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U.D.C. 541.6:541.64

THE PART PLAYED BY STRUCTURAL PHENOMENA IN DETERMINING THE PROPERTIES OF POLYMERS†

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We have all been accustomed to relating the properties of polymers in the first place to the chemical composition, structure, and dimensions of their molecules. The detection of structural formations in a wide variety of polymers, however, is making it necessary to devote increasing attention not only to the actual molecules of the polymers but also to their mutual arrangement and packing. The part played by these structural formations in determining the properties of polymers is often as great as in the case of metals, silicates, and other solids.

Despite the very great variety of morphological forms, it is now possible to distinguish the chief types of structural formation in polymers, in both crystalline and amorphous states.

The simplest type consists of the globular structures, formed by one or many polymer molecules, coiled up into spherical particles. This type of structure is characteristic of amorphous polymers in the vitreous state, although almost any polymer can be obtained in the form of amorphous globules. The formation of globules is accompanied by the loss of an appreciable number of the properties characteristic of linear molecules, and globular polymers are generally brittle and are broken by mechanical shock. Globular structures may also be present, infrequently, in elastic polymers. In this case the globules uncoil on deformation, and the polymers exhibit elastic properties, but have a reduced strength. Thus this type of structure does not favour good mechanical properties. Typical globular structures for polyacrylic acid, polyvinyl chloride, and fluorocarbon rubber are shown in Fig.1. The mechanism of formation of these structures

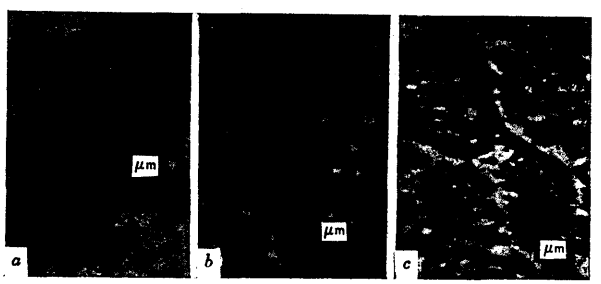


Fig.1. Globular structures:
a) polyacrylic acid; *b*) polyvinyl chloride; *c*) SKF-26 fluorocarbon rubber.

† Paper presented at the International Symposium on the Chemistry of Macromolecules, Prague, 1965.

was the subject of a paper presented at the Symposium on Polymers in Wiesbaden and has been described in a number of papers[1-7].

Increased rigidity of the molecular chains or decreased intramolecular interaction produces a type of structure consisting of straight chains, which are, however, aggregated into bundles. These structural formations consist of tens or hundreds of chains and are the simplest structural units from which all subsequent types of structure are formed. In amorphous glasses, long thin bundles of chains may be formed, and these, as a result of subsequent aggregation, may form dendrites with regular shapes and very large dimensions of several hundred microns. This type of linear amorphous structure is illustrated in Fig.2, which shows the sodium salt of polyacrylic acid and the bundles and dendrites of the copolymer formed by acrylic acid and diethyl vinylphosphonate[2,8].

In the elastic state in amorphous polymers, another very typical type of structure is produced — banded structures consisting of formations which now have much greater dimensions. These structures are characteristic of almost any polymer in the elastic state, but because of experimental difficulties they were detected only comparatively recently. Fig.3 gives as examples the structures of natural rubber in the amorphous state, the copolymer of butadiene and styrene, and vinyl octanoate[9-11]. These banded structures are apparently secondary formations. When specimens are prepared for electron-microscope study at very low temperatures or in the initial stages of crystallisation, it is also possible to see the formation of the simplest fibrillar structures in rubbers (Fig.4).

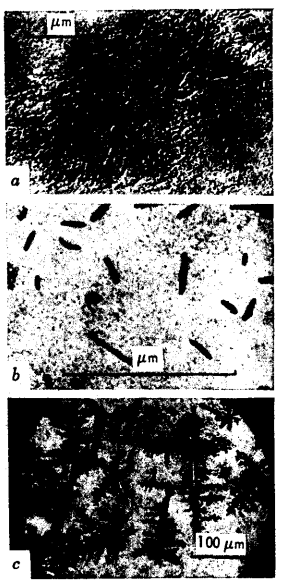


Fig.2. Fibrillar structures of amorphous polymers:
a) rods formed by the sodium salt of polyacrylic acid; *b*) bundles formed by the copolymer of acrylic acid and diethyl vinylphosphonate; *c*) dendrites of the same copolymer.

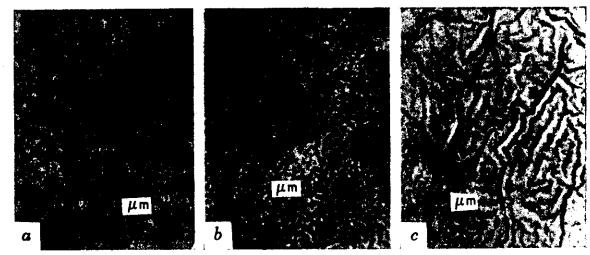


Fig.3. Banded structures:
a) natural rubber; *b*) butadiene–styrene rubber; *c*) vinyl octanoate.

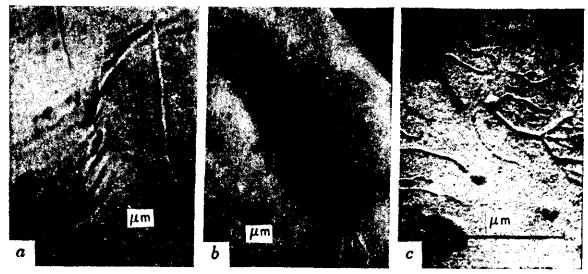


Fig.4. Simplest fibrillar structures in rubbers, produced by crystallisaton (*a* and *b*) and at low temperatures (*c*).

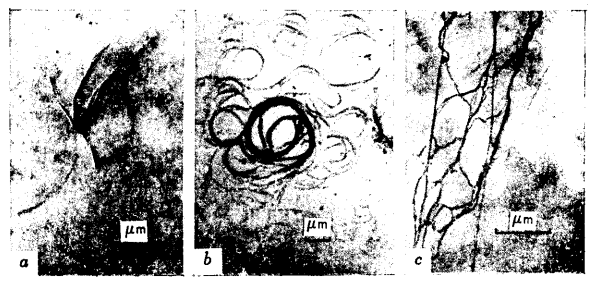


Fig.5. Bundle-like structures in crystalline polymers:
a) polypropylene; *b*) polyamide copolymer; *c*) polyethylene.

As in amorphous polymers, the simplest structural formations in crystalline polymers are bundles of chains. Fig.5 gives examples of such formations in polypropylene and a polyamide–polyethylene copolymer[12]. Further combination to give more complex formations may take place by two different mechanisms: the formations may combine by the familiar mechanism first discovered by Keller[13], to give planes which form spherulites and single crystals, or they may combine to give larger linear formations or fibrils which undergo further aggregation, again with the formation of spherulites and single crystals. Fig.6 shows typical spherulites and crystals of lamellar type formed by isotactic polystyrene[14]. Formations of this type given by polystyrene have been well studied. Typical fibrillar formations are also illustrated in Fig.7, which shows spherulites and crystals of polypropylene[15].

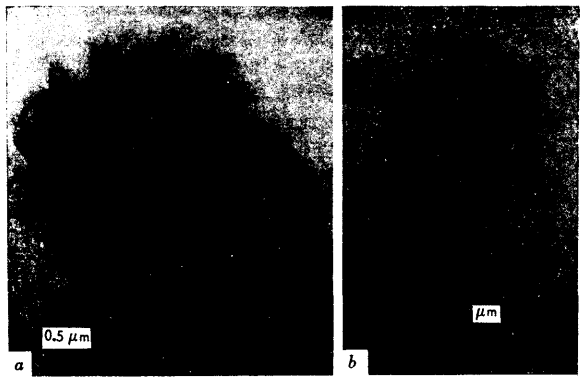


Fig. 6. Spherulite (*a*) and crystals (*b*) of the lamellar type of isotactic polystyrene.



Fig. 7. Spherulites (*a* and *b*) and crystals (*c*) of polypropylene with fibrillar structure.

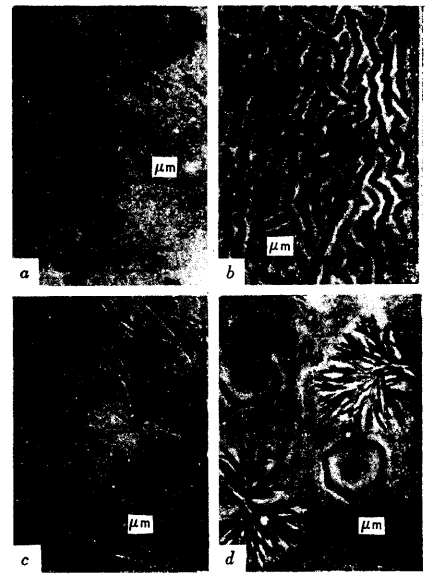


Fig. 8. The four basic structural forms observed in polymers:
a) globular structures of polyacrylic acid; *b*) banded structures in amorphous butadiene–styrene rubber; *c*) fibrillar structures of polypropylene; *d*) spherulites and crystals of isotactic polybutylene.

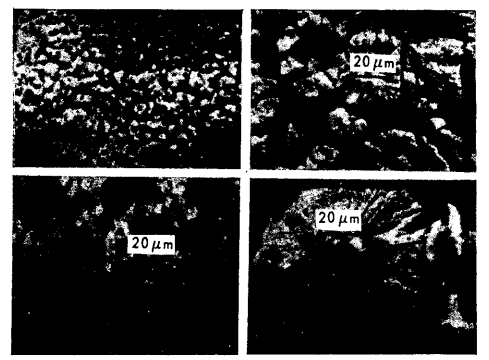


Fig. 9. Spherulitic structures of various dimensions in gutta-percha.

Thus among the great variety of structural forms in polymers, it is possible to distinguish clearly four basic types of structure: globular structures, usually produced in amorphous polymers obtained by polycondensation; banded structures, typical of all polymers in the elastic state (rubbers); fibrillar structures, characteristic of extensively ordered amorphous addition polymers and the initial stages of crystallisation; and finally the large structural formations in crystalline polymers — spherulites and crystals. The four characteristic types of polymer structure are illustrated in Fig. 8.[16]

It can now be confidently stated that the formation of globular and coarsely-crystalline structures has an unfavourable influence on the production of satisfactory mechanical properties. The coiling of linear chains into globules usually leads to the loss of elastic properties, and the mechanical heterogeneity of coarsely-crystalline polymers leads to the ready formation of cracks and to premature breakdown. The formation of simple fibrillar structures is always favourable. Banded structures have as yet been little studied, but they apparently occupy an intermediate position. Thus decrease in the dimensions of coarsely-crystalline formations and uncoiling of globules with conversion into linear formations should lead to an improvement in mechanical properties. The influence of the dimensions of the crystalline formations can be illustrated for the case of gutta-percha. The dimensions of the spherulites produced can be readily altered by altering the thermal conditions of crystallisation. Fig. 9 shows photomicrographs for gutta-percha specimens with spherulites of different dimensions, and Fig. 10 shows stress–tensile strain plots for the same specimens. It can be seen that merely by decreasing the dimensions of the spherulites it is possible to increase the tensile strength and elongation on rupture several times over[17-20].

By altering the conditions of the preparation, Slonimskii[21] was able to convert the globular form of the polyester of isophthalic acid and phenolphthalein into a fibrillar form, with a corresponding marked change in the mechanical properties. Fig. 11 and the Table give respectively

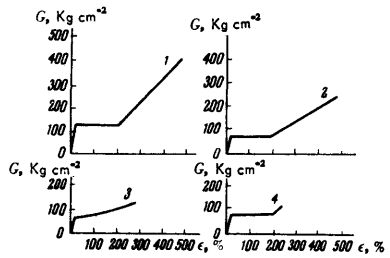


Fig. 10. Stress–tensile strain relations for the gutta-percha specimens whose structures are shown in Fig. 9.

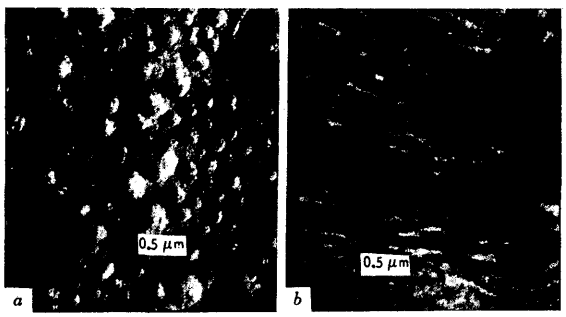


Fig. 11. Globular (*a*) and fibrillar (*b*) structures of the polyester formed by isophthalic acid and phenolphthalein.

TABLE. Properties of the polyester formed by isophthalic acid and phenolphthalein, with globular and fibrillar structures.

Property	Globular	Fibrillar	Property	Globular	Fibrillar
Molecular weight	28 000	28 000	Elongation at rupture, %	10—20	50—80
Softening temperature, °C	270	290	Specific impact strength,		
Tensile strength, Kg cm^{-2}	640	740	Kg cm cm^{-2}	2—3	6—10

photomicrographs of the structures and the mechanical characteristics of the linear and globular polyesters. These examples show that structure may have a considerable influence on mechanical properties and that it is important to be able to control the structure[17-21].

The simplest problem in this field is possibly the control of the dimensions of the coarsely-crystalline formations or spherulites. Spherulitic structures are typical of most readily-crystallising polymers, and there are now several examples of control of this type. Firstly, we have the introduction of synthetic crystallisation nuclei, which act as centres for the formation of spherulites. The greater the quantity of such centres introduced, the smaller will be the dimensions of each spherulite. The dimensions of the spherulites can also be altered by thermal treatment of melts to alter the number of natural nuclei. In this case, however, recrystallisation phenomena with consequent aging of the polymer material are possible. Synthetic nuclei make it possible not only to alter the dimensions of structural formations, but also to preserve them, with a consequent increase in the stability of the material[22-25].

As an example of the action of synthetic nuclei, Figs. 12 and 13 give respectively the structures and deformation curves for pure isotactic polystyrene and for polystyrene containing indigo particles to act as nuclei. Analogous behaviour is shown by many and possibly all crystallising polymers capable of forming structures having large dimensions[24].

It is also possible to alter the dimensions of the structural formations, and hence the properties, by introducing low-molecular compounds, which act as surface-active

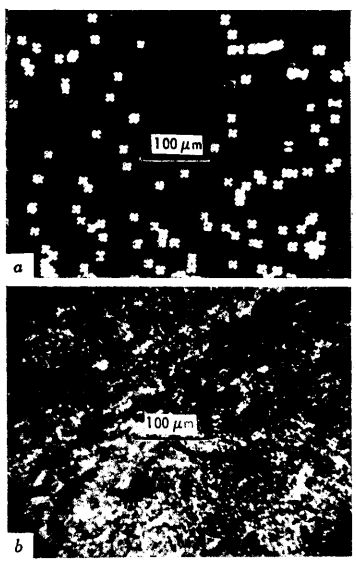


Fig. 12. Structure of specimens of isotactic polystyrene: *a*) pure; *b*) containing indigo.

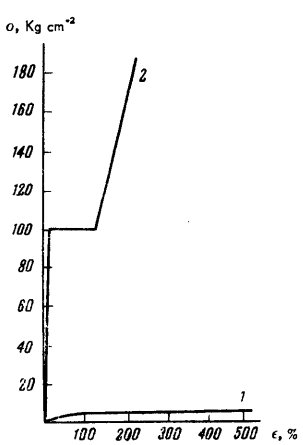


Fig. 13. Deformation curves for the elongation of specimens at 110°:
1) pure isotactic polystyrene; 2) isotactic polystyrene containing indigo.

substances. These are sorbed on the surface of the structural formations, and the dimensions and shapes of the latter are altered in a fashion analogous to that familiar for crystals of low-molecular substances. Fig. 14 gives photographs of the spherulites for nylon 66 with and without the addition of 1,4-dimesidinoanthraquinone. We see again the sharp change in structure, again accompanied by a change in properties[26]. It must be remembered, however, that low-molecular substances introduced into crystalline polymers may produce a quite different effect, particularly when added in comparatively large quantities. By distributing themselves over the interfaces between the simplest structural formations, for example bundles of chains or fibrils, they increase the mobility of the latter and lead to the development of brittle structures. Fig. 15 shows photographs of the structures of pure isotactic polystyrene and polystyrene containing 20 vol.% of cetyl chloride.

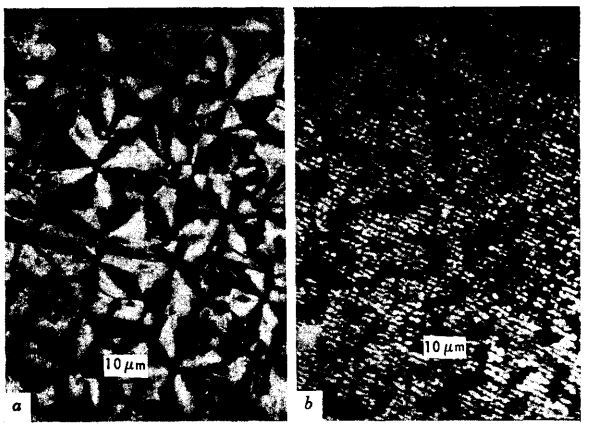


Fig. 14. Structure of nylon 66: *a*) pure; *b*) containing 1,4-dimesidinoanthraquinone.

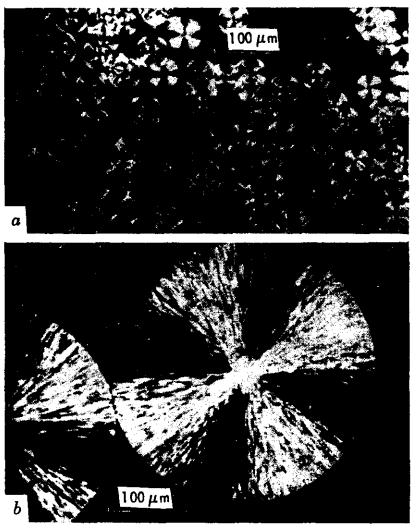


Fig. 15. Structure of isotactic polystyrene: *a*) pure; *b*) containing cetyl chloride.

Brittle spherulites are produced and the specimen becomes weak and brittle. This is why attempts to plasticise crystalline polymers by means of the usual plasticising agents often leads to the opposite of the expected results — the production of brittleness in the specimens being plasticised[27].

Mention may be made of the grafting of polymers as a means of controlling structures; this was described at the previous symposium in Paris[28]. The grafting of any other polymer generally hinders the formation of higher structures, whereas it does not prevent the development of simpler structures, more favourable for the production of the required mechanical properties. We shall not consider this question in more detail.

Up to the present we have dealt only with physical methods for influencing structure formation processes. Complete change from the most disordered structures to the most perfect structures can of course be achieved by changing the structure of the actual polymer chains, and this subject will be considered later in this paper.

Up to the present we have been discussing isotropic structures. In nature and technology, however, a very important part is played by anisotropic polymeric formations — fibres and fibrous materials. Most synthetic fibres are obtained by elongating originally isotropic or almost isotropic fibres. To trace the origin of oriented structures, it is extremely important to know whether relationships exist between the structure, and hence the properties, of oriented fibres and the structure of the original material from which the fibre is prepared by elongation. Orientation, particularly in crystalline polymers, usually takes place abruptly, with the production of so-called "necks". It was observed at an early date[29] that this process occurs as a phase transformation. It might be suggested that the production of a "neck" is accompanied by complete breakdown of the structures which existed in the isotropic polymer and the production of completely new structures in an oriented state. It was recently shown, however, that a direct relationship exists between the original structure and the structure produced on orientation. When a film of crystalline polymer exhibiting a spherulitic structure (for example polypropylene) is extended, the abrupt formation of an oriented polymer is readily observed. If observations are made of individual spherulites, it can be seen that they are preserved in the extended film. They are usually difficult to observe in fibres, since after elongation they become very long and fine, but they can sometimes be readily seen. Fig. 16 shows the conversion of a polypropylene spherulite into the oriented state[30]. It can be clearly seen that the spherulite is preserved after orientation. It can be shown that these elongated spherulites are only pseudomorphs; the interface between the spherulites is preserved, but not their internal structure. If, however, this oriented film is very carefully heated to a temperature several degrees below the melting point of the crystalline polymer, it contracts and returns almost completely to its original dimensions. In the process, the original spherulites are also restored. Thus the elongation of the spherulites, even when it takes place with the formation of a "neck", may be a reversible process. This phenomenon of the reversible deformation of large crystalline formations has been demonstrated for a number of materials and is apparently fairly common[17,31]. From this it follows that the simpler structural elements making up the spherulites or crystals remain unchanged during orientation and that, moreover, they may preserve

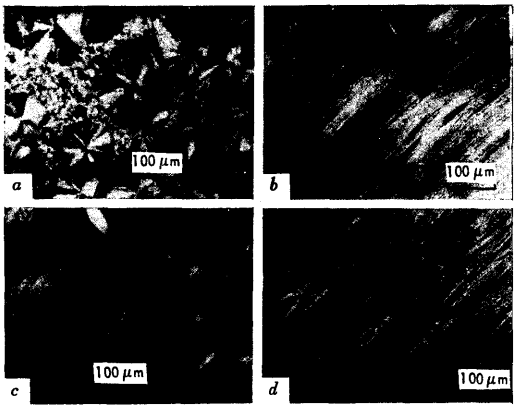


Fig. 16. Change in the structure of polypropylene during extension: *a*) original specimen; *b*)–*d*) extended films.

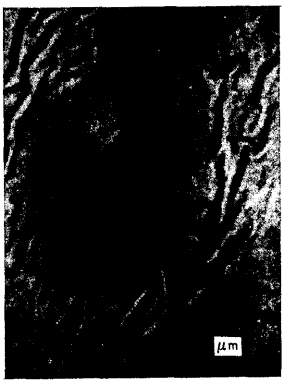


Fig. 17. Conversion of banded structures into crystalline fibrils in polychloroprene.

their mutual arrangement. This phenomenon indicates essentially that large reversible deformations may take place in crystalline polymers without fusion, merely as a result of mutual displacement of the bundles of chains or fibrils.

This phenomenon shows that a close relationship exists between the structures of fibres and the original isotropic materials, and that the structure of fibres begins to be formed even before their orientation. The influence of the structure of fibres on their mechanical properties has been studied for many years, but always on the assumption that the actual orientation process determines the complete structure of the oriented polymer. It is found that the structure of fibres begins to be formed much earlier, even in the isotropic state, and possibly even earlier in melts or solutions, or directly in the polymerisation process! The fact that the structure of oriented fibres influences their properties is generally accepted, and need not be mentioned further.

Thus the development of the properties of solid polymers is closely related to structure formation. This naturally leads to the question of the extent to which the phenomena of structure formation are encountered in elastic polymers and finally the question of where and how the structures begin to be formed — whether they are produced only in the solid state or begin to be produced in the melts or solutions or possibly directly in the processes of polymerisation and polycondensation.

Mention has already been made of the discovery of banded structures in typical rubbers. Similar structures have also been found to be typical of other polymers in the elastic state. The most perfect structural forms in elastomers can be observed only at low temperatures. In crystallising rubbers, however, it is possible to observe the complete change from banded structures to crystalline fibrils and large crystalline formations — spherulites and single crystals. This change has already been described for polybutylene[28]. The conversion of bands into crystalline fibrils is typical, and examples of this change are given in Fig. 17 for polychloroprene. It can be seen that crystallisation is not the original source of order in polymers, but that, on the contrary, ordering in the amorphous state is a necessary prerequisite for crystallisation, which is the last stage in the ordering process. We are thus faced with the question of how the properties of an elastomer change on going from the simplest banded structures to crystalline fibrils and then to spherulites and single crystals.

We are accustomed to the idea that crystallisation always leads to a decrease in elastic properties and to a decrease in elongation. Combined study of properties and structure shows, however, that the earliest stages in crystallisation do not always lead to a decrease in elongation. The production of well-formed fibrils apparently always leads to an increase in strength, and, for a small change in the modulus of elasticity, to an increase in elongation at rupture. We have the effect of "self-reinforcement" which is found in rigid polymers and was first observed clearly for polycarbonates[32,33]. The elastic properties are lost not when the crystalline fibrils are produced but only when the coarsely-crystalline structures — primarily spherulites — are formed. An example of the change from amorphous to crystalline structures is provided by the series of copolymers of ethylene with vinyl acetate. Pure polyethylene has a clearly defined spherulitic structure. The copolymer containing more than 25% of vinyl acetate is a typical amorphous elastomer with a banded structure. With increase in the concentration of vinyl acetate, the crystallinity of the copolymer decreases and the elongation increases, but the strength passes through a maximum. This maximum corresponds to a stage where the crystallinity of the copolymer is still high (Fig. 18). The structures of pure polyethylene and the completely amorphous copolymer, and the structure of the copolymer with maximum elongation, are shown in Fig. 19. The copolymer with maximum elongation shows a clearly defined fibrillar structure and is a transparent typical resilient elastomer.

So far these transitions have been little studied, but even now it can be stated that a definite degree of ordering is necessary for the production of effective mechanical properties in elastomers. The degree of ordering produced in amorphous banded structures is inadequate and a fundamental problem in the production of structures in rubbers is to increase the degree of ordering until well-defined fibrils are formed, both by the use of fillers and by stereospecific polymerisation and copolymerisation. Extremely characteristic phenomena are observed in thin polymer films. Fig. 20 shows the structure of isotactic

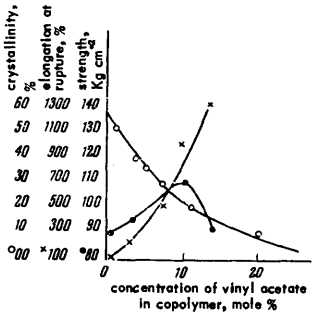


Fig. 18. Composition dependence of the properties of the copolymer of ethylene and vinyl acetate.

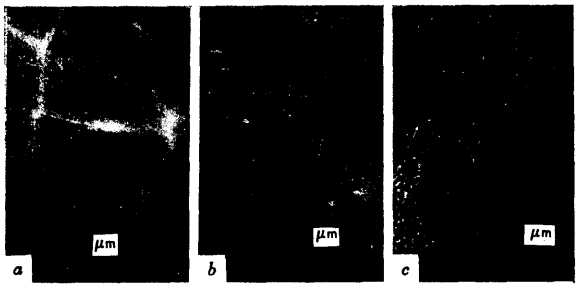


Fig. 19. Structures of pure polyethylene (*a*), the copolymer of ethylene and vinyl acetate at maximum elongation (*b*), and the amorphous copolymer of ethylene and vinly acetate (*c*).

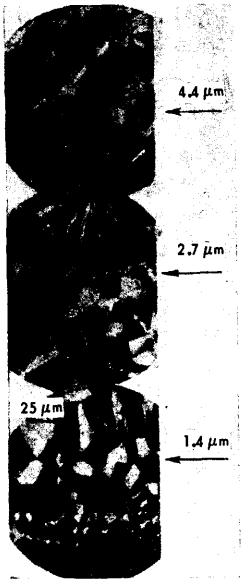


Fig. 20. Change in the structure of isotactic polypropylene with change in film thickness from 1.4 μm to 4.4 μm.

polypropylene in a layer of adhesive whose thickness is varied from several tenths of a micron to one micron. It can be seen that, with decrease in the thickness of the film, the dimensions of the spherulites at first increase, after which, when a definite critical thickness has been reached, they disappear and are replaced by fibrillar structures. Thus for a number of crystalline polymers at least[34], there exists a definite limit of thickness below which large crystalline formations cannot be produced. Thus in the thin polymer layers (produced on surfaces), with thicknesses of several microns, in foams, in reinforced systems, and in systems with high concentrations of fillers, either large or fibrillar structures may be produced depending on the thickness with corresponding consequences for the development of mechanical properties.

Thus detailed study has shown that structure formation is not exceptional but is a common phenomenon for all types of rigid and elastic polymers. It has also been shown that the influence of structures on mechanical properties is important and must always be taken into account.

Where does the formation of structures begin, however? In very dilute solutions polymers are probably present in the form of individual molecules. Similarly it may be confidently assumed that in melts at sufficiently high temperatures all the structures disappear and the polymer is converted into a system of disordered entangled molecules. The change from these infinitely dilute or molten systems to rigid structured polymers, however, may take place over a fairly wide range of temperatures and concentrations. Thus for each polymer it is necessary to estimate the concentrations or temperatures at which structures begin to be produced, since the start of structure formation corresponds to the start of the development of properties.

The fact that very rapid crystallisation takes place in a number of polymers indicates the existence of a fairly high degree of order in the melt. Papers presented at the previous Symposium in Prague gave information on the state of polymers in melts, based on electron diffraction studies[35,37] which showed the existence of a high degree of order in the arrangement of the polymer molecules. The existence of ordered structures in melts is also indicated by the adsorption properties[36] and by the fluidity of the melts[38,39]. Possibly the most graphic demonstration of the existence of structures in the melts is obtained by heating a coarsely-crystalline polymer above its melting point under the microscope and then cooling the melt. In this experiment the microscopic structure of the specimen being studied is very often completely restored. Photographs of polypropylene before and after fusion (with heating to a temperature 20 deg above the melting point) (Fig. 21) are almost indistinguishable. The same spherulites are produced at the same crystallisation centres. This "memory" is preserved in molten polypropylene on heating to a temperature 20–25 deg above its melting point. If the specimen is heated to higher temperatures, however, the number of nuclei gradually begins to decrease and the number of spherulites decreases, with a corresponding increase in their dimensions. Finally, after a definite temperature has been reached (for polypropylene this temperature lies 150–200 deg above the melting point) all traces of the original structures preserved in the melt disappear and the entire crystallisation picture changes sharply. The same polypropylene specimen, after being heated to 350°, has a finer spherulitic structure (Fig. 22). It can be seen how the foundations for the structures are



Fig. 21. Structure of polypropylene film before (*a*) and after (*b*) fusion.



Fig. 22. Structure of polypropylene film after fusion at 350°.

created in the melt and how the temperature conditions in the melt determine the structure and hence the properties of the polypropylene specimen. There is thus no doubt that structures exist in molten polymers although up to the present no one has been able to observe these structures directly.

Quite recently, however, it has been possible to observe directly the formation of structures in solutions. By using as solvents substances which show absolutely no tendency to crystallise and which form glasses on cooling, it is possible to obtain solutions of polymers in the vitreous state. It is highly probable that, when a solution is converted into a glass, it retains the structure which it had in the liquid state. By breaking the glass and taking a replica from the surface of the fracture, it is possible to study the structure of the solutions. The electron-microscope photographs of replicas obtained from 0.1% and 0.5% solutions of poly-α-butylene in vitreous rosin (Fig. 23) show the start of structure formation at a concentration of 0.1% and clearly defined structures at 0.5%.[40]

These results were confirmed by a different method. By dissolving a polymer in a solvent with a low critical point and heating the solution above the critical temperature, we

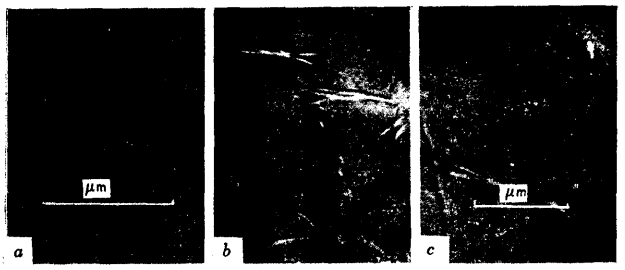


Fig. 23. Replicas from solutions of poly-α-butylene in vitreous rosin at concentrations of 0% (*a*), 0.5% (*b*), and 0.1% (*c*).

obtained a solution in a gas, with the same density as the original liquid. In this case also it may be assumed that the structure of the solution will not change significantly. If we break a heated ampoule containing such a solution in a vacuum, we expand the gas without the production of an interface and scatter the species present in the solution throughout the entire volume of the vessel. If we place at the foot of this vessel pieces of gauze with the thin carrier films usually employed in electron microscopy, we can collect these particles and examine them in the electron microscope. An example is provided by a solution of polybutylene in propane, heated to 115°. This experiment gave results completely analogous to those described above for vitreous solutions[41].

In the same way it is possible to follow the formation of globular structures in solutions. As noted above, almost any polymer can be obtained in the globular state from extremely dilute solutions. With increase in the concentration of solutions containing coiled molecules, however, aggregation of the molecules also begins. In the case of globular formations this leads to an increase in the dimensions of the globules, since the aggregating globules combine together to form larger globules containing not one but an appreciable number of polymer molecules. Rearrangement of the globules into linear structures may take place only at comparatively high concentrations. Fig. 24 shows photographs obtained for solutions of isotactic polyacrylic acid in liquid ammonia with a small quantity of water above the critical temperature. At a concentration of 0.05% each globule contains 1–4 polymer molecules, with increase in the concentration to 0.5% the number of molecules in each globule increases to between 9 and 70, and at a concentration of 1% the number of molecules in each globule increases to 120 and rearrangement to a linear structure begins.

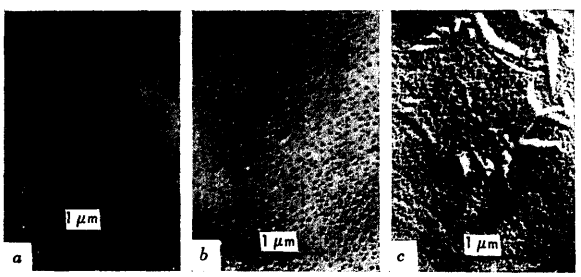


Fig. 24. Structure of isotactic polyacrylic acid in liquid ammonia solution at concentrations of 0.05% (*a*), 0.5% (*b*), and 1% (*c*).

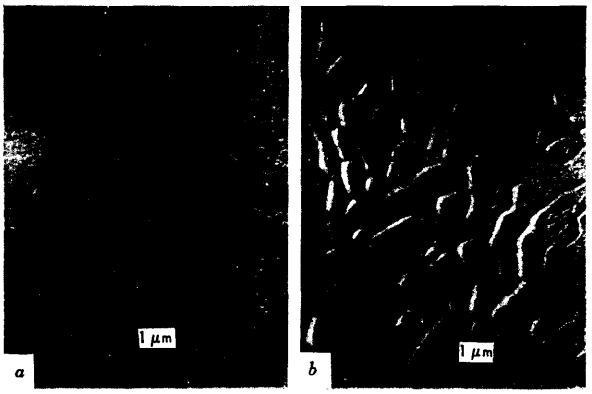


Fig. 25. Structure of polystyrenesulphonic acid in liquid ammonia solution at concentrations of 0.2% (*a*) and 1% (*b*).

Fig. 25 shows analogous photographs for polystyrenesulphonic acid; in 0.2% solution each globule contains between one and twenty molecules, whereas at a concentration of 1% the structure is completely fibrillar.

Thus these few results show that structures are produced in solutions at low concentrations and that concentrated solutions naturally contain structures which are extremely similar to the simplest types of structure found in solid polymers. Nucleation of the structures and hence the start of the development of properties takes place even in comparatively dilute solutions and hot melts.

It is also possible to make the more far-reaching assumption that structures may be produced directly in the polymerisation process. Several years ago the production of coarse fibrous structures was observed on the surface of heterogeneous catalysts during the polymerisation of ethylene and propene[42,43] and the polymerisation of a number of solid monomers[44]. When the temperature of the experiment exceeds the glass temperature of the polymer, however, there is always a danger of molecular rearrangement and the formation of structures as a result of secondary processes. The only polymerisation experiment free from criticism is one in which the monomer and polymer are solid and are at a temperature lower than the glass temperature. Such experiments were carried out recently by polymerising solid monomers directly in the electron microscope, where the electron beam itself initiated the polymerisation. The materials studied were phenylmethacrylamide, *p*-biphenylylmethacrylamide, and sodium acrylate. Fig. 26 shows electron-microscope photographs of polyphenylmethacrylamide and polybiphenylylmethacrylamide obtained by polymerising the solid monomers, and Fig. 27 shows an electron-microscope photograph of sodium polyacrylate obtained under the same conditions.

It can be seen that, instead of the continuous thin film which should have been obtained for regular polymerisation throughout the entire volume of the monomer, typical bundle-like structures are in fact produced, accompanied by a small number of globules. The actual polymerisation process is readily observed under the electron microscope and provides an example of the direct production of structures in the polymerisation process. It is as yet difficult to say anything regarding the extent of such phenomena, but it is now known that they are possible. If, however,

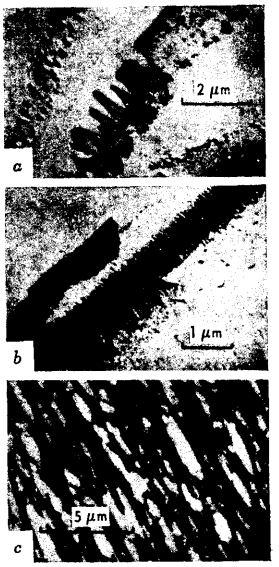


Fig. 26. Structures of polybiphenylylmethacrylamide (*a*) and polyphenylmethacrylamide (*b* and *c*) obtained by polymerisation of the solid monomers.

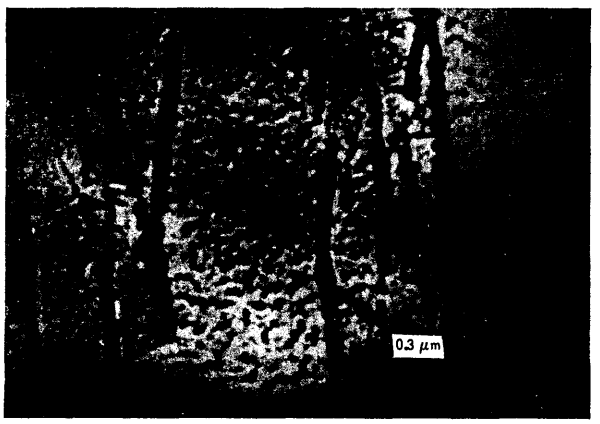


Fig. 27. Structure of sodium polyacrylate obtained by polymerisation of the solid monomer.

structures can be formed directly in the polymerisation process, this can and must influence the polymerisation process itself, particularly the free energy changes during polymerisation. The total free energy change is always equal to the sum of the free energies of conversion of the monomer into the polymeric molecules and the formation of structures from individual polymeric molecules. In most cases, when the heats of polymerisation are large and the polymerisation–depolymerisation equilibria are displaced towards very high temperatures, the free energy changes in structure formation are unimportant. When the heats of polymerisation are small, however, as for example in the polymerisation of rings, structure formation may play an important part and there may even be cases

where polymerisation becomes possible only when structure formation takes place. Several cases are known where polymerisation takes place only when the resulting polymer crystallises and does not take place when the polymer cannot crystallise (α-methylstyrene, α-pyrrolidone, and α-piperidone[45-47]. Crystallisation is most favourable for displacement of polymerisation–degradation equilibria towards polymerisation, but it may be assumed that very strong interaction between the chains and the formation of amorphous structures may be sufficient. Processes such as the polymerisation of nitriles may be possible only as a result of structure formation by the polymeric chains with conjugated double bonds[48].

We cannot deal in detail here with the part played by all structural phenomena in polymerisation and we would merely mention that structure formation also influences the kinetics of polymerisation, leading to the characteristic phenomena of autocatalysis[49], that phase transformations in solid monomers are responsible for very rapid polymerisation in the solid phase[50-54], and that polymerisation in complexes makes it possible to carry out a number of polymerisation processes which are not undergone by the pure monomers[55-59]. An equally important factor is the influence of the state of aggregation of the monomer on the structure of the resulting polymeric molecule. Thus in the polymerisation of diketen, initiated by metallic magnesium, two different isomeric forms of the polymer may be obtained, depending on the state of aggregation of the monomer. Polymerisation of solid monomer obtained by the joint condensation of the vapours of the monomer and metallic magnesium at a temperature several degrees below the melting point gives a polyether. Polymerisation at or above the melting point, however, gives a different isomer — a poly-β-diketone[60]. Similarly, acetaldehyde polymerised in the solid state in the presence of metallic magnesium, introduced into the monomer by joint condensation of the vapours, gives polyacetal. When the same system is polymerised above the melting point, polyvinyl alcohol is formed[61]. In both cases the difference between the polymerisation temperatures above and below the melting point amounts to only a few degrees. The formation of the different polymeric isomers is undoubtedly determined entirely by the state of aggregation of the monomer. Thus it is also necessary to make allowance for the part played by structural phenomena in the polymerisation stage, particularly in the case of polymerisation in the solid state and in those cases where structures are produced directly in the polymerisation process. The most general conclusion to be reached from the foregoing is that structures are extremely common in polymers of all types and that structures are produced at very early stages in the formation of solid polymers in solutions, in melts, and in the polymerisation process. If this is correct, polymers in most cases cannot be regarded as homogeneous systems like ordinary liquids. The occurrence of structure formation implies the existence of interfaces, differences in densities, and irregular distribution of mechanical stresses. This is related to the influence of the structures on mechanical properties. The heterogeneity of polymers should also influence their other properties, and particularly chemical reactions involving the polymers and the processes involved in the swelling and plasticising of polymers.

In fact, low-molecular substances introduced into a polymer may be distributed in different ways. The most usual result is regular distribution of the substance throughout the entire bulk of the polymer, corresponding to true dissolution of the low-molecular substance in the polymer. This leads to corresponding changes in mechanical properties and particularly to a decrease in the glass temperature, proportional to the mole fraction[62] or volume fraction[63] of the added plasticiser.

In polymers showing structure formation, however, another possibility arises. If the low-molecular substance (plasticiser) is insoluble in the polymer but wets it, it may be distributed along the interfaces between the structures, acting as a lubricant between them and thus increasing the mutual mobility of the individual elements of the structure. Very small quantities of plasticiser may then produce very marked effects, but at the same time saturation should take place rapidly and addition of excess plasticiser will not be accompanied by a further decrease in the glass temperature or modulus of the polymer. These phenomena, described as inter-bundle or inter-structural plasticising, have been detected particularly in cellulose esters[64-68]. Fig. 28 shows the dependence of the glass temperature of nitrocellulose on the concentration of various plasticising agents, introduced via the solution. For dibutyl phthalate, which shows unlimited solubility in nitrocellulose, the glass temperature decreases continuously with increase in concentration. Castor oil is insoluble in nitrocellulose, and its addition in very small quantities (see the upper right hand section of Fig. 28) leads to a sharp decrease of the glass temperature, but its effect rapidly reaches a limit beyond which no further change takes place (curve *2* in Fig. 28). We thus see two different types of plasticising — that by a soluble plasticising agent and that by an insoluble plasticising agent, which is distributed only at the interfaces between the structures. The effect of the insoluble plasticising agent is unusually pronounced — the addition of 0.1% produces the same effect as the addition of 10% of the soluble plasticising agent, but saturation takes place equally rapidly. An analogous situation is observed in the plasticising of acetylcellulose. Curve *1* in Fig. 29 illustrates the effect of the soluble plasticising agent 2-methyl-1-nitropropan-2-ol, and curve *3* illustrates the effect of the insoluble plasticising agent butyl stearate, which acts between the bundles. We can see the same typical effect of unusually small quantities of the inter-bundle plasticising agent, with rapid attainment of the limit at a concentration of only 0.05%. The sparingly soluble plasticising agent trimonochloroethyl phosphate occupies an intermediate position.

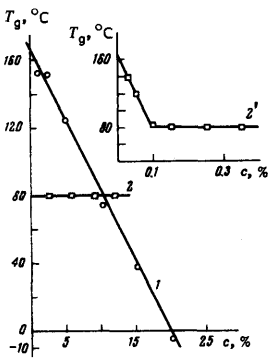


Fig. 28. Dependence of the glass temperature of nitrocellulose on the concentration of plasticiser added via the solution: 1) butyl phthalate; 2) and 2′) castor oil.

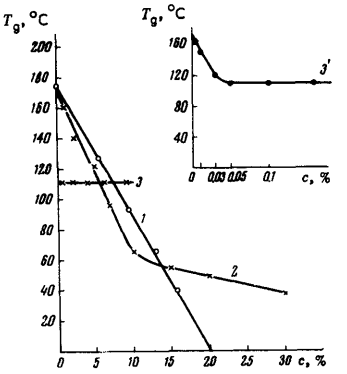


Fig. 29. Dependence of the glass temperature of cellulose triacetate on the concentration of the plasticiser:
1) 2-methyl-1-nitropropan-2-ol; 2) trimonochloroethyl phosphate; 3) and 3′) butyl stearate.



Fig. 30. Successive stages of structure formation in polychloroprene rubber vulcanisates broken down mechanically by rolling (*a* and *b*).

Analogous phenomena have recently been observed for other polymers[69-71].

We must not forget other effects associated with inter-structural plasticising. A small quantity of a low-molecular substance present at the interfaces increases the mobility of the structural formations and facilitates the production of higher supermolecular structures. This is not dangerous in the case of amorphous polymers, but in crystalline polymers it may lead to a sharp increase in the rate of recrystallisation with the formation of brittle structures, so that the result is not plasticising but the production of brittleness[72].

Chemical reactions in polymers also often take place similarly as in heterogeneous systems. A paper presented at the Symposium in Paris described structural phenomena observed in the production of graft polymers. The general conclusion was that the grafting process usually takes place not in the entire bulk of the polymer but only at the interfaces between the structural formations, and that the resulting graft polymers usually show the phenomena of "micro-layer formation", that is a change to heterogeneity[73].

Another example of a chemical process which takes place in polymers similarly as in heterogeneous systems is vulcanisation. It has for long been known that vulcanised rubbers from crystallisable raw rubbers retain the ability to undergo crystallisation. The explanation given was that crystallisation takes place only in small sections of the chains. It has recently been possible to show that rubbers vulcanised in the normal way retain not only their ability to undergo crystallisation but also their abilitiy to form higher structures, as far as the formation of single crystals. Fig. 30 shows the various successive stages of the ordering and crystallisation of polychloroprene, vulcanised by Tonox to a vulcanisation network frequency corresponding to the average production of one bond per 300 carbon atoms. The vulcanised specimens were rolled until the soluble state was attained, after which specimens for electron-microscope study were obtained from solution in carbon tetrachloride. It is obvious that even after vulcanisation the rubber still contained a sufficiently large number of unbranched chains and linear structural formations, without which the formation of large

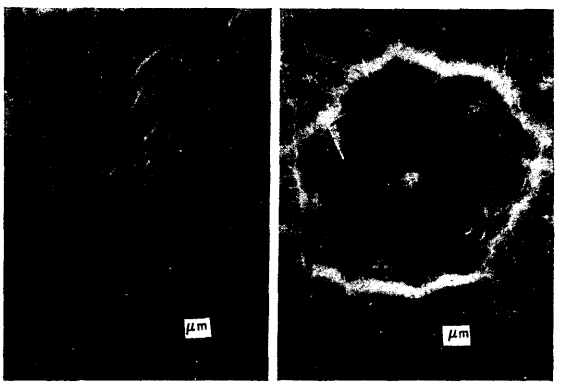


Fig. 31. Structures produced in polychloroprene rubber thermovulcanisates.

structures and single crystals is impossible. This takes place only when the vulcanisation bonds are distributed irregularly in the rubber, which is possible only in heterogeneous systems.

Fig. 31 illustrates analogous structure formation in polychloroprene heat-vulcanisates. Thus thermochemical decomposition also takes place irregularly throughout the entire bulk of the rubber[74,75].

A curious feature is that it is also possible to detect phenomena associated with the presence of structural formations in solutions in the study of chemical reactions involving polymers. In the chlorination of high-density polyethylene in carbon tetrachloride solution in the concentration range 0.1-0.5% at 115-125°, the chlorination product is divided into two fractions immediately after the solution is cooled — fractions soluble and insoluble in cold carbon tetrachloride. The concentrations of chlorine in these fractions differ by a factor of 2-3, the total chlorine concentrations being 14-22% for the soluble fraction and 4-8% for the insoluble fraction. This phenomenon persists up to 130°, after which a homogeneous product is formed, soluble or insoluble in chlorobenzene, depending on its chlorine content. A curious feature is that this

temperature is extremely close to the melting point of polyethylene crystals and evidently corresponds to complete breakdown of the structural formations in solution. The experiments were carried out by rapidly mixing solutions of polyethylene and a solution of chlorine in chlorobenzene, to avoid possible non-uniformity in the chlorination by the gas[76]. Analogous phenomena are observed in the chlorination of gutta-percha[18].

In this paper an attempt has been made to present basic data on the formation of structures in polymeric substances in all their states, on their nucleation, and on the part which they play in polymerisation processes, the development of mechanical properties, and their influence on the chemical behaviour of polymers. Structural phenomena must not now be regarded as exceptional but as an integral part of all processes leading to the development of the most important properties of polymers.

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CHARACTERISTIC FEATURES OF NON-EQUILIBRIUM POLYCONDENSATION†

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CONTENTS

I. Introduction 439
II. Types of polycondensation 439
1. Non-equilibrium polycondensation 440
2. Interfacial polycondensation 440
3. Polycondensation in solution 440
4. Dehydration polycondensation 440
5. Dehydropolycondensation 440
6. Polyrecombination 441
7. Polycyclisation 441
III. Exchange reactions 442
IV. The rule of the non-equivalence of functional groups 443
V. Molecular weight distribution of polymers 446

† Reported at the International Symposium on Macromolecular Chemistry in Prague, 1965.

I. INTRODUCTION

Recently there has been extensive development of new polycondensation processes leading to the preparation of a number of hetero-chain polymers which include many compounds of great practical interest since these are substances with high thermal stability, interesting electrophysical properties, biological activity, etc. Among these processes mention must be made in particular of interfacial polycondensation, dehydropolycondensation, and especially oxidative dehydropolycondensation, and also the polyrecombination reaction, the polycyclisation reaction, and certain others.

For clarity we shall adopt the conventional definition of polycondensation as a process involving the formation of high-molecular-weight compounds in which in addition to the polymer a low-molecular-weight product is formed, most often water, hydrogen chloride, and similar substances. Because of this the elementary composition of the polymer formed differs from that of the initial monomer or the initial mixture of monomers.

In the general case the polycondensation reaction of two starting materials can be represented by the following equation:

$$x\mathrm{a}-\mathrm{A}-\mathrm{a}+x\mathrm{b}-\mathrm{B}-\mathrm{b}\rightarrow\mathrm{a}-(-\mathrm{AB}-)_x-\mathrm{b}+2(x-1)\,\mathrm{ab}$$

and in the case where both functional groups enter into the composition of the same initial molecule, the reaction equation is

$$x\mathrm{a}-\mathrm{A}-\mathrm{b}\rightarrow\mathrm{a}-(-\mathrm{A}-)_x-\mathrm{b}+(x-1)\,\mathrm{ab}.$$

II. TYPES OF POLYCONDENSATION

We now know that, depending on the structure of the starting materials and the method of carrying out the reactions, polycondensation can be achieved in two different ways, namely: (1) as equilibrium polycondensation and (2) as non-equilibrium polycondensation. In addition there are probably certain reactions which exhibit the features of both types of polycondensation. Unfortunately reactions of this intermediate type have so far been little investigated.

A characteristic feature of equilibrium polycondensation is a low equilibrium constant. Very many examples of equilibrium polycondensation are known. Examples which have been particularly thoroughly investigated are the formation of polyamides or polyesters in the reactions, on heating, between dicarboxylic acids and diamines or glycols.

Equilibrium polycondensation constitutes a classical method of synthesising polymers which has been known for a long time. It has been studied thoroughly in many instances and its principal features have been established in a large number of investigations and have been described in reviews and monographs[1-9].

On the other hand, non-equilibrium polycondensation is a new process which was discovered relatively recently