STRUCTURE OF POLYMER MOLECULES AND SUPERMOLECULAR STRUCTURES

V. A. KARGIN

Khimicheskoe Otdelenie, Akademia Nauk, S.S.S.R., Moskva, S.S.S.R.

From year to year we become more and more convinced of the important role played by structural phenomena in forming the properties of polymers. Mechanical properties are determined not only by changes in shape conformation and by motion of individual molecules of the polymers, but by the behaviour of larger and more complex structural formations as well. The interphase boundaries of these formations, known as supermolecular structures, are the sites where chemical reactions in polymers are most likely to begin and centres of crack formation and incipient destruction to arise. It has been found that extensive occurrence of ordered structures is typical not only of crystalline, but also of amorphous polymers, namely, glasses and rubbers.

Despite the complex morphology of structural formation in polymers it should not be forgotten that all these structures are built up of separate polymeric molecules. At first glance it seems self-evident that direct relations must exist between the properties of macromolecules and their ability to form supermolecular structures. In any case, the entire crystal chemistry of low-molecular substances is built on the assumption that such relations are inevitable.

This is all quite correct for crystals of low-molecular substances whose molecules have strictly definite shapes and sizes. But with respect to the immense molecules of polymers, in which variability of shape is inevitable, all these assumptions become much less clear. Indeed, there is always a direct relation between the properties of any structure and the properties of its structural elements. But these structural elements are not necessarily separate molecules. For example, the properties of some tactoid structure consisting of colloidal particles will, of course, be related to the geometry and size of those colloidal particles, but will have no direct relation to the properties of the molecules of the substance constituting the colloidal particles.

The shapes of most polymer molecules may vary within wide limits. When studying the simplest phenomena of structure formation quite a long time ago we came definitely to the conclusion that there are two ways by which structures can form. Sufficiently flexible molecules roll up into spherical coils or globules which form in very much the same way as the drops of a liquid under the action of surface tension. But if the macromolecules are sufficiently rigid the simplest linear structures result. No separate linear polymer molecules have been observed so far. Evidently in the great majority of cases, if not always, they aggregate into chain bunches usually containing several dozen molecules. These simple structural formations—globules and

bunches—are the structural elements, the simplest supermolecular structures which combine to produce more and more complex structural forms in polymers². These observations were first made 10 years ago and reported to the Symposium in Wisbaden³. Since then a large amount of data has accumulated and it may be asserted that many polymers can be obtained both in the linear and globular forms, because each of these forms results in an entirely different type of supermolecular structure. The very possibility of polymeric matter existing both in the globular and in the linear form shows that, if only the composition, structure, and size of the chain molecules are known, the supermolecular structure which the polymeric substance will form cannot be predicted. On the other hand, there is no doubt that if the formation of two forms of the simplest supermolecular structures is possible, only one of them is equilibrrious. It is therefore necessary to consider in greater detail the conditions of their formation and the possibilities of their conversion into one another. The first factor to be taken into account in this connection should be the physical state of the polymer and the temperature of formation of the structures. In the elastic state, equilibrium structures may be expected. In the glassy state, structural transformations are so difficult that the polymer retains its original structural form.

The most general method is to produce polymers in the globular state from dilute solutions by evaporating the solute below the glass temperature of the polymers. Since the polymer molecules are rolled into globules in very dilute solutions, they remain fixed in this form. In this way a very great variety of polymers, ranging from polyolefins⁴ and polyamides to gelatin and casein⁵, can be obtained in the globular form. For many polymers, globular structures arise directly on their formation. Poly-condensation resins with high softening temperatures, such as epoxides or phenolics almost always give globular structures on preparation, though globular structures are also obtained with polyvinyl chlorides⁶ and even fluorine-containing rubbers⁷. Finally, it should not be forgotten that in the globular form chain molecules are the least ordered and therefore any polymer in this form is amorphous. The rate of ordering in polymers is never high, and when a polymeric substance is precipitated from solution the rate of its separation is, as a rule, higher than the rate of ordering of its molecules. That is apparently why the first stage of precipitation of polymers as a separate phase or as separate particles is always the formation of amorphous particles, which may consist of one or many molecules. This process is typical not only for polymers, but for any substance separating as an insoluble precipitate from solutions. As far back as the twenties of this century, Haber⁸ drew attention to the importance of the ratio of the rates of ordering and separation of a substance. Later Berestneva and the present author⁹ showed for a large number of examples that the first stage of formation of colloid particles is always the formation of primary amorphous particles of spherical shape. This is natural, because being amorphous, they are isotropic and the rate of their growth is the same in all directions. The next stage is ordering of the molecules of the precipitated substance, which in the case of low-molecular substances results in crystallization. As a result of this the primary particle breaks up into a large number of minute, crystalline particles which form the colloid solution. *Figure 1* shows the consecutive states of formation of a colloidal solution of

(a) freshly prepared sol;
(b) 1 or 2 hours after preparation; (c) several days later

TiO₂, beginning with large spherical amorphous particles which break up subsequently, due to ordering, into minute crystalline particles. All this results from the fact that the rate of separation of TiO₂ from the solution is much higher than the rate of its ordering.

This is no formal analogy. It is known that in the case of polymers also, ordered supermolecular structures form comparatively slowly both in amorphous and in crystalline polymers owing to the large size of the interacting polymer molecules. It may therefore be expected that when a polymeric substance forms, or separates from solutions, or melts, it falls out at first in the least organized form, namely, in globular form, especially if this occurs at temperatures where the molecular motion of the polymer molecules is very low. There are exceptions, when the polymer forms immediately as well organized structures, but I shall return to this later.

Hence, we should expect the simplest structures to form first; these may be unbalanced and on approaching equilibrium, will come into more perfect forms. If this transition is very slow the polymer may exist in various intermediate forms as globules, fibrils and more complex formations. In this case all perceptible relations between the composition and structure of the polymer molecules and their ability to form supermolecular structures will be obliterated. Only in the case where the structural transformations occur quickly can we expect equilibrium to be reached and direct relations to exist between the molecular build and supermolecular structure. Hence, we must examine how the transition from the simplest to the most perfect equilibrium structures occurs in polymers, and the rates of these processes for various classes of polymers and for various conditions of formation of supermolecular structures.

I have already said that below the glass temperature globular structures are quite stable in the absence of extraneous influences, and the globules

Figure 2. Replica of the spalled surface of block polyvinyl chloride

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are retained as separate structural units with well-defined interfacial boundaries. The photograph of a replica of a spalled surface of polyvinyl chloride shown in *Figure 2* may serve as an example.

When the temperature rises and the polymer passes into the elastic state

Figure 3. Isotactic polystyrene out of decaline solution: (a) freshly prepared; (b) after 3 months; (c) after 6 months; (d) after 10 months

further ordering begins. The globules merge like the drops of a liquid into larger globules which now contain numerous polymer molecules rather than one. Finally, after a critical size is reached the globules rearrange into linear or band structures typical of any polymer in the elastic state, or into bunches and fibrils characteristic of polymers with more rigid chains¹⁰. The rate of these transitions in pure polymeric substances is not very well known, but it is not high even in solutions. I should like to give a few examples of how the transitions from the simplest structures to more elaborate ones are accomplished when working even with very dilute solutions.

If a melt of isotactic polystyrene is cooled quickly to a low temperature it becomes amorphous and dissolves readily in hydrocarbons. If preparations for electron-microscopic photography are made out of such a solution after storage of the latter for different lengths of time, the entire sequence of structure formations can be observed beginning from the simplest structureless species and globules down to quite perfect single crystals. It is striking that even in solutions, where conditions would seem to favour mobility of the polymer molecules the most, these ordering processes take weeks and months¹¹. *Figures 3 and 4* show the structure patterns formed as a result

Figure 4. Isotactic polystyrene crystallized from a melt at 160°C

(a) (b) (c)
 Figure 5. Copolymer of sodium ethylene sulphonate with acrylic acid (20:80) : (a) freshly prepared solution; (b) (c) after a month

of rapid evaporation of isotactic polystyrene solutions after various storage times. Only the last photograph shows the final state of structure formation—the formation of a crystalline substance. All the foregoing structures are amorphous, as is evidenced by the electron-diffraction pattern (taken of the most perfect structure prior to crystallization, that of long and thin fibrils).

Figure 6. Copolymer of sodium ethylene sulphonate with acrylic acid (20:80): (a) one month after preparation; (b) (c) after 3 months; (d) after a year

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It can be seen how slowly the transition to more perfect structures occurs and how easy it is to register intermediate, non-equilibrium stages of structure formation. Adding to this the polymorphism of the crystalline forms of isotactic polystyrene, it can readily be understood that under ordinary conditions of working with this polymer, when the time and conditions of specimen preparation do not, as a rule, favour the establishment of equilibrium, a large number of various structural forms may easily result,

Figure 7. Optical photographs of copolymer of sodium ethylene sulphonate with acrylic acid (20:80): (a) freshly prepared solution; (b) after storing for 6 weeks

obliterating any direct relation between the properties of the initial molecules and the supermolecular structures formed.

I should like to give one more example of the sequence of various stages of structure formation, entirely free from the complications of crystallization phenomena. Perhaps the most interesting from the standpoint of studying structure formation phenomena are polyelectrolytes and their copolymers, because both the flexibility of their molecules and their intermolecular interaction can easily be varied by changing the salt composition of the medium. At the same time they possess a striking ability to form sometimes very perfect large structures without crystallization due only to ordering of their molecules in the amorphous state (this process being accomplished in several stages¹²). *Figures 5, 6 and 7* are (as in the case of polystyrene) a series of electronmicroscopic photographs of specimens of the copolymer of sodium ethylene sulphonate and acrylic acid, obtained by rapid evaporation of the same solution after different periods of storage. These latter photographs refer to more concentrated solutions from which large structures, up to visible sizes, are formed. One can see the consecutive transition from monomolecular globules to polymolecular formations, the merging of the latter into intermediate, sometimes shapeless formations, the appearance of linear structures of a very peculiar and complex type, and finally, their transition into very perfect fibril structures, up to the formation of large dendrites.

In dilute solutions their formation is very slow. This does not mean, of course, that concentrations and temperatures cannot be found at which even very perfect structures can be obtained quite rapidly. But this series of tests again demonstrates how easily polymorphism can be achieved even in strong polyelectrolytes and their copolymers. These copolymers of sodium ethylene sulphonate and polyacrylic acid are irregular and do not crystallize completely, just like the copolymers of vinylphosphonic acid and its acrylic acid esters, described above.

The behaviour of polystyrene sulphonic acid is very much the same¹³. *Figures 8 and 9* illustrate the structure formation pattern of this polymer under conditions similar to those described above. I shall restrict myself to these examples, although at present many cases of slow structure formation could be cited both for amorphous and for crystalline polymers. I have quite deliberately been speaking of structure formation in amorphous polymers all the time because ordering in the amorphous state is a necessary prerequisite for crystallization. Therefore, the sources of polymorphism are inherent in the formation of polymeric structures prior to crystallization, and the extensive development of polymorphism is the main obstacle to establishment of relations between the structure of polymeric molecules and the formation of supermolecular structures. The general course of structure formation is very similar for a great variety of polymers, but depending on the conditions it may stop at various stages of the process. Naturally, in polymers with rigid chains and large intermolecular interactions, having high glass transition temperatures and existing as glasses under ordinary conditions, the early, primitive structural forms will 'freeze'. But at the same time, under adequate conditions accelerating structure formation these polymers will form perfect structures. On the other hand, polymers with flexible and not

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strongly interacting molecules (rubbers) covers this path quickly, but the final and probably equilibrium structural forms of these polymers are comparatively simple.

These are the band structures characteristic of any polymer in the highly elastic state¹⁰.

Figure 8. Sodium polystyrene sulphonate (M.W. 300,000) (a) freshly prepared solution, pH = 6; (b) 2 weeks after preparation, pH = 6

Of course, the rate of formation of the structures depends on a number of other factors as well, namely, the molecular weight, the regularity of structure and the degree of branching of the chains. For this reason different structures may not infrequently be observed to coexist within an ordinary

Figure 9. Sodium polystyrene sulphonate (M.W. 300,000): (a) 4 weeks after preparation, pH = 6; (b) after 6 weeks, pH = 6

specimen of a polymeric substance. An example is shown in *Figure 10* which is a photograph of partly-brominated gutta-percha, showing globules, fibrils and spherulites, i.e., the entire sequence of structures from the simplest to the highest form¹⁴. Hence, (owing to the stepwise, multi-stage nature of structure formation in polymers and the ready appearance and fixation of non-equilibrium structures) the conditions of formation influence the

Figure 10. Partly-brominated gutta percha (16.3% Br), out of chloroform solution at 50°C

appearing supermolecular structures not less, at any rate, than the nature of the polymeric molecules themselves. The flexibility of polymeric molecules, their intermolecular interaction, and, of course, their molecular weight and degree of branching are the factors which affect structure formation in a very general way. (The regularity of the macromolecules plays an essential part only during crystallization.)

But flexibility and intermolecular interaction are constant characteristics only in the case of pure polymers. In solutions and other multicomponent systems these characteristics vary widely. Therefore on polymerization in solutions, on separation of polymers from solutions on plasticizing and in mixtures of polymeric substances, the same polymer may form various types of structures depending on the influence of the medium. Perhaps the

Figure 11. Conformational coil-helix transition. (a) aqueous solution of sodium salt of poly-L-glutamic acid. (b) aqueous solution of poly-L-glutamic acid, pH = 4.5

Figure 12. Poly-L-glutamic acid out of aqueous solution, pH = 3.7. Specimen prepared by thermal attachment method, ($T = 45^\circ$)

Figure 13. Poly- γ -benzyl-L-glutamate out of chloroform solution

most typical are polyelectrolytes, especially weak acids, where, depending on the pH or salt composition of the solution, the undissociated flexible molecules which roll up into coils in acid media, can easily pass into drawn out charged chains in alkaline media, to form linear structures. An old and well-known example is polyacrylic acid which forms globules, and its alkali salts, which give typical linear structures¹. Other phenomena occur in solutions of polypeptides in which conformational coil-helix transitions occur within a very narrow pH interval. For example, the sodium salt of

Figure 14. Poly- γ -benzyl-L-glutamate out of dichloroacetic acid solution

polyglutamic acid is a strong electrolyte whose behaviour is quite analogous to that of sodium polyacrylate and which forms the same linear structures on aggregation of drawn-out charged chains. Such a structure is shown in *Figure 11*. However, when the solution is acidified to pH = 4.5, instead of globules, as is the case for polyacrylic acid, polyglutamic acid forms a fibrillar structure, a photograph of which is given in *Figure 11b*. Well-formed fibrils can be seen to have appeared approximately of the same size, about 200 Å in cross-section and 0.5 microns long. It is curious that comparatively perfect structures not only form in the solid polymer after evaporation of the solvent, but are already existent even in dilute solutions. An investigation of solutions containing 0.03% of glutamic acid, by means of the thermal

attachment method, showed the existence of well-formed aggregates containing several tens of molecules (*Figure 12*). Thus we see that conformational transitions sharply influence the formation of supermolecular structures. It is interesting that the reverse is also true, i.e., the formation of supermolecular structures promotes the transition of coils into helices.

These phenomena are typical not only of aqueous solutions. With glutamic acid esters such conformational transitions occur when polar solvents are substituted for non-polar ones and *vice versa*. *Figure 13* shows photographs of the structures of polybenzyl glutamate obtained from chloroform solution, where its molecules exist in the form of helices. The photographs in *Figure 14* are of the same polymer out of dichloroacetic acid solution, where the polymer exists in coil conformation. In the first case we see well-defined fibrillar structures, and in the second, shapeless formations. It can be seen how the order arising at the molecular level affects the formation of supermolecular structures. I would like to add that all the structural formations I have been talking about are amorphous, as is evidenced by the electron diffraction pattern¹⁵.

I have given only a few examples of the effect of the solvent on the formation of supermolecular structures owing to changes in conformation of the polymer molecules. Many more similar examples could be given, especially for crystallizing polymers for which the importance of selecting the correct solvent is widely known.

All this reduces to the fact that by using various solvents for polymers already obtained, or during polymerization, various structures can be obtained for the same polymeric substance. Of course, after removing the solvent, some of these structures will become non-equilibrium ones, but if the polymer is under conditions of low rates of structural transformations, these non-equilibrium structures will be practically stable. We again come to the conclusion that non-equilibrium states form easily in polymers, and that this is one of the primary factors hindering the establishment of direct relations between the structure of the polymeric molecules and the formation of supermolecular structures. (These relations are only of a very general nature.)

Finally, what interests us primarily in supermolecular structures is their influence on the properties of polymeric bodies. Having outlined the basic types of polymeric structures, we may consider that each of these types will have a definite corresponding complex of properties, of which mechanical properties are of the greatest interest. However, this seemingly quite self-evident proposition is not always true. Sometimes polymers of globular structure exhibit elastic properties, although in the globular state these properties would be expected to disappear. Usually, the larger the spherulites in crystalline polymers, the more brittle the polymeric material¹⁰. But this rule is not always valid. (There arises the question as to the causes of these invalidities and of the unambiguity of the relations between the supermolecular structures and the mechanical properties of polymers.)

The assumption that there exists a direct relation between the type of supermolecular structure and the properties of a material is connected with a very important condition. The structure of a material should remain practically unchanged until the specimen fails. But if structural transfor-

mations occur in the specimen during deformation, the structure at the moment of breakdown will not be that of the initial specimen, but that formed as a result of the mechanical influence to which the polymer was subjected. Evidently, in this case no correspondence can even be expected to exist between the initial structure and the properties at big deformations. These phenomena of structural transformations occurring during deformation are very typical of polymers.

An old example of structural transformation is the formation of a 'neck' on

Figure 15. Electron microscopic photograph of neck of polyethylene extended to 150%

deformation, described for the case of crystalline polymers some time ago by Karothers. (It is also observed in amorphous polymers with developed structures and is formally described as a phase transformation¹⁶.) The nature of this phenomenon remained obscure for a long time, but electron microscopy revealed that 'neck' formation is observed on a microscopic scale as well, and is actually a jumpwise transition from one supermolecular structure to another with a sharp interphasal boundary. I would like to remind you of the well-known example of polyethylene¹⁷ (*Figure 15*) where a sharp boundary can be seen between the isotropic and the oriented parts of the specimen. Next we see the formation of a 'neck' on deformation of a large spherulite of isotactic polystyrene (*Figure 16*) where a sharp boundary can

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also be discerned between the unchanged and the oriented portions of the spherulite. (In addition, secondary formations can be seen which have resulted from recrystallization of the oriented parts, and these are also separated by sharp boundary lines¹⁸.) Finally, an excellent example of jumpwise development of deformations and changes in structure is the

Figure 16. Optical photographs of necks of isotactic polystyrene crystallized from a melt and extended

extension of polyoxypropylene in the form of large spherulites¹⁹. *Figures 17 and 18* show the deformation pattern of this polymer in different scales, revealing a sharp transition from one structure to the other. But such phenomena are not only observed for crystalline polymers and linear structures. Comparatively recently we observed similar phenomena during the deformation of

Figure 17. Extended sample of polyoxypropylene

a polymer with a globular structure⁷. Fluorine-containing rubbers possess a typical globular structure, the globules being regular in shape and close in size. The existence of a globular rubber is in itself surprising, because as long as a polymeric molecule is in globular form it should be devoid of all the typical properties of a polymer. However, when such a rubber deforms, its globules change gradually to linear conformations. In this process the globules themselves are not deformed and there is a sharp boundary between them and the newly formed oriented linear part, this boundary being just as sharp as in the deformation of the spherulites of crystalline polystyrenes. *Figure 19* is a photograph of undeformed rubber, and *Figure 20* is the same rubber stretched, at different magnifications. Here we distinctly

Figure 18. Different sections of an extended specimen of polyoxypolypropylene

see the picture of transition of the globules into oriented structureless filaments. The display of elastic properties in this case is related to destruction of the globules. We again come up against the same phenomenon, viz., breakdown of the initial structure and jumpwise transition to an entirely different type of structure.

Figure 19. Fluorine-containing SKF-26 rubber out of acetone solution

Thus we must distinguish between two types of phenomena in polymer deformation. In the first, the initial structure is preserved up to the moment of failure. When this is the case the general properties of the material can be judged from its structure. In the other type the structure changes sharply during deformation and the relation between the initial structure and the properties of the material is obliterated. Evidently, structural transformations are possible during deformation only when the material possesses sufficient molecular mobility, and for this the material must be at a temperature above glass transition. Below this temperature structural transformations no longer occur and the initial structure is preserved right up to the moment of failure of the specimen. We again see how great is the part played by the transition temperatures and the physical state of the polymeric substance in the transformation of supermolecular structures. Below the glass temperature various non-equilibrium structures become fixed, and do not change

even when subjected to extraneous mechanical influences. Above this temperature supermolecular structures may change into one another both spontaneously and due to external forces.

We are accustomed to the idea that major deformations in polymers are always due to changes in shape and shifting of the individual polymer molecules. That is why, even when the polymer possesses a supermolecular structure, one usually attempts to explain such deformations by the fact

Figure 20. Extended film of fluorine-containing SKF-26 rubber out of acetone solution

that some unordered 'amorphous' portion is left in it. Meanwhile it is essential to know the contribution of the supermolecular structures themselves, especially when they consist of long, thin and sometimes also sufficiently flexible fibrillar formations. Are there cases where the deformation properties are not directly related to the properties of the separate molecules, but only to those of the supermolecular formations?

Recently we were successful in obtaining sufficiently-perfect, large-spherulite structures of polypropylene which exhibited the ability to undergo big deformations much below the glass temperature, which for polypropylene is -30°C . Already at -40° both atactic propylene and polypropylene possessing a fine spherulite structure are ruptured without perceptible elongation. Meanwhile specimens with large spherulites show ultimate elongations of 150–200% at temperatures of -40° to -60°C . Even at the temperature of liquid nitrogen the deformation may be as high as 120 or 140%²⁰.

It is quite natural that at such temperatures, considerably below the glass transition temperature and the brittle point (corresponding to the last dielectric loss maximum), there is no molecular mobility. The development of deformation cannot be related to the flexibility and displacement of

individual macromolecules, or, which is the same, to the presence of any amorphous portions. Another proof of this is the brittleness of amorphous polypropylene at these temperatures. Hence, big deformations in crystalline propylene with a very perfect structure can be related only to the shift of large structural elements, these being well-formed supermolecular structures.

Figure 21 shows photomicrographs of the consecutive stages of extension

Figure 21. Consecutive stages of development of big low-temperature deformations and x-ray photograph of specimen extended to 120% at -55°C

of large-spherulite propylene with spherulites 80–150 microns in size. Both stretching and photographing were done at -55°C . The same figure shows an x-ray photograph of a specimen extended to 120% at -55°C and photographed at the same temperature. Though extended to 120% the specimen showed no texture on the x-ray photograph! We found that deformation involves the displacement of blocks so large that their displacement did not even cause any texture to appear.

Thus we now have two extreme cases, namely, rubbers at high temperatures where deformations are due almost entirely to changes in conformation and displacement of macromolecules, and very-well-formed structures at low temperatures, where the deformations are due solely to the displacement of elements of supermolecular structures. The majority of real polymeric materials serve under intermediate conditions, and the current problem is to determine the contribution of each of the described phenomena to the general properties of the materials.

To conclude, it seems to me that the extraordinary simplicity of rise and fixation of non-equilibrium states in polymers excludes the existence of direct and unambiguous relations between the structure and composition of macromolecules and the appearance of supermolecular structures. Such relations may be only of a very general nature and can be considered only with reference to the physical state of the polymeric substance.

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