STRUCTURE AND PROPERTIES OF POLYMERS*

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UDC 678:[539.2+539.3]

The history of the development of the structural mechanics of polymers is reviewed and the more important of its future tasks are noted.

The relation between the structure and properties of polymers is naturally a very important problem of polymer research, since the better it is understood, the more effective the work of the chemists and plastics engineers. Thus, the investigation of the relation between polymer structure and properties is a fundamental theoretical task with far-reaching practical implications. This is undoubtedly the reason for the rapidly increasing volume of research being done in this area of polymer physicochemistry.

The development of research on the relation between polymer structure and properties can be divided into two stages.

During the first stage (approximately from 1930 to 1956), which was preceded by successful chemical and physicochemical research demonstrating the existence of chain macromolecules, their flexibility, determined by their enormous length-to-diameter ratio, and the possibility of significant relative rotations of the individual parts of the molecule without loss of integrity, the kinetic theory of equilibrium rubber elasticity was developed [1-5]. This theory was received as a brilliant explanation of a series of striking anomalies observed in rubbery polymers, for example, the enormous values of the mechanically reversible strains (many hundreds of percent), the unusually low values of the moduli of elasticity (of the order of 1 kgf/cm^2), the increase in the modulus of elasticity of heated elastomers, the release of heat in loaded polymers during extension and its absorption during contraction, etc.

The subsequent studies of a number of Soviet physicists in the area of the kinetics of polymer deformation processes [6-18] showed that the idea of flexible and entangled chain macromolecules was consistent with the observed effects and could be used to establish fundamental laws. All this, and the success achieved in exploiting these ideas in the synthesis of new macromolecules and the investigation of electrical and other physical properties, gradually pushed into the background the previously dominant colloido-chemical concept of polymers† as colloids whose particles possess an unusual affinity for the solvent, which sought to explain the anomalous behavior of polymer solutions. It was found that these ideas did not advance the study of the relation between polymer properties and structure.

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* Presented at the 2nd All-Union Conference on Polymer Mechanics, Riga, November 10-12, 1971.

† It should be noted that colloid chemistry, the study of the structure and properties of disperse systems, i.e., all types of heterogeneous systems consisting of a solid, liquid, or gaseous homogeneous medium in which particles of another solid, liquid, or gaseous phase are dispersed, was for many years extremely fruitful in connection with the investigation of so-called lyophobic colloids, for example, insoluble, very finely divided substances suspended in water (aqueous dispersions, emulsions, foams). The colloid chemistry of such systems, based on the latest (at that time) physical and chemical techniques, was scientifically so well-founded that many of its ideas were rather too hastily applied to a second group of colloidal systems — lyophilic colloids, which included polymers. The latter were assumed to be colloids since their solutions contained large particles of colloidal size and thus, according to the notions of the day, could not be molecular solutions.

Although the colloido-chemical approach to polymers was to be deemphasized, nonetheless colloid chemistry remained an important branch of polymer physicochemistry, since many methods of synthesizing (for example, emulsion polymerization) and processing polymers lead to the use or to the formation of typical colloidal systems (for example, latexes, various polymer dispersions used for the impregnation, etc. of fibers and fabrics, and so on).

Moreover, the very existence of macromolecules, large particles comparable in size with the colloidal particles of lyophobic colloids, leads to certain similarities in the behavior of lyophobic colloids and polymers (for example, the inability to filter through microporous materials).

Thus, the first stage in the development of modern ideas about the relation between polymer structure and properties was characterized by a sudden switch from the colloido-chemical approach to the notion of flexible macromolecules and by a series of very important theoretical and practical consequences that followed from this switch. At this point, in addition to the kinetic theory of rubber elasticity, it is also necessary to mention the successes of the theory of relaxation phenomena in polymers, which revealed the molecular nature of the nonequilibria in stressed polymeric bodies, provided an explanation of the frequency and temperature dependence of the compliance, established the existence of three physical states of amorphous polymers, revealed the nature of the flow anomalies observed in polymers and polymer solutions, and threw light on polymer orientation processes; among the more important results of this stage one might also note the discovery of the physical significance of the plasticization of polymers, the swift development of the statistical-thermodynamic theory of polymer solutions, and new insights into the molecular mechanism of formation of polymer gels, rubbers,and other three-dimensional polymers and the physical structure of crystalline polymers.

The guiding principles of this period may be formulated as follows:

1) An isotropic amorphous polymer is a homogeneous body consisting of a random arrangement of more or less flexible macromolecules; isotropic crystalline polymers are formed as a result of the ordering of parts of the macromolecules into small microcrystals.

2) The physical properties of a polymer are completely determined by the arrangement and behavior of the constituent macromolecules.

The application of these principles to the mechanical properties of polymers naturally led to the notion that the reversible strains are due to a change in the shape of the flexible macromolecules (i.e., to a change in the conformations, as the chemist put it), while the irreversible strains are caused by the displacement of whole macromolecules; the entire complex of relaxation effects was attributed to delays in the regrouping of the interacting flexible macromolecules; the mechanical (and in general physical) anisotropy of polymers was a consequence of the straightening and orientation of the macromolecules; the strength characteristics of a polymer were related with the interaction energies of the long macromolecules and their bond energies (it was assumed that polymer fracture was a consequence of the relative slippage of the macromolecules or of bond breakages, if this required less energy).

At first, research was concentrated on synthetic rubbers, in most cases incapable of crystallization owing to the highly irregular structure of the macromolecules. In the first approximation these polymers satisfied the above-mentioned basic principles and therefore the development of the theory and its application started off well. However, after 1945 increasing attention was given to polymers with regular, yet flexible macromolecules. These readily crystallizing polymers (for example, polyethylene, nylon, Kapron, etc.), which were quickly commercialized, naturally gave rise to a great deal of research on their structure and properties leading to the conclusion that a reexamination of the basic principles was in order. The rapid development of electron microscopy and other methods of investigating the physical structure of polymers soon led to the discovery of the inhomogeneous structure of crystalline, and then amorphous polymers. In 1956 all this research culminated in the hypothesis [19] of a complex supermolecular structure, which was quickly and broadly confirmed [20].

These developments in our understanding of the physical structue of polymers produced the following guiding principles which are still accepted today:

1) All polymers, isotropic and anisotropic, liquid and solid, amorphous and crystalline, consist of supermolecular formations (i.e., aggregations of macromolecules) of various degrees of complexity and of different size. In a number of cases the existence of supermolecular formations makes it impossible to treat polymers as homogeneous or even continuous bodies.
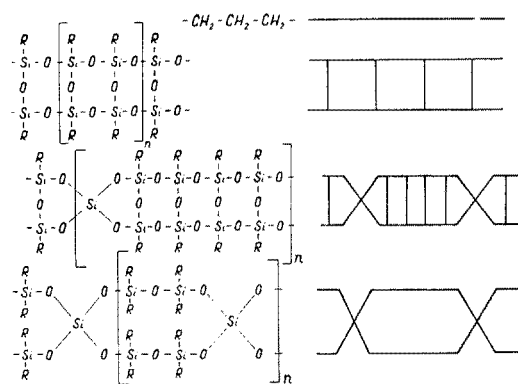
$-CH_2-CH_2-CH_2-$

Fig. 1. Certain new structural types of macro-
molecules.

2) The physical properties of any polymer are determined by the nature and properties of the con-
stituent supermolecular formations which, in their turn, depend both on their own characteristics
(structure and size of the supermolecular formation, relations between the various elements of
the supermolecular structure) and on the characteristics of the macromolecules (size, flexibility,
and chemical structure, which determines the intra- and intermolecular interactions).

The application of these principles to the mechanical properties of polymers requires such bodies
to be treated in some cases as continuous and homogeneous and in others as inhomogeneous and discrete,
even as microstructures. Polymer melts and solutions are closer to the first type, crystalline polymers
closer to the second. Thus, research on the mechanical properties of polymers called for a simultaneous
study of their physical structure. The merging of structural and mechanical research led to the develop-
ment of a new branch of polymer mechanics — polymer structural mechanics [21-24].

The possibility of ordering the macromolecules in various supermolecular formations (fibrillar or
globular in shape) and their subsequent aggregation into larger formations, etc. brought into the foreground
the study of the origin and growth of various elements of the physical structure. The conditions favorable
to the development of specific types of physical structure were discovered and the mechanical properties
of polymers with the same chemical, but different physical, structures were investigated. It was shown that
the physical structure has an important influence on the entire complex of mechanical properties of poly-
mers [25-29]. Recent studies of different polymers have broadly confirmed these initial conclusions and
have provided a much deeper knowledge of the conditions of formation of the various types of supermolec-
ular structure.

This first step in the field of polymer structural mechanics naturally prompted investigators to study
the stability of the various forms of supermolecular formations under a variety of conditions of tempera-
ture and mechanical stress and, moreover, to find ways of controlling the physical structure of polymers.
This key problem of creating from a given polymer a polymeric material with the physical structure best
suited to the conditions under which it is to serve, i.e., with a structure giving the optimum combination
of mechanical and other physical properties for a particular product, has already been solved in a number
of quite important cases [24], but it remains a most important problem of modern polymer mechanics.

One consequence of the development of these new structural concepts is the need to enlist the aid of
a number of branches of physical chemistry closely related with colloid chemistry. The presence of super-
molecular formations of colloidal dimensions, the undoubted significance of surface phenomena in the case
of polymeric bodies with a microdiscrete structure and a number of other factors makes it necessary to
conduct a strict critical examination of the resemblances and differences between polymeric and typical
colloidal systems on the basis of the achievements of modern physical and colloid chemistry.

So far we have been concerned with the main body of physical and mechanical research into the rela-
tion between polymer structure and properties, but there have been other interesting developments based
on and complementing these results.

Technology is constantly demanding new materials with different combinations of physical properties.
There is a need for polymeric materials with sufficient elasticity and strength at very low and very high
temperatures, under high-vacuum conditions, in various liquid and gaseous media, under exposure to var-

ious kinds of radiation, etc. Naturally, in solving these very difficult technical problems any path likely to lead to success is followed. One such path involves the synthesis of macromolecules with different structural characteristics (see Fig. 1).

The physical properties of these macromolecules, in particular, their flexibility and, moreover, their ability to coalesce into supermolecular formations are almost uninvestigated. Naturally, the structural mechanics of these polymers has not yet been developed. At the same time, a comparison of ordinary chain macromolecules of variable stiffness and other types with respect to their ability to form aggregations and the relations between their structure and possible types of physical structure and hence groups of mechanical properties would be of considerable theoretical value. A deeper insight into the role of the chemical structure of the macromolecules in the formation of the structure and properties of the polymeric body would undoubtedly also lead to new applied results.

The requirements of technology, in addition to prompting a search for polymers of previously unknown composition and structure, have also led to the creation of complex composite materials (mixtures of polymers, porous and foam plastics, polymers with various organic and mineral powdered, fibrous, and other fillers, microscopic metal-polymer combinations, ceramo-polymers, reinforced polymeric materials with various micro- and macrostructures, etc.). These materials are all intended to serve different purposes and in each case it is necessary to establish the relation between structure and properties. Unfortunately, in this very important area of polymer mechanics, despite certain successes, there are still many blanks. Although in the case of glass-reinforced plastics we have already accumulated a certain sum of knowledge about the relation between the structure of the material and its properties and on the effect of the properties of the resin and the fibers on the properties of the composite (see, for example, [30]), we still know little about the possibility of creating a particular set of material properties by varying the combination of resin and organic or heteroorganic fiber or by regulating the supermolecular structure of the resin and the fiber itself. The same can be said of other composites, although in certain cases enormous amounts of empirical data have been accumulated and await generalization and application in the interests of modern structural mechanics. This will require a fusion of the structural mechanics approach and material design, doubtless with fruitful results.

It is impossible not to mention one particularly interesting method of creating new polymeric materials, that is, the creation of different surface and internal structures. There are various ways of achieving this result. The physical structure at the surface and in the interior of the polymer can be differently controlled [24, 31-33] or the chemical and at the same time the physical structure of the surface may be modified [34, 35]. The structural mechanics of such bodies is still in an early stage and the possibilities for theoretical and practical development are extensive.

We now turn to the question of structural research in the areas of polymer elasticity, plasticity, strength, and friction. It is necessary to distinguish two types of elastic, i.e., reversible, deformation in polymers, namely, elasticity, in the narrow sense of the word, and high elasticity. The first type, which for the sake of brevity we shall refer to simply as elasticity, is typical of glassy and highly crystalline polymers, the second of elastomers. High elasticity is believed to depend on conformational changes of the macromolecules during deformation, elasticity on the forces of interaction between neighboring atoms belonging to the same or different macromolecules.

The theory of equilibrium high elasticity is based on the concept of randomly entangled flexible macromolecules; i.e., it does not reflect modern ideas on orderedness in amorphous polymers. Individual attempts to take into account the spatial correlation of the macromolecules [36, 37], although interesting, have still not led to any significant shift in the theory. The creation of a new theory of high elasticity, solidly founded on the concept of supermolecular organization of the macromolecules, is to be anticipated. Such a theory, while incorporating the undoubted achievements of the existing theory, would obviously be closer to reality and hence more effective.

In the area of the theory of elastic relaxation phenomena, i.e., the theory of nonequilibrium high elasticity, and moreover the theory of nonequilibrium structural changes in stressed glassy and crystalline polymers, the situation is somewhat different. Here, a variety of modern physical methods have been used to establish the many types of structural transformations responsible for relaxation processes, and the significance of the delay both in molecular rearrangements and in various structural transformations at the supermolecular level is gradually being revealed.

Since the phenomenological description of relaxation processes [10, 38, 39] in polymers is quite well developed, an obvious task of structural mechanics in this area is to establish relations between the param-

eters of the phenomenological equations describing relaxation processes (i.e., the parameters of the kernels of the linear and nonlinear Boltzmann–Volterra equations) and the molecular and supermolecular characteristics of polymers.

In connection with the theory of equilibrium elasticity of rigid glassy and crystalline polymers it should be noted that there is an obvious need to express the modulus of elasticity in terms of the structural characteristics.

The development of the theory of plasticity of polymers is of enormous practical importance, since it is an essential tool of the plastics engineer. The difficulty is that irreversible strains in polymers are always accompanied by reversible strains, which in a number of cases are very hard to isolate. Moreover, the physical structure of melts and solutions is still very poorly understood. Thus, here it will be necessary to develop both phenomenological and structural concepts and to combine them to produce a structural theory of plasticity.

The structural theory of polymer strength is in the development stage. Two important examples deserve special attention. Firstly, it is known that the multiple deformation of elastomers ultimately leads to fracture. The number of cycles to failure depends on temperature, the amplitude of the applied force, and a number of other factors. It is noteworthy that almost up to the moment of failure the static strength characteristics of such a specimen are more or less independent of the number of deformation cycles. This elastomer fatigue effect has been thoroughly studied [40-43] and it has been shown that after each deformation, even if it is small, macromolecules are broken at the chemical bonds with the formation of a terminal free radical. However, these free radicals do not survive, but interact with so-called inhibitors present in the polymer. As the inhibitor is consumed, in some microregion there ultimately appears a free radical in whose neighborhood the inhibitor has been exhausted. There then develops a chain reaction leading to a radical change in the composition and chemical structure in this microregion, i.e., to the formation of a microdefect. Rapid development of a microdefect leads macroscopic fracture of the elastomeric specimen. Thus, fatigue changes in elastomers are based on a mechanochemical process.

The second example is the fracture of rigid polymers subjected to a constant stress. As shown with the aid of modern physical methods of structural investigation [44-48], the fracture process, whose duration depends on the magnitude of the stress and temperature, is also based on a multiplicity of macromolecular breakages, i.e., a mechanochemical process. Consequently, it has been possible to demonstrate a close relationship between changes in the chemical structure of the macromolecules and the polymer fracture process. However, we still know very little of the effect of the supermolecular structure on the fracture mechanism, although the existence of such an effect follows clearly from the different strengths (or lifetimes) of polymers of the same chemical structure but different supermolecular structure. The development of a structural theory of strength based on a consideration of the mechanochemical processes in polymers with different physical structures is under investigation at the present time.

Finally, it is impossible to ignore the problem of friction and wear. The successful development of new friction and antifriction polymers and their rational use must depend on the creation of a structural theory of friction of polymeric materials. This is a particularly difficult problem because when the surface of a polymeric material interacts with any other surface – polymer, metal, etc. – the effect is to create a complex state of stress leading to the development of a whole series of relaxation processes and, moreover, a process of fracture in the most heavily loaded microregions; mechanochemical processes associated with the state of stress are also initiated and lead to chemical changes in the polymeric material in the friction zone and even to chemical interaction with the material of the other rubbing surface. In addition, various physical structural transformations at the molecular and supermolecular levels, caused by mechanical action and rapid local temperature changes, take place in the friction zone. The picture is further complicated by the presence of electric charges (as a result of triboelectrification). These produce a series of secondary chemical and physical effects. It is obvious that progress in this area can only be made on the basis of the closest cooperation among all the specialists involved.

Unfortunately, so far it is mainly the chemists and physicists who have contributed to the theory of polymer structural mechanics, while the engineers have provided support only in the area of applications.

Further progress in solving the structural problems of polymer mechanics would be an important contribution to science and would undoubtedly lead to rapid advances in the production, processing, and application of polymeric materials.

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