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Abstract

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MECHANICS OF POLYMER MOLECULES

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1. A number of facts observed during rolling, crushing, and mechanical deformation of polymeric substances are interpreted theoretically as a consequence of the mechanical rupture of polymer molecules (^1).

In recent years it has been experimentally proven that, as a result of mechanical ruptures of polymer molecules, free polymer radicals (macroradicals) are formed, which can be used as centers of radical polymerization (^2, ^3).

New scientific disciplines are being developed—mechanochemistry (^3) and physicochemical mechanics (^4).

2. Ideas about mechanical intramolecular stresses (^5) and about valence bonds as quasi-elastic rods (^6) arose long ago.

If one assumes that the act of mechanical rupture is preceded by a stage of elastic stretching, then the methods of mechanics can be applied to the study of the elementary act of stretching and rupture of a polymer molecule. It is known that the first stage of stretching of a flexible polymer molecule under the action of external forces is its straightening as a result of a change in the configuration of the molecule, leading to a decrease in the entropy of the system. The mean statistical value of the modulus of elasticity (a_s) for "configurational-entropy" deformation of an idealized hydrocarbon polymer molecule can be estimated as a value of the order of $1 \cdot 10^{-8}$ dyn/bond (^7,8). For a formal estimate of the change in the energy of a molecule under mechanical deformation, it is useful to introduce the concept of "specific energy density" (g_s), calculated as the quotient of the work of stretching divided by the volume of the stretched segment of the molecule. The specific energy density for configurational deformation is small and amounts to $g_s \simeq 0.05 V_s$ kcal/cm^3, where V_s is the work of stretching in kcal/mol. For V_s of the order of 200 kcal/mol, $g_s \simeq 10$ kcal/cm^3.

The postulated elastic stretching of a polymer molecule, occurring through the stretching of valence angles and valence bonds, can take place only after complete straightening of the molecule. If the length of the completely straightened molecule is taken as unity, then the modulus of elasticity (a_c) in the initial stage of elastic stretching of a hydrocarbon polymer chain is, in a very rough approximation, estimated as a value of the order of $2.5 \cdot 10^{-3}$ dyn/bond (^9) or $5.6 \cdot 10^{-3}$ dyn/bond (^7). When approximating the dependence of stress (σ)

on elongation (ε) by Hooke' s law, the order of strength of the C–C bond is roughly estimated as $5.7 \cdot 10^{-4}$ dyn/bond ($\hat{}7$). In our opinion, these data for estimating the stiffness and, especially, the strength of a polymer molecule are greatly underestimated, since they do not take into account the substantial increase in the slope of the potential curve as the covalent bond is stretched and the role of other factors. It may be assumed that the order of magnitude of the modulus is $a_c \simeq 7\text{–}12 \cdot 10^{-3}$ dyn/bond; then

the strength of a C–C bond can be estimated as a quantity of the order of $0.2 \cdot 10^{-2}$ dyn/bond*, and the relative elongation at rupture (ε_z) will be no less than 0.2—0.3. Regardless of the values of the parameters of the mechanical properties, the potential energy accumulated under elastic extension must be commensurate with the dissociation energy of the covalent C–C bond (V_0), since extension must provide for the stretching of all valence angles and all valence bonds forming the molecular chain. The specific energy density under elastic extension (g_c) is very large and amounts to $g_c \simeq 54V_c$ cal/cm^3, where V_c is the work of extension, in kcal/mol; at $V_c = 20$ kcal/mol, g_c has a value of the order of 10^3 cal/cm^3, i.e., two orders of magnitude greater than under configurational-entropic deformation. This is a conclusion resulting from the extension of the basic principles of mechanics to the consideration of the phenomenon of mechanical stretching of a polymer molecule.

3. An elastically stretched polymer chain may be regarded as a quasi-elastic rod, which contracts spontaneously when the external action is reduced, owing to the potential energy accumulated during stretching, and in doing so performs work against external forces. This process will prove reversible if no excitation (activation) of the valence bonds occurs and no chemical transformations take place. However, owing to the considerable increase in the internal energy during elastic stretching of the valence bonds, the probability of excitation–activation of the bonds must be great; there is hardly any reason to doubt the statistical character of this effect. The degree of activation at rupture of an elastically stretched polymer molecule must be especially significant. Attempts are known to estimate experimentally the magnitude of the energy of mechanical activation without theoretical consideration of the elementary act of stretching and rupture of a polymer molecule ([10]).

4. For the mechanics of polymer molecules, consideration of the elementary act of rupture of an elastically stressed polymer molecule is of fundamental importance. The thermodynamic equilibrium of an elastically stretched molecular chain is determined by the relation between the elastically stressed state of the molecule and the action of external forces. In mechanical rupture of the chain, i.e., when the integrity of at least one single atomic bond is disrupted, the state of thermodynamic equilibrium, simultaneously with rupture of the covalent bond, will be disrupted owing to the elimination of the possibility of external mechanical action on the molecule.

To estimate the relation between the work of external forces on elastic stretching of a molecular chain and on the formation of macroradicals during mechanical rupture, it is sufficient to take into account the number of valence bonds (n) in the stretched molecule. If it is assumed that rupture occurs at the site of one of the valence bonds, then the relative fraction of the work of external forces expended on the formation of two macroradicals will prove very small, since it will constitute only $1/n$ of the total work of stretching a molecule of n units. This important circumstance must be taken into account not only in the theoretical estimate of the work of formation of macroradicals, but also in estimating the magnitude of the surface energy upon formation of an interface in the case of rupture of a polymer body ([11]).

The energy accumulated during elastic stretching of a molecular chain is very considerable, and it will be the greater, the closer in magnitude the work of stretching a single valence bond is to the dissociation energy of C—

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*Taking the mean effective cross section (s_0) of polymer molecules to be $25 \cdot 10^{-16}$ cm^2, we obtain, respectively, the values of the elastic modulus

$$E_c = \frac{a_c}{s_0} \simeq 3.5 \cdot 10^6 \text{ kg/cm}^2$$

and the rupture stress

$$f_z = \frac{\sigma_z}{s_0} \simeq 0.8 \cdot 10^6 \text{ kg/cm}^2.$$

C-bonds. For an accurate estimate of the value of the specific energy density before rupture of a molecule, knowledge of the average value of the dissociation energy proves insufficient, because of the manifestation of fluctuations in the energy of valence bonds, which must obey statistical laws. Therefore, the strength of an elastically stretched molecular chain must depend on time. In the mechanical rupture of an elastically stressed molecular chain, thermodynamic equilibrium must be disturbed instantaneously. Then, owing to the exclusion of the possibility of performing mechanical work, along with the process of activation of valence bonds there must occur a transformation and dissipation of energy. Establishing the ratio of the energy expenditures for these transformations is an important, but as yet unsolved, problem. In the mechanical rupture of an elastically stressed polymer molecule, dissipative processes must have an explosive character if the rate of spontaneous contraction of the parts of the ruptured molecule is sufficiently great.

There are grounds for assuming that the dissipative processes in the elastic rupture of a polymer molecule are fundamental. In particular, it is natural to suppose that the strong electrification and heat evolution observed during the "cold" plasticization (15—20°C) of polyisobutylene on rolls are caused by

mechanical elastic rupture of molecules. In the thermal dissociation of elastically unstressed polymer molecules, dissipative effects, naturally, should not be expected. It is also important to note that, in the mechanical rupture of local intermolecular van der Waals bonds or hydrogen bonds, there is likewise no reason to expect energy dissipation, since there will be no elastic stretching in this case, because of the substantially lower mechanical stiffness of these bonds and owing to the possibility of successive rupture of these bonds.

However, in discussing this question it is no longer possible to confine oneself to the mechanics of polymer molecules; it is necessary to touch upon the problems of deformation of polymer systems. It should be specially noted that the concepts being developed are based on assertions concerning the surprisingly great stiffness and mechanical strength of covalent chemical bonds (C—C, C —O, C—S). Thus the concepts being developed are based on the fundamental assertion of a radical, qualitative difference between strong covalent chemical bonds and substantially less strong physical bonds. It is precisely this feature of the structure of polymer molecules that proves essential both from the point of view of chemistry and from the point of view of mechanics. Unfortunately, this circumstance is not only not taken into account, but is often tacitly called into question or even rejected.

5. At present there is still no possibility of directly experimentally studying the elementary act of elastic stretching and mechanical rupture of a polymer molecule. There are also no reliable, trustworthy initial data for a theoretical quantitative estimate of the mechanical and energy parameters considered in this article. However, these circumstances should not impede the development of the mechanics of polymer molecules.

The concepts of the mechanical rupture of polymer molecules, accompanied by the formation of polymer radicals and the activation of valence bonds, have served as the basis for developing a program of work on the synthetic modification of polymers ([2], [3]), as well as work in the field of studying certain technological problems and of studying the special features of the molecular mechanism of deformation of polymer bodies ([12]).

However, the concepts of the elastic stretching of polymer molecules are still used to an insufficient degree, and the concepts of the dissipative processes accompanying the elastic rupture of polymer molecules are still not used at all. Meanwhile, recognition of the presence of the effect of energy dissipation in the elastic rupture of polymer molecules makes it possible to outline—

to find new ways of solving certain important problems in the field of polymers.

The development of a program of work may be based on a general rule according to which, in studying the mechanical deformations of a polymer body, one should take into account the possibility of the occurrence of elastic stretching and mechanical rupture of polymer molecules, accompanied not only by the formation of radicals and activation of valence bonds, but also by dissipative processes. The rule formulated should also be used in solving problems of

the strength of solid bodies; for this purpose it is recommended to determine whether a given solid contains polymer molecules whose elastic stretching may have a substantial influence on the mechanical properties of the body even at a negligible content of polymer molecules, owing to the very great strength and stiffness of the latter.

6. An important section of the recommended program of work is the study of the mechanical stretching of polymer systems. We have shown the possibility of developing a molecular theory based on recognition of the decisive significance of the elastic stretching of flexible polymer hydrocarbon molecules during deformation of an elastic body (13).

By assigning great importance to elastic rupture, one can interpret the nature of triboelectricity during the mechanical rupture of polymer bodies, and also understand the cause of electrification when polymer bodies are rubbed against solid bodies. Finally, if one assumes that elastic rupture of polymer molecules occurs during mechanical deformations of animal and plant tissues, it becomes possible to formulate a hypothesis for interpreting the cause of the directed growth of these tissues. Thus, the ideas being developed may be used in the study of a fairly wide range of phenomena in the field of polymers and solid bodies.

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Note: Figure translations are in progress. See original paper for figures.