem of the length of the stretched chain as a function of the acting force, one may use a specific mathematical technique, which is a modification of the method of the Markov chain.[68] The theory is especially graphic for a one-dimensional model of the rotational-isomeric chain. In this model, each link is represented by a vector of standard length l, directed to the right or to the left. Rotational isomerism is represented in the model by varying probabilities of having the same or opposite directions of two adjacent vectors. In the absence of external forces, the probability of vectors to the right or to the left is the same, and the mean length of the chain is zero. If a force f is applied, directed from left to right, the probability of orientation of a vector l in the direction of the force will be increased by the factor $\exp(fl/kT)$, while the probability of orientation of the vector in the opposite direction will be decreased in the same ratio. The mean length of a chain consisting of N links is equal to[67]

$$\bar{h} = N l \frac{\sinh a}{\sqrt{\sinh^2 a + w^2}}, \qquad (31)$$

where $a = fl/kT$, $w = \exp(-\Delta F/kT)$, and ΔF is the difference in free energy between the rotational isomers. From (31) it follows that, when $a = f = 0$, $\bar{h} = 0$; and when $f \to \infty$, $\bar{h} \to Nl$. That is, the chain becomes completely extended. When $\Delta F \to \infty$ (complete rigidity of the chain), $\bar{h} = Nl$, independently of f. If both rotational isomers are equally probable, corresponding to the case of free rotation, $\Delta F = 0$, $w = 1$, and

$$\bar{h} = N l \tanh a \qquad (32)$$

a formula analogous to the expression for the paramagnetic moment per unit volume of a substance consisting of atoms in a ^2S state (e.g., atoms of the alkali metals):[69]

$$M = N\mu \tanh \frac{\mu H}{kT}. \tag{33}$$

The agreement of formulas (32) and (33) is determined by the fact that, in the latter case, the essential feature is that the spin of $\frac{1}{2}$, can have only two orientations in the external field. The theory of the stretching of the one-dimensional chain is equivalent to the theory of ferromagnetism of Ising, in its application to a one-dimensional model[70] (see also reference 71). The stretching of the chain is a typical cooperative process. Further study of the polymer chain in three-dimensional space confirms the conclusions drawn from the study of the one-dimensional model.[72] For small forces, $fl \ll kT$, $a \ll 1$, and hence, from (31) it follows that

$$\bar{h} \cong Nl \frac{a}{w}. \tag{34}$$

At the same time, the mean square length of the one-dimensional chain in the absence of forces is

$$\overline{h_0^2} = Nl^2 \frac{1+\eta}{1-\eta}, \tag{35}$$

where

$$\eta = \overline{\cos \varphi} = \frac{\cos 0° + \cos \pi \cdot w}{1+w} = \frac{1-w}{1+w}$$

and hence

$$\overline{h_0^2} = Nl^2 \frac{1}{w}. \tag{36}$$

Substituting (34) into (36), we find that

$$\bar{h} \cong \frac{f}{kT} \overline{h_0^2}. \tag{37}$$

For $N \gg 1$, this formula may be rewritten in the form

$$f = \frac{kT}{\overline{h_0^2}} h. \tag{38}$$

Here f is the average force pulling the ends of the chain together, when they are separated by a distance h. For a chain in three dimensions, an analogous formula is valid:

$$f = \frac{3kT}{\overline{h_0^2}} h. \tag{39}$$

Formula (18) may be written for an isolated chain in the form

$$f = \left(\frac{\partial F}{\partial h}\right)_T = \left(\frac{\partial F}{\partial h}\right)_T - T\left(\frac{\partial S}{\partial h}\right)_T = f_{energ} + f_{entr}, \tag{40}$$

from which we find the expression for the energy component of the force

$$f_{energ} = f + T\left(\frac{\partial S}{\partial h}\right)_T = f - T\left(\frac{\partial f}{\partial T}\right)_h \tag{41}$$

or, substituting in (39),

$$f_{energ} = fT \frac{\partial \ln \overline{h_0^2}}{\partial T}. \tag{42}$$

Formula (42), which was derived in reference 73, does not depend on the model used, but is completely rigorous. It connects the energy component of the elastic force produced by the rotational isomerization on stretching with the temperature dependence relation of the mean square length of the macromolecule. This is natural, since the change in the "undisturbed" dimensions of the chain upon temperature change is also determined by the phenomenon of rotational isomerization. If, as often happens, a more extended configuration of the chain corresponds to lower energy, then $\partial \ln h_0^2/\partial T$, and hence also f_{energ}, are negative, and the energy component of the force facilitates stretching. In reference 73, it was shown that, if the energy difference between the rotational isomers is of the order of kT, then f_{energ} is of the same order of magnitude as f. The existence of the energy component of the force does not, however, change the expression for the total elastic force of the form (38) in the Gaussian region of stretching, since the entropy and energy forces associated with rotational isomerization compensate for each other.[73] The energy component of the force in the bulk polymer is expressed in a similar way. From formulas (18) and (29), it follows that

$$f_{energ} = -fT\left(\frac{\partial \ln K}{\partial T}\right)_V. \tag{43}$$

The network theory for chains having hindered internal rotation gives[74]

$$K = \frac{const}{\overline{h_0^2}(T)}. \tag{44}$$

Formulas (43) and (44) lead again to (41), which is now applicable to the bulk polymer.[66] Thus, the theory does not lead to a pure entropy character for the elasticity of rubber. The experimental verification of the theory is based on (18):

$$f_{energ} = f - T\left(\frac{\partial f}{\partial T}\right)_{V, L}. \tag{45}$$

However, the measurement of the quantity $(\partial f/\partial T)_{V,L}$ is difficult. It is more convenient to use the approximate equation

$$f_{energ} \cong f - T\left(\frac{\partial f}{\partial T}\right)_{p, \lambda}. \tag{46}$$

Here, p is the pressure, $\lambda = L/L_0$, where L_0 is the length of the unstretched sample (in deriving formula (29) we assumed $L_0 = 1$). The thermodynamic equation

$$\left(\frac{\partial f}{\partial T}\right)_{V,\,L} \cong \left(\frac{\partial f}{\partial T}\right)_{p,\,\lambda} \qquad (47)$$

arises from the real properties of rubber,[58,4] but does not follow from the network theory, which contradicts experiment in this respect.[66] In the simplest case of three rotational isomers, corresponding to angles of 0°, ±120°, in which the energy of the twisted (gauche) isomers is greater by ΔE that that of the trans-isomer (polyethylene), we have[73]

$$\bar{h}_0^2 = Nl^2 \frac{1+\cos\alpha}{1-\cos\alpha} \frac{2+w}{3w} \qquad (48)$$

and, according to (42)

$$f_{\mathrm{energ}} = -f \frac{1}{1+w/2} \frac{\Delta E}{kT}. \qquad (49)$$

Rotational isomerization during the stretching of polymers may be directly demonstrated by the dependence of the infra-red spectra of the polymers on the degree of extension.[75] The theory of this phenomenon is given in reference 76. The result obtained in the study of gutta-percha is especially clear. This polymer exists in two crystalline modifications, corresponding to more or less coiled rotational isomers. The first modification is stable, the second metastable. However, when gutta-percha in the stable modification is stretched, bands appear in the infra-red absorption spectrum corresponding to the more extended isomer.[77]

In a recent paper by Flory, Hoeve, and Ciferri,[78] the rotational-isomeric theory of stretching was confirmed by direct measurement of the energy component of the force. Cross-linked polydimethylsiloxane and polyethylene were studied. In the first case, $f_{\mathrm{energ}} \cong 0$, and in the second, $f_{\mathrm{energ}} \cong -f/2$. The equality of f_{energ} to zero for polydimethylsiloxane is in agreement with the generally accepted conception of the low degree of hindrance of internal rotation about the Si—O bond. Interpreting the experimental data for polyethylene with the aid of Eq. (49), and assuming that $\Delta F \cong \Delta E$, Flory and his co-authors have obtained the value $\Delta E = 540$ cal/mole. This is in agreement with the spectroscopic data for the difference in energy between rotational isomers in paraffins of low molecular weight[79] and in polyethylene.[25]

Further development of the theory of the intramolecular interactions in polymers and their influence on the elastic properties requires that the calculations be made concrete by application to particular polymers.

We shall return now to intermolecular interactions. Gee[58] has already stated that the discrepancies between the network theory and experiment are connected with the existence of definite correlations of the chains with respect to one another. Such a correlation implies a certain degree of local order of the chains. This must naturally have an influence on the entropy of the network and its changes upon deformation. It is as if the chains helped one another to extend.

In a recent paper, V. A. Kargin, A. I. Kitaĭgorodskiĭ, and G. L. Slonimskiĭ[80] have shown with great definitiveness a significant degree of order in amorphous polymers, in comparison with substances of low molecular weight. This degree of order results from the chain structure of macromolecules. Even in the absence of significant intermolecular forces in non-polar polymers, the chains try to lie parallel. Apparently, in an amorphous polymer the pattern is not that of separate chains with configurations which are independent from one another, but that of bundles of chains having a single configuration. It is just this condition which is emphasized in reference 80. Recently V. A. Kargin and his associates have directly shown the presence of these bundles in amorphous polymers by means of electron microscopy. They showed also that the bundles are capable of curvature as a whole.[81] Thus, we may suppose that in an amorphous bulk polymer that the chains are curved together with other chains belonging to the same bundle. In fact, it is the bundle, rather than the individual chain, which is the element of the statistical ensemble. Consequently, one may not consider that the configurations of chains in the amorphous network are completely analogous to the configurations of isolated macromolecules in solution — the chains in the network are not subject to Gaussian statistics. Rotational isomerization on stretching must take place concordantly in neighboring chains. The bundle structure of the amorphous polymer implies that the intramolecular volume effects have a relatively weak influence on the stretching of the sample. Thus, the further development of the theory of elasticity of bulk polymers is connected with the taking into account of cooperative phenomena — the "mutual aid" of chains in stretching. Evidence in favor of the concepts presented here is given by the data of structure analysis and organic crystal chemistry,[80,81,82,83] by the sign of the discrepancy between the curves for $f(L)$ obtained experimentally and from the "gaseous" network theory, and also by the previously indicated circumstance of the improved agreement of the network theory with experiment for swollen polymers. Naturally, swelling must decrease the role of intermolecular cooperation.

The theory of cooperative phenomena encounters great difficulties even in the case of systems

composed of small molecules. Nevertheless, we may suppose that the fundamental theoretical problem of the statistical thermodynamics of rubber will be solved in the near future.

All that has been said above refers to the thermodynamic equilibrium behavior of rubber. Its kinetic properties, which determine the relation of stress and strain to time, have no less, if no more, important meaning (see references 10, 11, 12, 13, 14, 51, and 54). It is not possible for us to discuss all these questions here, but certain problems associated with the relaxation properties of polymers will be discussed in the following section.

4. THE VITRIFICATION OF LOW-MOLECULAR-WEIGHT LIQUIDS AND POLYMERS

Rubber-like properties of polymers are connected not so much with the chemical structure of the individual substance, as with the overall chain structure of the macromolecules. In principle, any polymer may become rubber-like in a definite temperature range — the appearance of high elasticity ordinarily hinders the crystallization of the polymer. All non-crystalline polymers are brittle, glassy substances below a certain temperature; at temperatures above the glass-transition temperature T_g, they are transformed into a viscoelastic state. In order for high elasticity to exist, cross-links must be created between the chains to hinder flow — the vulcanization of rubber consists in just this process. Finally, at still higher temperatures, the polymer becomes a viscous fluid.

As has been shown by experiment, the general characteristics of the vitrification of polymers have no differences in principle from the characteristics of the vitrification of liquids of low molecular weight. Let us examine the nature of the glassy state. Apparently, this state does not even correspond to a relative minimum of the thermodynamic potential. The transition from the liquid to the glassy state, and vice versa, is not a thermodynamic transition, as may be shown directly from the dependence of the transition temperature T_g on the rate of cooling or heating. The slower the cooling is carried out, the lower the glass-transition temperature T_g. The behavior of substances on crystallization and vitrification may be illustrated by a graph showing the dependence of the specific volume on the temperature (Fig. 7). On crystallization at the freezing point T_f, an abrupt change in the volume takes place. On the contrary, at the glass-transition point T_g, there is no discontinuity in the curve $V(T)$, only a break in the
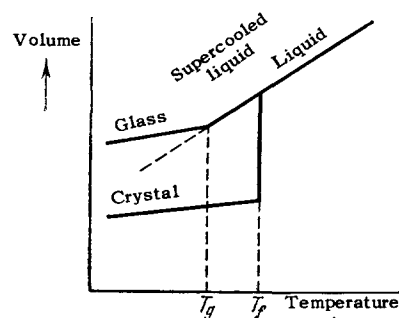

FIG. 7. Crystallization and vitrification.

curve being observed. The function $V(T)$ for a supercooled liquid is shown by the broken line. We see that the glassy state does not coincide with the state of the supercooled liquid.

In vitrification, the values of the volume, heat content, and entropy vary continuously. On the other hand, the values of the volume coefficient of thermal expansion α, the coefficient of compressibility κ, and the heat capacity C_p show discontinuities. In the softening of polyvinyl acetate, a maximum is observed in the curve $C_p(T)$ similar to that occurring at a λ-point.[84] These facts have compelled us to consider vitrification to be a second-order phase transition. However, as has been stated, this transition is not a thermodynamic equilibrium transition. According to current conceptions, in the development of which the papers of P. P. Kobeko (see reference 12) have played an important role, vitrification is associated with the slowing down of molecular rearrangement. The movement of the molecules slows down as the temperature is lowered. The time τ for transition of the molecule from one equilibrium position to another, and thereby also the viscosity of the liquid, depends strongly on the temperature.

According to Ya. I. Frenkel'[85]

$$\tau = A e^{\frac{U}{kT}}, \tag{50}$$

where U is the activation energy necessary for surmounting some potential barrier separating one equilibrium position from another. With a given rate of cooling, a moment arrives when the rearrangement of the molecules can no longer keep up with the decrease in temperature, due to the sharp increase in τ. The structure of the substance becomes a non-equilibrium structure. At a temperature below T_g, the structure of the glass is approximately that of the liquid in the vicinity of T_g. Kinetic conceptions of the nature of the glassy state have been developed in the papers of P. P. Kobeko,[12] Tool,[86] Kautzmann,[87] and Davies and Jones.[88,89] Using the method of the thermodynamics of irreversible processes, Davies and Jones showed that a relaxation mech-

anism of the described nature must lead to a relation between the discontinuities in α, κ, and C_p similar to the relation corresponding to a second-order phase transition:

$$\Delta C_p \Delta \varkappa = TV (\Delta \alpha)^2. \tag{51}$$

A model kinetic theory of vitrification has been propounded in the paper of M. V. Vol'kenshteĭn and O. B. Ptitsyn.[90] Kinetic units (e.g., molecules in a liquid of low molecular weight, or links in a polymer chain) are considered, which may occur in two states with differing energies, separated by an energy barrier. The solution of the corresponding kinetic equation, taking into account the time rate of temperature change, leads to the condition for vitrification:

$$\left(\frac{d\tau}{dT} \right)_{T=T_g} = -\frac{1}{q}, \tag{52}$$

where q is the rate of cooling of the system. This solution was obtained with the single assumption that the kinetic properties of the system which are characterized by τ depend more strongly on T than the equilibrium properties do. The theory shows that, on cooling to the temperature T = T_g satisfying the condition (52), the equilibrium concentrations of the kinetic units in the two states being considered become "frozen." Thus, the changes in the specific volume and the heat content associated with the described mechanism are interrupted. According to (52), the value of T_g itself depends on the rate of cooling. The theory gives a qualitative explanation for all the phenomena observed in the transition to the glassy state, and in particular, explains the dependence of the position and height of the maximim in the $C_p(T)$ curve on the rate of heating. The theory also explains the trend in the concentration of hydrogen bonds on vitrification,[91] which was studied in references 92 and 93, as well as the dependence of T_g on the pressure, which was studied by N. I. Shishkin.[94] The theory predicts hysteresis effects on cooling and subsequent warming, as has been confirmed by a series of experiments. In particular, hysteresis has been found in the temperature dependence of optical properties, such as the optical activity[95] and the luminescence intensity of plastics into which luminescent substances have been introduced.[96] The theoretical concepts presented here have formed a basis for a theory of molecular light scattering in glasses.[97]

However, the simple model theory taking into account only one relaxation process with a single relaxation time τ is inadequate. Naturally, it gives only a qualitative, and not a quantitative,

agreement with experiment, since a real substance is characterized not by a single relaxation time, but by a complex relaxation spectrum. This is especially true of polymers.

Not all substances of low molecular weight can be vitrified. Compounds which form intermolecular hydrogen bonds, such as alcohols and carbohydrates, are easily vitrified. Also, the hydrocarbons of low molecular weight vitrify, their intermolecular interactions having the nature of dispersion forces and being relatively weak. Vitrification is thus governed not so much by the strength of the intermolecular interactions, as by the mobility of the molecules.

In distinction from substances of low molecular weight, practically all polymers may be obtained in the glassy state. This may be explained apparently by the large values of and by the sharper dependence of τ on the temperature. A molecular theory of the relaxation properties of polymers has not yet been devised, and its creation encounters significant difficulties. The model and phenomenological theories are inadequate for the interpretation of the experimental data obtained in the study of polymers by the methods of mechanical and electrical losses, by means of the absorption and dispersion of ultrasound, and by the method of nuclear magnetic resonance. Bueche[98] has undertaken an attempt to study the influence of the mobility of macromolecular chains on the process of vitrification of polymers; however, these studies do not yet permit us to connect the characteristics of vitrification with the chemical structure of the macromolecules. Nevertheless, the necessity of devising a molecular theory of the vitrification arises directly from the needs of technology. At present, considerable effort is being applied to the obtaining of heat-resistant plastics characterized by high values of T_g. There is now also a problem of cold-resistant rubbers, of the preservation of high elasticity at low temperatures. The lowering of T_g may be attained, on the one hand, by a suitable choice of the polymer, and on the other hand, by using plasticizers. Plasticization consists in the introduction into the polymer of substances of low-molecular weight. The lowering of T_g which takes place in this way was explained in a paper by S. N. Zhurkov,[99] on the basis of the conception of blocking of the polar groups of the polymer by the small molecules. V. A. Kargin presented another point of view, according to which the basic role of the plasticizer consists in the separation of the polymer chains.[100] One may suppose that the essential role is played in polar polymers by Zhurkov's mechanism and

in non-polar polymers by Kargin's mechanism.

Some theoretical papers of Gibbs and DiMarzio[101,102,103] were published recently, in which concepts were developed on the nature of vitrification, essentially different from those given above. In these papers, a statistical calculation is carried out with the aid of a lattice model. The chains, which are distributed in the lattice, are characterized by a certain rigidity. Following Flory, who used the same method in the theory of the crystallization of polymers,[104] Gibbs and DiMarzio express the rigidity of the chains in terms of rotational isomerism. The orientations of the links are defined with respect to those of the two preceding links; one of the orientations is assigned an energy different from that assigned to the other orientations, the other discrete orientations all being equal in energy. An interaction exists between the chains, having an energy proportional to the number of vacant lattice sites, i.e., the number of empty cells, since this energy is determined by the number of van der Waals contacts which are broken when the given number of vacancies is introduced. The partition function is calculated for the chains as a function of the temperature. The rigidity of the chains increases on lowering the temperature (the proportion of the rotational isomers with higher energy decreases), and the number of vacancies decreases, i.e., the energy of intermolecular interaction increases. As the study of the partition function shows, at a certain temperature T', the number of possible disordered packings of the chains in the lattice becomes less than unity. In other words, at $T = T'$, changes in the configurations of the chains cease. The free energy, the internal energy, the entropy, and the volume of the system vary continuously through the transition at T', while the temperature derivatives of these quantities — C_p and α — vary discontinuously at T'. Thus, statistical thermodynamics leads to the existence of a second-order phase transition at T'. The theory gives a value of T' depending on the rigidity of the chains and the energy of intermolecular interaction. Gibbs and DiMarzio advance the hypothesis of the identity of T' with the "equilibrium" glass-transition temperature. In the opinion of Gibbs and DiMarzio, relaxation phenomena must be eliminated at a sufficiently low rate of cooling, although they do not deny the practical role of such phenomena. In other words, the basis of vitrification is a true second-order thermodynamic transition; the vitreous state is in principle an equilibrium state, and is a fourth state of aggregation of matter. This state is characterized

by the most stable amorphous packing of long chain molecules, and is particularly inherent in polymers consisting of macromolecules whose rigidity depends on the temperature.

The hypothesis of Gibbs and DiMarzio arouses serious objections. First, the attempts at quantitative comparison of the theory with experimental data on vitrification[102] are not very convincing. Second, experiment shows that the discontinuity in C_p decreases as the rate of heating of the glass is decreased without approaching a finite limit which would correspond to the second-order phase transition. Third, (and this is the most fundamental objection), the experimental data give evidence that the nature of vitrification of polymers and of substances of low molecular weight is identical. Substances consisting of small molecules with weak intermolecular interactions vitrify, for example, branched-chain paraffins. However, the presence of long-chain molecules is essential to the theory of Gibbs and DiMarzio. Finally, it is hardly possible to conceive of a fourth state of matter having the symmetry of a liquid. Thus, there is at present no basis for rejection of the conception of the purely kinetic nature of vitrification. It is not clear whether the effect calculated by Gibbs and DiMarzio could be observed experimentally; it is possible that it actually exists, but in a temperature range far from the glass transition range. In any case, the papers of Gibbs and DiMarzio are of considerable theoretical interest. In an obvious manner, the model used in the calculations takes into account the cooperative character of the process of regrouping of the chains in the amorphous polymer, as determined by the intra- and intermolecular interactions. The further development of both the kinetic theory of vitrification and the thermodynamic theory of phase transition in polymers is closely connected with the study of cooperative processes.

5. THE CRYSTALLINE STATE OF POLYMERS

X-ray data indicate the presence of three-dimensional crystalline order in a series of polymers; evidence of this is given by the sharp lines on powder patterns. Reflections are observed from a rather large number of planes.[105,106] Crystalline polymers have a very valuable technical significance, since they include the synthetic and natural fibrous materials, and the strength of fibers is essentially connected with their crystal structures. Certain important plastics are also crystalline, such as polyethylene, polytetrafluoroethylene (Teflon), and many others. Detailed

studies of the mechanical properties of crystalline polymers, demonstrating, in particular, the existence of a recrystallization process on stretching, have been carried out by V. A. Kargin and T. I. Sogolova.[107]

In most cases, polymers are not completely crystallized. For example, evidence of this is given by the occurrence on the x-ray diagrams of diffuse haloes, characteristic of amorphous substances, along with the sharp lines. The empirical quantity, the "degree of crystallinity," of a polymer is determined from the ratio of intensities of the sharp lines to the diffuse halo. The essential fact is that the values of the degree of crystallinity obtained in this way agree with the values obtained dilatometrically by comparison of the densities of the amorphous and the partly-crystallized polymer. Finally, the completely independent method of determining the degree of crystallinity by infra-red spectra gives the same results. This method is based on the difference between the spectra of the crystalline and the amorphous polymer;[108] the meaning of this difference is found by the study of the crystals and melts of low-molecular-weight substances of analogous structures, and amounts basically to the influence of rotational isomerism on the spectra. Both low-molecular-weight substances consisting of sufficiently long chains (e.g., the paraffins), and polymers crystallize in the form of one definite rotational isomer. In the melt or in an amorphous substance, a mixture of rotational isomers is involved. Hence, the spectra of the crystalline and amorphous polymer are different.

Thus, the concept of the degree of crystallinity appears to have a real physical meaning. The width of the x-ray diffraction maxima in incompletely-crystallized polymers corresponds to the small dimensions of the crystallites — of the order of several hundred Angstrom units. The same dimensions of the crystalline formations are found from the results of small-angle x-ray scattering studies.[109,110,111] The structural details of the crystallites have been completely deciphered for many polymers.[106,112] Along with the incompletely-crystalline polymers, which have the character of polycrystals containing an appreciable fraction of amorphous material, in recent years some practically completely crystallized polycrystalline polymers have been obtained. These are the stereospecific polymers[26] (see above). Finally, even single crystals of polymers have been obtained — polyethylene and a series of proteins.[113,114] These single crystals give good Laue diagrams. In many

polymers, spherulitic crystals are characteristically formed, and are easily observed with the polarizing microscope. Through study of sections of polymers in the electron microscope, V. A. Kargin has discovered single-crystal formations in them.

The basic physical problem concerning crystalline polymers is the following. What are the structural, thermodynamic, and kinetic characteristics of a system consisting of long-chain macromolecules which determine the limit of crystallization and the specific thermal properties? The solution of this problem will have a general theoretical and a great practical significance.

Under ordinary experimental conditions, incompletely-crystalline polymers do not have definite melting points, but rather broad melting ranges. This range depends on the conditions, and in particular, on the crystallization temperature,[115] which occurs outside the temperature range of melting. This indicates the non-equilibrium state of the polymer under the given conditions, as there is no temperature at which the crystalline and amorphous polymer coexist in equilibrium. The kinetics of crystallization is substantially complicated by the circumstance that the entities which must crystallize are chain molecules whose links cannot move independently. The rate of nucleation depends on the existing degree of crystallinity; thus we are dealing with a specific cooperative process. Both nucleation and growth of the crystallites take place in a very viscous medium, and are slow processes. Supercooling of an amorphous polymer may be brought about without any especial difficulty. The kinetic theory of the crystallization of polymers which has been recently developed[116,117] is still far from taking these circumstances completely into account. Nevertheless, it is clear that the indicated peculiarities of partly-crystalline polymers are of kinetic origin, and might vanish if the experiment were designed so as to ensure attainment of equilibrium. If heating were carried out sufficiently slowly, melting points would be observed which would be independent of the previous history of the sample and would be quite reproducible. It is essential here that the polymer being studied should not be oriented, i.e., that the crystallites within it should be distributed at random; otherwise anomalously high values of T_f may be found[117,118,119] It is obvious that the dependence of T_f on the history of the sample is not of thermodynamic, but of kinetic nature. Curves of the temperature dependence of the relative volume of

the polymer, when obtained by sufficiently slow heating, distinctly show a normal first-order thermodynamic transition, characterized by a definite T_f.[117] On slow heating, annealing of the non-equilibrium, supercooled amorphous material takes place, and may even be accompanied by an increase in the degree of crystallinity. In fact, in the treatment of certain fibrous materials, heat is applied to increase the degree of crystallinity and strength of the material. The technical significance of the questions under discussion is obvious. The increase in crystallinity on heating and also on swelling of the polymer has been established by the following methods of structural investigation: infra-red spectra[120] and x-ray diffraction.[121] Thus, the amorphous regions in a crystalline polymer are in a non-equilibrium state. Crystallization in these regions is hindered by kinetic factors. In this sense, polymers are similar to other polycrystalline substances which contain amorphous material forming structural defects. However, the defects in polycrystalline polymers are especially significant. V. A. Kargin showed that crystalline polymers are the least ordered of any crystalline materials (whereas amorphous polymers are the most ordered of all amorphous materials).

The second reason for incomplete crystallization is not kinetic, but structural in nature. Even if we ignore the disturbances in the regularity of real polymer chains (branching, adventitious substituents on the chain) and ignore the inhomogeneity in length of the chains (molecular weight). the structure of macromolecules in most cases is such that the system is inhomogeneous and incapable of complete crystallization. Let us consider, for example, the polystyrene chain (p. 69) containing N links. Since the phenyl group C_6H_5 may be found in two positions, to the right or the left of the basic chain, 2^{N-1} stereoisomeric modifications of the macromolecule are possible (considering its symmetry number to be 2). For sufficiently larges values of N, all of the macromolecules in a given sample will be different. Yet, this does not imply complete lack of crystallizability. First, modern studies in the field of polymer synthesis have shown that far from all of the 2^{N-1} stereoisomeric modifications of the macromolecule can be realized in practice. Irregular atactic polymers apparently consists of blocks of isotactic and syndiotactic links, and therefore do not have completely irregular structures. The possibility of partially ordered packing of such chains is obvious. Second, experiment has shown that for sufficiently long chains (even with low

molecular weights), defect crystals may be formed containing molecules with some deviation in structure within the unit cell.[123] Structural factors thus do not eliminate, but only limit the crystallinity. The existence of structural limitations is directly confirmed by the fact of practically complete crystallinity of stereospecific polymers. Atactic polystyrene is amorphous; the isotactic polymer may be completely crystalline.

A crystalline polymer containing amorphous material must be considered to be a single-phase system, normally found in a non-equilibrium state. It is a highly defective polycrystal, and naturally, the defects (the amorphous regions) may not be considered as a separate phase.

The chief structural peculiarity of the systems being discussed is the small dimensions of the crystals in comparison with the lengths of the polymer chains. The point of view was formerly generally accepted that one and the same chain may pass through a series of crystalline and amorphous regions (see, for example, references 4 and 12). However, the structure of the single crystals of Keller is evidence for another possibility. The linear dimensions of these crystals are also significantly less than the chain length; yet, the chains are completely packed within them in the form of a sort of "accordion." It is possible that in polycrystals as well, the chains may be completely packed within the crystalline, or within the amorphous regions. The theoretical study of these questions is extremely important. Yet, it is not at all clear why macromolecules should find an advantage in bending repeatedly in forming a crystal. It is indubitable only that the flexibility of macromolecules plays here a determining role, as it does in the other physical properties of polymers.

Thus, the nature of the crystalline state of polymers presents an important and interesting physical problem. Its complexity is determined by a combination of kinetic and thermodynamic factors. As has been stated, a spherulitic structure is characteristic of polymers in a number of cases. The reasons for this situation, i.e., the mechanism of initiation and growth of spherulites have not been sufficiently clear up to now. It is possible that essential roles are played here by the high viscosity of the medium and by local anisotropy associated with the chain structure of the macromolecules.

The configuration of polymer chains in crystalline regions is apparently determined by two factors, intramolecular and intermolecular.[123] The first factor determines the most stable rotational

isomer, whose stabilization in the crystal generates a planar zigzag or helical structure of the chain. The second factor determines the densest packing of the macromolecules in the crystal, according to the concepts developed by A. I. Kitaĭgorodskiĭ.[83] The actual configuration of the chains in crystals, which may be determined by x-ray diffraction, arises through concurrence of the two cited factors. It is obvious that the theoretical study of this configuration is quite essential for understanding the structures of crystalline and amorphous polymers; hence, it is essential for the further development of the configurational statistics of polymer chains. The study of the structure and mobility of macromolecules in a state of densest packing is very interesting also from the biological aspect. The structure of biological polymers on the supermolecular level has in any case a highly ordered, if not crystalline, character. An example is the structure of fibrous proteins. The structure of the individual molecules of biological substances — proteins, DNA (deoxyribonucleic acid) — is determined by the same factors as the structure of ordinary polymers. A helical structure is characteristic of biopolymers — the α-helix of Pauling and Corey for polypeptides, the double helix of Watson and Crick for DNA — each being stabilized by hydrogen bonds. As has already been shown, such a structure may be subject to cooperative disruption at a definite temperature.[15] A theory of the helix-random coil phase transition in the isolated macromolecular chain was recently propounded by Zimm[124] (see also reference 125). The existence of high mobility of the macromolecules in a crystalline polymer at a sufficiently high temperature has been shown directly by the method of nuclear magnetic resonance. The feature concerned is that of orientational melting, according to Ya. I. Frenkel'.[85] A. I. Kitaĭgorodskiĭ designates the corresponding state of a substance as "gasocrystalline."

The theory of the melting of crystalline polymers has been developed in a series of papers. Even on slow heating, a melting range of several degrees is often observed. This may naturally be explained by the smallness and heterogeneity of the dimensions of the crystallites, and by their considerable defect character. With the small dimensions of the crystallites, an essential role in the melting process is played by the surface free energy. Equilibrium melting of a partly-crystalline polymer is a diffuse first-order phase transition.[126] Melting is complete at a completely definite temperature.

Flory presented a statistical theory connecting the melting range with the defect character of the crystals.[127,117] Starting with the conception of chains which pass through crystalline and amorphous regions, Flory obtained the following expression:

$$\frac{1}{T_f} - \frac{1}{T_f^0} = \frac{R}{h}\left\{\frac{1}{n\lambda} + \frac{1}{n-\lambda+1}\right\}, \qquad (53)$$

where T_f^0 is the melting point for a pure polymer crystal of infinite length, h is the heat of fusion per structural unit, n is the number of such units in the chain, and λ is the fraction of the polymer in the amorphous state. The lowering of T_f with respect to the ideal crystalline polymer is the greater, the shorter the chains. The theory shows that the introduction of a solvent will increase the difference $T_f - T_f^0$. The introduction of differing links into the chain (copolymerization) acts in a similar way. The presence in an actual polymer of chains of different lengths leads to a broadening of the melting range, which ends at the temperature characteristic of the longest chains.

The basic results of Flory's theory may be obtained also from general thermodynamic considerations.[4] This theory gives a reasonable explanation for the lowering of T_f caused by the presence of a solvent, inhomogeneity of the polymer, or finite length of the chains. However, Flory's theory is not a complete statistical theory of solutions of crystalline polymers. It does not answer the question of the relation of the degree of crystallinity and the dimensions of the crystallites to the concentration of the solvent. The quantities characterizing the degree of crystallinity and the dimensions of the crystallites enter into the expression for the free energy as independent variables, and only occur separately. Nevertheless, these quantities are connected together. An ideal statistical theory must lead automatically to definite values of the indicated quantities for a given temperature and concentration. Such a theory must necessarily be based on a concrete molecular mechanism of the process, and must take into account its cooperative nature. Flory has also developed a statistical-thermodynamic theory of the crystallization of polymers on stretching.[128]

Several attempts have been undertaken to explain the molecular mechanism of melting of polymers by connecting this process with the flexibility of the macromolecules. As early as 1943, Bunn advanced a hypothesis that the peculiarities of the melting of crystalline polymers are determined by the internal rotation in the chains.[106] M. V. Vol'kenshteĭn and O. B. Ptitsyn[129] have pro-

posed a rotational-isomeric theory of melting. The mechanism of melting consists in the transition from a single rotational isomer existing in the crystal to a mixture of isomers in the melt, possessing increased entropy and energy. The theory connects the T_f of the polymer with the flexibility of the chains and the energy of intermolecular interaction. The more flexible the chains are, and consequently, the greater is the relative content of twisted rotational isomers, the lower is the value of T_f of the polymer, other conditions remaining equal. A result of the theory is the dependence of the heat of fusion on the flexibility of the chains, i.e., the difference in energy of the rotational isomers.

In spite of the obvious correctness of the physical concept, reference 129 is primarily of qualitative significance. The theory is limited to the study of an isolated chain, and does not take into account the cooperative character of the process.

The same conceptions about rotational isomerism were utilized in the paper of Flory[104] mentioned above; here he developed a quantitative statistical theory. Beginning with a lattice model, Flory showed that when the chains are sufficiently rigid, the crystalline, ordered state of the polymer is stable. Roughly speaking, if the chains are sufficiently rigid, they may fill the lattice only by lying parallel to one another like matches in a match box. Since the rigidity depends on the temperature, increase in the latter increases the proportion of metastable rotational isomers, and thus, T_f is connected with the difference in energy between the rotational isomers. The theory of Flory does not take intermolecular interactions into account. M. V. Vol'kenshteĭn has shown that the theory of Flory does not give quantitative agreement with experiment; such agreement may be obtained if the excitation of torsional oscillations is taken into account, along with rotational isomerism.[130] The further development of the theory will require the study of the intermolecular interactions (cf. reference 103).

It is obvious that a rigorous statistical theory of both the crystalline and the amorphous states of polymers will be based on a thorough study of intra- and intermolecular cooperative phenomena.

We see that there is a close connection between the problems described in the different sections of this article. Thus, theoretical work in any field of polymer physics is of general significance. The state of polymer physics at present permits us to trust in the rapid development of the molecular theory, which in the near future is to become an important aid to technology.

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Translated by M. V. King