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Structure of Amorphous Polymers

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A critical survey is made of experimental results obtained by the application of direct structural methods—X-ray, electron, and neutron diffraction, electron microscopy, and several other physical methods—to amorphous linear polymers. A list of 162 references is included.

CONTENTS

I.	Introduction	69
II.	Nomenclature of structures of different degrees of order	70
III.	Classical structure analysis of amorphous polymers	70
IV.	Results of electron microscopy	73
V.	Other physical methods of investigation	77

I. INTRODUCTION

For many years research workers have paid steady attention to the structure of polymers at a supermolecular level. Special progress has been made in studying the structure of crystallising polymers—the folding of polymeric molecules, detected originally in thin films [1] and in single crystals [2-4]—which was very reliably transferred also to crystallites present in blocks and in the fibres of most polymers [5-7]. A wide range of supermolecular crystalline structures has been discovered and studied in detail [5-7], and a systematic classification has been developed [8].

Less attention has been paid to the structure of amorphous polymers, firstly because of the opinion that polymers in the amorphous state were structureless, and secondly because application of the usual structural methods

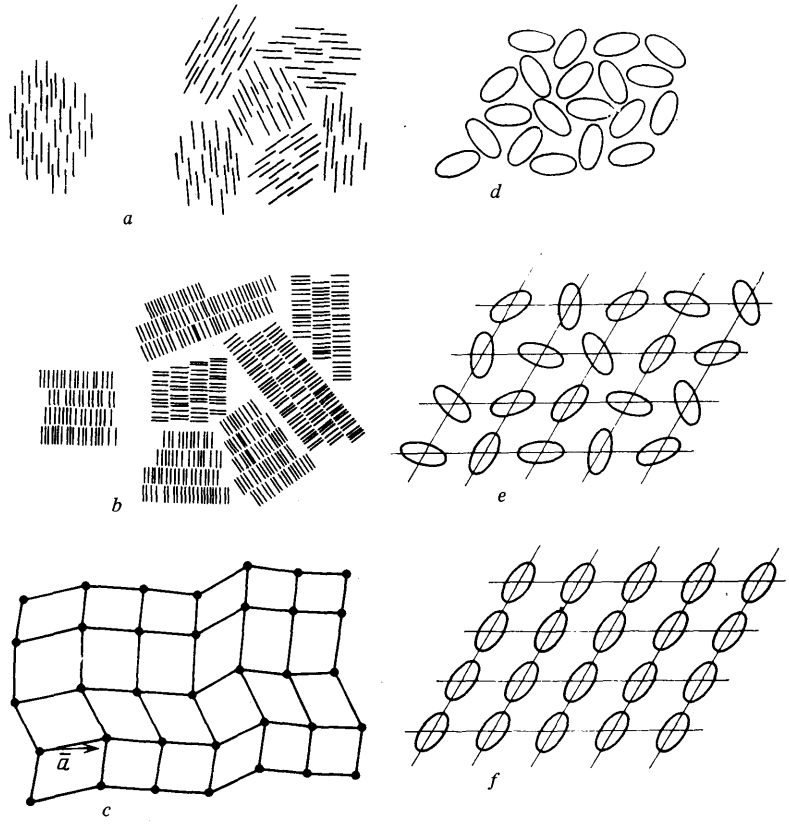


Figure 1. Schemes of packing of rod-shaped molecules: *a*) nematic structure; *b*) smectic structure (according to Friedel); *c*) ideal paracrystalline lattice (according to Hosemann); *d*) liquid packing of cross-sections of macromolecules; *e*) gasocrystalline; *f*) crystalline (according to Kitaigorodskii).

to amorphous substances yielded little information. Systematic study of the structure of amorphous polymers was initiated in 1957 by the work of Kargin et al.,[9] whose underlying idea, as expressed by one of the authors 17 years later[10], was that the structure of a polymer in the amorphous state should be similar to its structure in the crystalline state. Although the bundle model of the structure of amorphous polymers, in the form in which it was presented in that[9] and other publications of these workers[11, 12], is now regarded as unsatisfactory, the actual concept of a high degree of structural order permeates the majority of current models of the amorphous state.

The present Review traces the main trends and results in the experimental study of the structure of amorphous polymers, and the extent of agreement with the most generally accepted current models of the amorphous state.

II. NOMENCLATURE OF STRUCTURES OF DIFFERENT DEGREES OF ORDER

A multitude of organic compounds exist in Nature that, over a certain temperature range, are intermediate between liquids and crystals with respect to the degree of molecular order and hence physical properties[13,14]. They comprise elongated molecules, and for this reason are able to form molecular aggregates with different degrees of ordering. The structure and the properties of liquid crystals have now been investigated for more than half a century, so that almost the whole terminology used to describe noncrystalline packages of macromolecules was developed for liquid crystals.

All types of intermediate ordering were generally termed "mesophases" (from *mesos*—intermediate and *phasis*—phase) or "mesomorphs", the "mesomorphic" state. In 1933 Rinne suggested for one- and two-dimensional mesophases, in contrast to a three-dimensional crystalline phase, the term "paracrystal", thereby emphasising that the majority of liquid crystals are *para*-substituted benzene derivatives. Somewhat earlier, in 1922, Friedel had independently suggested the term "nematic mesophase" (from *nematos*—fibrous, filamentous) for a unidimentional mesophase, and "smectic" for a two-dimensional mesophase. These structures are shown diagrammatically in Fig. 1*a*,*b*.

These terms already came to be applied in the same sense to analysing polymer structures in the early papers of the 1930s.[15] The term "paracrystal" was then made more specific by Hosemann in 1950 in his paracrystalline model of the structure of polymers as a whole, including regions of all degrees of order[16,17]. This worker postulated the presence of a three-dimensional lattice in the arrangement of atoms in a polymer, with all three parameters of the unit cell not constant but conforming to some coordination statistics (Fig. 1*c*). The type of statistics and the consequent lattice disturbances are determined by the degree of molecular order—from liquid to monocrystalline—in different polymers or in different portions of the same polymer.

In 1959 Kitaigorodskii proposed[18] the new term "gasocrystalline" structure for certain highly ordered nematic and smectic forms. If the axes of the long molecules are located at the points of a regular (crystalline) two-dimensional hexagonal lattice and the molecules perform random ("gaseous") rotations about their axes, a model of the gasocrystalline state is obtained (Fig. 1*e*). This structure will exhibit a nematic or a smectic character according as neighbouring molecules undergo random or coordinated displacements respectively.

In 1963 Vainshtein[19] discussed in the greatest detail possible types of aggregates of chain molecules. The simplest and most natural organisation of chain molecules into three-dimensional aggregates, also satisfying the principle of densest packing[20], was taken to be a parallel arrangement with a varying degree of order and with the parallelism maintained in varying degree. Having placed the chain molecule with its axis passing through a branch point of one of the five possible ideal two-dimensional networks (Fig. 2*a*,*b*), this author then examined every type of disturbance of the initial position of this molecule, various combinations of which are summarised by the scheme in Fig. 2*c*. Thus the structure of a given polymer can be regarded as established when the type of aggregation of chain molecules to which the given structure corresponds has been found experimentally and the quantitative characteristics of the disturbances involved have been determined. Later in the monograph[19] theoretical consideration was given to the character of the X-ray diffraction from all types of aggregates of chain molecules, the results being illustrated by optical diffractograms from models or X-ray diffraction patterns of model materials.

III. CLASSICAL STRUCTURE ANALYSIS OF AMORPHOUS POLYMERS

Application of X-ray diffraction to the study of natural and synthetic polymers began immediately on the appearance of industrial equipment for structural analysis. Most of the polymers known at that time were amorphous, so that greater attention was then paid to their structure than at the present time, with the abundance of well crystallised polymers, more suitable for study by means of X-rays.

Firstly the X-ray patterns of monomers and corresponding polymers were compared[15]. The greatest differences were observed with polymers having large side-chains—poly(methyl acrylate), poly(vinyl acetate)–polystyrene, polycarbonate, polyindene—whose patterns exhibited two halos within a certain range of angles, whereas the corresponding monomers showed only one of them. The additional halo, always having the greater periodicity, was termed a "polymerisation ring". The reason for its appearance became clear when it was observed to contract on to the equator in the case of an oriented specimen (Fig. 3*c*). In the uniaxial stretching of a polymer the axes of the macromolecules are oriented preferentially in the direction of stretching, and therefore the equatorial reflection may be governed merely by the interchain distance. At the same time a good correlation was noted between the length of the side-chain and the periodicity of the equatorial reflection[21]. The fact that a "polymerisation ring"—or "intermolecular interference", as it came to be called later—is observed even in an isotropic specimen shows that the polymer molecules in a block are not randomly entangled but are arranged in parallel in microregions, each randomly oriented relative to its neighbour. In the terminology of liquid crystals such polymers have a nematic mesomorphous structure.

These ideas were developed as early as 1936, when Katz published his review[15], but they were forgotten during the postwar years, when the centre of gravity of structural investigations was transferred to well-crystallised stereoregular polymers. Experimental results gradually began to accumulate afresh: in 1950 Pritshk[22] demonstrated four

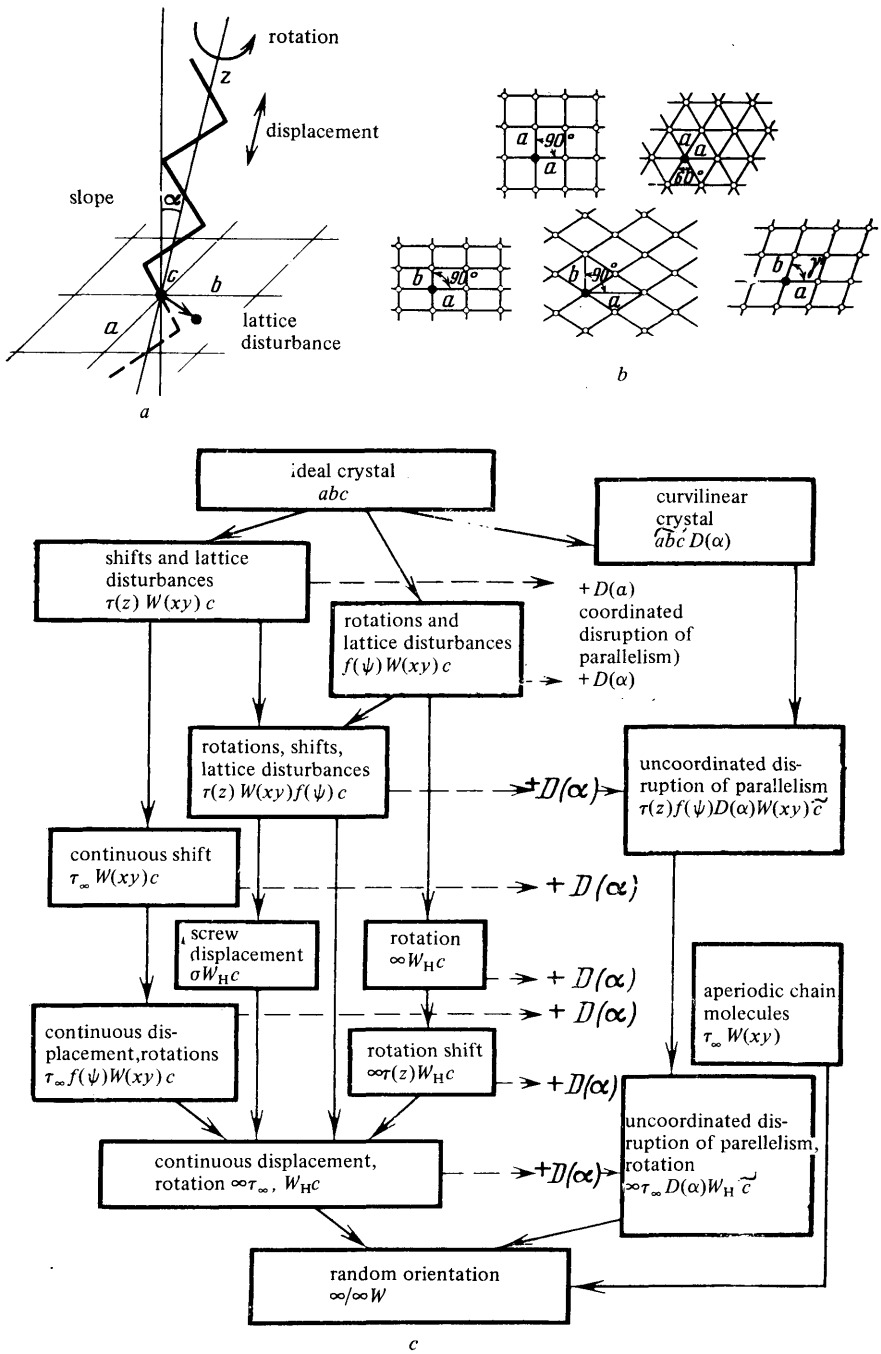


Figure 2. Packing of chain molecules (according to Vainshtein): *a*) types of disturbance of ideal packing; *b*) five regular two-dimensional networks; *c*) types of aggregation of chain molecules.

types of X-ray patterns obtainable with nylon-6, which he attributed to various combinations of liquid–amorphous, nematic, smectic, and crystalline structures; in 1951 Krimm and Tobolsky[23] reproduced the texture of atactic polystyrene discovered by Katz and Fuller during the 1930s; and in 1959 Kitaigorodskii[20] directed attention to polyacrylonitrile as the clearest example of a polymer having a gasocrystalline structure[18] (Fig. 3*a*). A nematic type of structure was noted in molten and amorphised specimens of poly(vinyl chloride)[24,25], poly(vinylidene chloride)[26], their copolymers, and chlorinated poly(vinyl chloride)[25]. The smectic state of isotactic polypropylene

was revealed by X-ray diffraction and dilatometrically[26,27]. The accumulation of experimental data was accompanied by attempts to systematise mesomorphous polymeric structures. For example, Ruscher distinguished seven different types of ordering of chain molecules[28]—amorphous, nematic, smectic, nematic–hexagonal, smectic–hexagonal, defect-crystalline, and ideally crystalline structures.

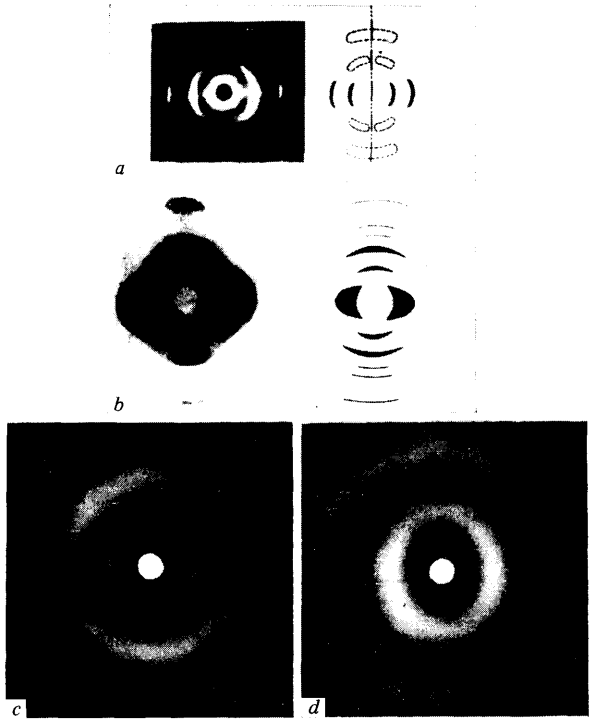


Figure 3. Effects of ordering on X-ray patterns of oriented amorphous polymers: *a*) two-dimensional long-range order[17] (gasocrystalline structure[18]) in polyacrylonitrile; *b*) one-dimensional long-range order in poly(ethylene terephthalate)[40]; *c*) interchain short-range order in polystyrene; *d*) as (*c*) in poly(methyl methacrylate).

As noted above, a rigorous and full classification of possible types of packing of chain molecules was given by Vainshtein[19]. Since the beginning of the 1970s increasing numbers of publications have appeared on the application to polymers of the analysis of radial distribution curves of electron density based on the dependence of the X-ray intensity on the scattering angle (or based on the potential distribution in the scattering of electrons). A comparatively large amount of structural information—interatomic distances in molecules, number of closest neighbours (coordination number), their mean distance, etc.—is given by radial distribution curves in the case of amorphous substances of low molecular weight[29]. For example, the examination of short-range order in cycloalkanes enables the molecular conformation (chair and boat forms of cyclohexane over different temperature ranges, the W form of cyclo-octane) and a coordination number of ~ 11.5 to be established[29] from the observed intramolecular distances. The molecules of n-alkanes, however, were packed in the liquid like cylinders of rotation, with a mean distance of 5.6 Å between their axes[29] and ~ 6 nearest neighbours.

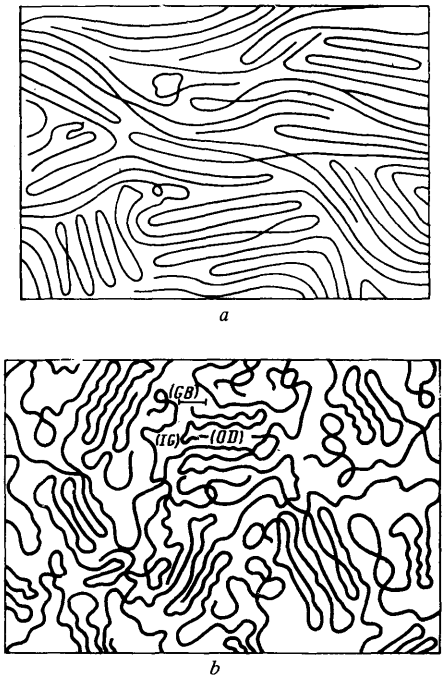
The greatest difficulties in analysing radial distribution curves are encountered in separating the contributions of intramolecular and intermolecular interference. This is probably why such analysis was first applied to atactic polystyrene[30] and its *para*-halogenated derivatives[31], for with this polymer, as we have already seen[15,23], the effects of intra- and inter-molecular interference are quite sharply separated even on the initial scattering curves. The statistical mean intrachain short-range order was found to be the same as in isotactic polystyrene, which has since been confirmed independently by nuclear magnetic resonance[31]. Among intermolecular distances, benzene rings in neighbouring chains were 5 Å apart, and their axes 9–11 Å apart.

This method has been used to investigate a large number of molten crystalline polymers—polyethylene[33,34], polychlorotrifluoroethylene, poly(ethylene sebacate), gutta-percha[34], natural rubbers from various sources[35,36], polyacrylonitrile[36], and polycarbonate[37]—by Ovchinnikov and his coworkers, who employed the set of interchain distances in the crystal lattices of the polymers to separate the maxima observed on the radial distribution difference curves into intramolecular and intermolecular. The general deduction for all the polymers was that the character of the short-range order in the melt corresponded to their structure in the crystalline state: i.e. a parallel arrangement of chain segments and their packing in the basal plane analogous to crystals (square, rectangular, hexagonal) are present also in molten crystalline polymers. In several cases transitions are observed from one type of packing to another: in molten polyethylene a change from rectangular (rhombic) to hexagonal packing was observed at 175–200°C,[36] and in polybutadiene one pseudohexagonal packing passed into another at ~ 75°C.[36] The number of intermolecular maxima on the difference radial distribution curve was regarded as a relative measure of the degree of perfection of the short-range order and the size of the ordered regions. Most frequently there were two, corresponding to regions of diameter ~ 25–30 Å, but sometimes three (polyacrylonitrile[36]) or one (gutta-percha[34]). Other workers[38] have obtained a similar result by this method for polycarbonate [bisphenol A polycarbonate]: the size of ordered regions for an amorphous specimen prepared by injection moulding, and also after annealing below the glass point (at 120°C for 3 h), was 20–30 Å, but after prolonged annealing above this point (at 190°C for 122 h) the size had increased to 50–60 Å.

Nevertheless, the ambiguity inherent in the separation of contributions by intramolecular and intermolecular scattering to the maxima on the radial distribution curves makes a different interpretation of the experimental results possible. Thus Fischer et al.[39] have attempted to assign all the maxima on the radial distribution curves of polyethylene to intrachain distances.

The difficulties in interpreting the X-ray patterns of amorphous polymers made theoretical consideration of this question necessary. A general solution of the problem of the diffraction of X-rays on amorphous polymers has not yet been found, but certain limiting or simple cases can be examined theoretically, and hence the main features of the X-ray patterns actually obtained from amorphous polymers can be predicted and explained[19].

The first noteworthy result is the character of the diffraction pattern to be expected with non-parallel packing of the chain molecules. The pattern of scattering should be saw-tooth in character: at scattering angles corresponding to the repeat period of the chain a sharp jump in intensity should be observed, followed by a slow fall. This applies even to 8 units in a linear chain segment. Such a pattern of scattering does not correspond to the experimental X-ray photographs. Further consideration of the diffraction from an individual curved macromolecule showed[19] that the periodicity should appear with oriented preparations as a single meridional reflection, but with isotropic specimens as a ring at the same angle of scattering. The effective chain segment with respect to diffraction is then 6–7 units long. A second effect in diffraction from a single curved chain is gaseous or liquid intramolecular scattering. If large side-groups are absent, this scattering should be apparent as a uniformly decaying background. If the monomer unit has a complicated structure, the intramolecular scattering will be characterised by diffuse maxima, as with molecular gases and liquids.



a *b*

Figure 4. Diagrammatic representations of structure of amorphous linear polymers: *a*) Vainshtein model[19]; *b*) Jeh–Geil model[103,107].

Parallel packing, as far as possible, is also advantageous in aggregates of curved chains[19]: portions with skew contacts between neighbouring molecules make hardly any contribution to the overall interference pattern, whereas portions with an approximately parallel arrangement of chains will give a new diffraction effect, consisting in the appearance of an interference spot on the equator of an oriented specimen (or an additional ring, in comparison with the scattering from a single chain, with an isotropic specimen). The presence of displacements and rotations of chains does not prevent the appearance of an equatorial reflection, and the spread in interchain distances merely results in blurring of this reflection. Qualitative estimates of the size of the interference region give 20–40 Å.

Thus three types of diffraction effects must be expected on the X-ray patterns from amorphous polymers (they can be reliably separated only in the case of oriented specimens)[19]—(i) a maximum (or maxima) on the meridian resulting from chemical periodicity in the chain molecule, (ii) a maximum on the equator as a consequence of interchain interference of roughly parallel chain segments, and (iii) a diffuse background of intramolecular scattering, with "liquid" maxima when the monomer unit is complicated in structure—all of which are in some measure apparent on the X-ray patterns of amorphous polymers, especially clearly with amorphous biopolymers (see Figs. 217 and 218 in the monograph[19]) but less distinctly with synthetic polymers owing to the considerably greater non-uniformity of molecular mass, branching, stereoregularity, and other characteristics. Examples of amorphous textures with meridional reflections are incompletely crystallised oriented poly(ethylene terephthalate)[40] (Fig. 3*b*) and fibres of certain polyamino-acids[41]; amorphous textures with equatorial reflections are exhibited by polystyrene[15,23], poly(vinyl acetate)[15], and poly(vinyl chloride)[26]. If intramolecular and intermolecular interferences greatly overlap, the X-ray patterns exhibit a tendency for one ring (usually the inner ring) to contract to an equator, and the other ring to a meridian, which occurs e.g. with a polycarbonate[42] and with poly(methyl methacrylate)[45] (Fig. 3*d*).

Thus the present-day possibilities of the theory and practice of classical structural analysis enable amorphous polymers to be regarded[19] as comprising (Fig. 4*a*) regions of 20–40 Å with roughly parallel packing of segments of macromolecules. A given molecule may pass through several regions or (if strongly bent) may enter the same region several times. "Skew" contacts are present between molecules in intermediate zones. Models in which the structure of an amorphous polymer is represented by bundles of macromolecules in which good or approximate parallelism of the molecules extends to a considerable length—or conversely by disordered microtangles each formed by a single molecule—cannot explain the observed character of the X-ray patterns[19]. The possibility of the chain folding is not excluded in the model illustrated by Fig. 4*a*, although it is not considered a decisive cause of the formation of regions with a parallel arrangement of chain segments.

IV. RESULTS OF ELECTRON MICROSCOPY

When considering the results of electron-microscopic investigations, we must bear in mind that electron beams interact with an object according to laws different from those governing the scattering of light[44]. A source of error in interpreting electron micrographs lies in so called artefacts, a term which is usually taken to imply peculiarities of the image that are due not to the structure of the object but to the method of preparing the specimen. Several typical examples of artefacts can be found in monographs on the technique of electron microscopy[44], and others will be noted below in connection with the results of the electron-microscopic study of the structure of amorphous polymers.

All publications concerned with the present topic can be arbitrarily divided, according to their specific purpose, into three groups. The first group comprises studies whose principal or subsidiary aim was to detect individual macromolecules on the electron micrographs. As early as 1940 Husemann and Ruska had reported[45] the presence of spherical particles of diameter 150–300 Å in specimens of iodinated glycogen, in good agreement with the calculated diameter of 240 Å for a molecular coil of the given molecular mass and macroscopic density. Spherical domains, roughly comparable with a single macromolecule, were later detected on micrographs of thin films from solutions of polystyrene[46-48], poly(methyl methacrylate)[46-48], and natural rubber[49].

The range of objects was expanded by using replicas from "brittle" fractures and ultrathin sections from block specimens. These methods have revealed, for example, two scales of dimensions in the observed structures—molecular of diameter 40–80 Å in poly(methyl methacrylate)[50] and 150–200 Å in melamine–formaldehyde resins[51] as well as in polyacrylonitrile[52]; and micellar of diameter 200–800 Å in poly(methyl methacrylate)[50,53], 700–900 Å in phenol–formaldehyde[42] and melamine–formaldehyde[51] resins [and in phenolic, dioctyl phthalate, epoxy, leached epoxy, and silicone resins[54]], and 200–840 A in polyacrylonitrile[53]—but recently the method of replicas from "brittle" fractures has been severely criticised[55-57]. Thus even at the temperature of liquid nitrogen cleavage is nonbrittle: because of local heating the polymer may undergo deformation under conditions of either forced elasticity, rubberlike elasticity, or viscous flow. Furthermore, experimental facts have been found[58] contradicting the initial assumption that a cleavage fracture bends the supermolecular structures. Thus the morphology recorded on replicas represents the actual process of fracture of the material, not the three-dimensional structure of the polymer.

With regard to the spherical particles observed in thin films mainly the interpretation of the results has changed. Thus Schoon et al.,[59,60] who investigated thin films (~ 100 Å) of polystyrene, poly(methyl methacrylate), butadiene–styrene copolymers, and also silicone replicas from these films, using several methods for comparing both films and replicas, and plasticising the polymers with various solvents, showed that two scales of spherical structures are actually observed, but no exact correspondence with the dimensions of individual molecules was established. They determined particle-size distribution curves from micrographs of narrow fractions of the polymers, and demonstrated that the first scale of particle diameters (47–62 Å for $M = (1-7) \times 10^5$ in polystyrene, 40–60 Å for $M = (2-70) \times 10^5$ in poly(methyl methacrylate), and 70 Å for $M = 10^5$ in the copolymer) are substantially smaller than the dimensions of a molecular coil of a polymer of the same molecular mass having the given macroscopic density. The second scale of particle diameters, representing aggregates of particles of the first range, exceed the calculated diameter of a single molecule by factors of 2–9. We shall return to the present interpretation of these results when discussing the third group of publications.

Observation of individual molecules under an electron microscope requires more complicated and rigorous procedures. For example, Richardson[61,62] used the vacuum sputtering of very dilute (~ 10^{-4}%) solutions of polymers—polystyrene, polyacrylonitrile, poly(methyl methacrylate), poly(vinyl acetate), etc.—in mixtures of a solvent with a precipitant in certain proportions. With very high molecular masses ($\gtrsim 10^6$), when the application of traditional methods is very difficult, electron microscopy is able, with a correct approach to problems of preparation, to cope successfully with the measurement of both the molecular mass and its distribution[63].

The second and largest group of publications on the electron-microscopic study of the structure of amorphous polymers is the product of research workers of Kargin's school, and has been the subject of several detailed reviews[11,64-68]. These studies were directed mainly at detecting experimentally the spontaneous ordering of micromolecules even in the case of non-crystallising polymers.

For this purpose a search was originally made for model substances differing in chain flexibility, and type of inter- and intra-molecular interaction (sometimes of exotic character), such as arsenic polymers (salvarsan)[68], polyacrylic acid[69], fluorinated and silicone rubbers[70], copolymers of the diethyl ether complex of vinylphosphinic acid with acrylic acid[71], etc. Application to such compounds of the usual preparation techniques (mostly film formation from dilute solutions) revealed two main types of organisation—globules, containing more than one coiled macromolecule, and fibrils (bundles of extended macromolecules). In several cases the latter were able to aggregate further to form regular polyhedra (methyl methacrylate–acrylate copolymer[68]) and well developed dendrites (copolymer of diethyl ether complex of vinylphosphinic acid and acrylic acid[71]). The so called "banded structures" were recognised as the most typical secondary formation, with such methods of preparation, from bundles of chains in any amorphous polymer.

The next stage was to study the structure of polymer solutions[67]. This complicated task involved the use or redevelopment of special techniques, such as one-step replicas from fractures of vitrified solutions[73], dissolving the polymer in a solvent at a temperature above its critical point (propane, colophony, ammonia) and "firing" the solution in a vacuum on to a support[74], thermal attachment[75,76]. Application of these methods to polymers differing in chain flexibility—e.g. in the sequence polystyrene, polyacrylonitrile, acetylcellulose, poly-(γ-benzyl glutamate)—showed that flexible molecules (polystyrene) do not form fibrils, whereas with rigid chains, as in poly-(γ-benzyl glutamate), the spontaneous aggregation of macromolecules in solution can be attacked only by special procedures. In the case of polymers having chains of intermediate rigidity (polyacrylonitrile and acetylcellulose) either globular particles (containing several dozen macromolecules) or fibrillar formations may appear depending on the ratio of solvent to precipitant.

It must be admitted that the structural studies of the Kargin school were treated with reserve by foreign workers[5,77], who remarked that "more detailed photomicrographs and electron micrographs of globules and bundles were absolutely essential" as proof of the results[5]. A tendency to reinterpret electron-microscopic data from several previous studies has recently begun to appear even in papers by Soviet investigators [sic][60]. It has been suggested[58], for example, that the "banded structures", which had been considered one of the main structural forms in amorphous polymers[65], should be regarded as artefacts of the preparative processes, since no diffraction data have yet been obtained that would support their presence in the bulk of a polymer. The appearance of images of such morphology on photomicrographs is attributed to wrinkling of the preparations under the influence of surface tension[58]. No confirmation has yet been obtained in other laboratories of the observation of large

faceted structures in amorphous polyacrylic acid[68] and its copolymers with the ether complex of vinylphosphinic acid[71], as also the detection of spherulites by Utsuo and Stein in industrial poly(vinyl chloride)[78] and by Natov[79] in atactic poly(methyl methacrylate) with 3% of poly(ethylene adipate). The absence from these papers of diffraction data casts doubt on the reality of such structures in amorphous polymers. Cases are known in which the authors themselves find a simpler explanation for the observations: thus the coarse crystalline formations in annealed gels of poly(vinyl chloride) with dioctyl phthalate[80] proved to be crystals of phthalic acid, a degradation product of the plasticiser[81].

In order to eliminate the influence of the surface relief of films, fractures, and cross-sections, which is an indication of the preparative processes rather than the structure of the material, several methods were proposed and have been used to etch the surface layers[56,82-88]. Although application of the "mildest" of them[83-86] to crystalline materials has little effect on the character of the images obtained[56], a radical change in the pattern is observed in several cases with amorphous polymers. Instead of the spherulitic formations often detected on replicas from fractures in amorphous polymers, e.g. polyurethane rubber[56] or poly(methyl methacrylate)[89] (arising, as is now understood, from the mutual intersection of the propagation fronts of fracture cracks), a globular morphology is observed in both cases after surface layers of the cleavage have vaporised in the gas-discharge plasma[56,90]. Still more surprising and unexpected is the transition from the clearly defined fibrillar morphology of replicas from cleavage planes of highly oriented specimens of poly(methyl methacrylate)[91] to the globular morphology of replicas from etched surfaces of cleavage planes in analogous specimens[90].

In the search for objective criteria of the correctness of an interpretation of electron-micrographs obtained from crystallisable polymers it was proposed that optical diffraction patterns should be compared with small-angle X-ray patterns[92] or with diffractograms obtained from block specimens in polarised light[60]. The diffuse character of small-angle X-ray patterns and optical diffractograms from amorphous polymers makes wide application of this test to amorphous preparations difficult, although it may prove useful in several cases. Fig. 5 gives electron-microscopic and optical diffraction results obtained by various workers for uniaxially oriented specimens of atactic poly(methyl methacrylate). The replicas of oriented films after being etched in the gas discharge exhibit globular formations and their aggregates of dimensions 200–2000 Å (*a* and *b*) with a somewhat distorted form when specimens are stretched at temperatures above the glass point[90]. The axial ratio of such particles was always appreciably smaller than the macroscopic degree of stretch if preparation was undertaken after removal of the stretching force, but corresponded to it when the load was maintained. The attempt to compare the Fraunhofer diffraction from a photomicrograph with the X-ray pattern of oriented poly(methyl methacrylate) at large scattering angles[58] (*c*) contradicts the very idea of the method of analysis of photomicrographs and is pointless. On the other hand, the "rhomboid" pattern obtained when polarised light is scattered by the specimen[93] (*f*), analogous to the scattering pattern for a set of anisotropic cylinders[93] (*e*), corresponds more closely to the fibrillar morphology found on replicas of unetched fractures (*d*). Results obtained[94] for isotropic and oriented amorphous films of poly(ethylene terephthalate) subjected to oxygen etching contrast with those for etched oriented poly(methyl methacrylate). An unoriented preparation reveals only globular formations of diameter 300–400 Å, but oriented specimens (amorphous texture[40]) exhibit elongated structural units 100–200 Å wide and up to 1 μm long.

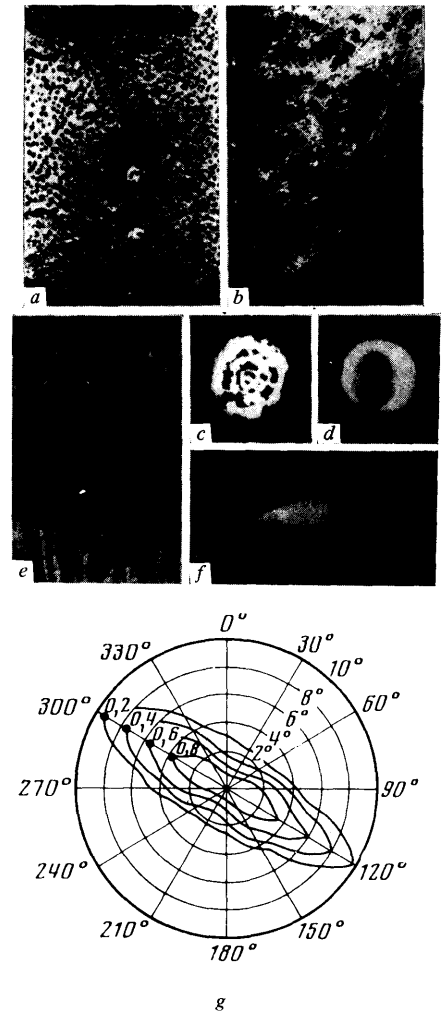


Figure 5. Morphology and diffraction of oriented poly(methyl methacrylate): *a*) electron-micrograph of replica from cleavage plane of 400% drawn polymer after ionic etching (magnification × 7000)[56,90]; *b*) as (*a*) × 70 000; *c*) Fraunhofer diffractogram from micrograph (*a*)[58]; *d*) X-ray large-angle diffraction pattern of block specimen[58,90]; *e*) micrograph of replica from cleavage plane without etching[91]; *f*) diffractogram obtained with polarised H_V light for polymer specimen stretched by 700%; *g*) theoretical intensity distribution of polarised light scattered by a set of anisotropic cylinders[8,93].

Hence the inclusion of ionic etching in the preparation of electron-microscopic objects eliminated the artefacts of the "brittle" cleavage method and of film formation from

dilute solutions, but at the same time introduced new artefacts, probably due to uncontrolled heating of the surface layer[95] and to the inadequately studied mechanism of polymer degradation under ion bombardment[96]. At the present time this method shows great promise for investigation of the phase morphology of multicomponent polymer systems, such as polymer and filler[97,98], mixtures of polymers[99,100], cross-linked systems[101], etc.

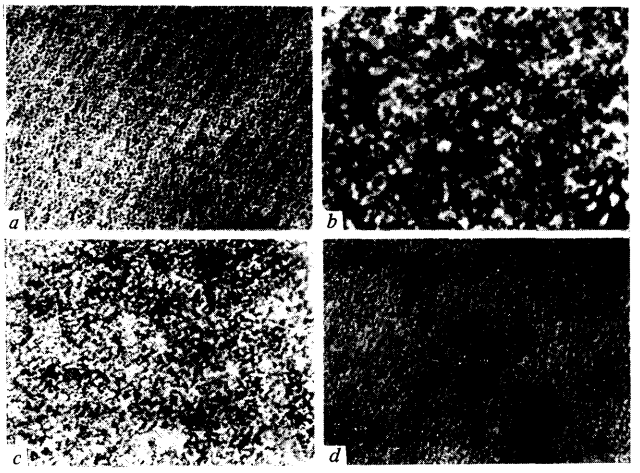


Figure 6. Granular (nodular, domainal) morphology of films of amorphous linear polymers: *a*) bright-field electron-micrograph of biaxially oriented (2 × 2 ×) amorphous film of poly(ethylene terephthalate) (shadowed with platinum plus carbon)[104]; *b*) dark-field micrograph of film of natural rubber[108]; *c*) bright-field micrograph of poly(methyl methacrylate) film (contrast enhancement with UO_2)[60]; *d*) as (*c*) (phase contrast)[115].

We have thus approached the third group of publications, reported the most complete utilisation of the current arsenal of aids to electron microscopy on preparations varying widely in their previous thermophysical history. Chronologically the first paper in this series was that by Frank et al.,[102] in which ionic etching revealed the granular structure of polycarbonate films. Grains of diameter < 100 Å were observed in films quenched in ice-water from a state of rubberlike elasticity (160°C); they could be enlarged reversibly to 200–900 Å by annealing at 110°C (glass point 150°C), and brought back to the previous size by being quenched again. The reversible character of the changes during the anneal–quench cycles, and the abrupt change in mechanical losses for an unannealed specimen in the region of 100°C, evident on the temperature curve of tan δ_{mech}, indicated the structural nature of this phenomenon.

Efforts by research workers of the Geil school soon detected granular structures (nodal, nodular, domainal) in amorphous specimens of poly(ethylene terephthalate)[103-104] (Fig. 6*a*), polycarbonate[105], polystyrene[106], and natural rubber[107,108]. Usually the granular structure (grain size 60–100 Å) was revealed simply by shadowing the films, so that artefacts were tested for by such well known procedures as iodination[104], contrast intensification with osmium tetroxide[108], various types of heat-treatment[103-111], uni- and bi-axial orientation[105,103,108], analysis of crystalline morphology developed from controlled variation of the nodular structure[103-105,108], and also chemical etching[109,110].

The application to amorphous polymers of dark-field microscopy[103,106,107]—a standard method applied to crystalline substances[44], including crystalline polymers[87,104,108]—represented a fresh advance in their electron microscopy. By tilting the illuminating system of the microscope to an angle corresponding to the Bragg angle of the inner amorphous halo of the polymer it is possible to obtain an image of the object by means of those electrons that are responsible for the appearance on the electron-micrograph of the segment of the diffuse ring that has passed through the aperture diaphragm. But it is known that inner halos on diffraction patterns of amorphous polymers are due mainly to intermolecular interference of parallel chain segments. As a consequence we might expect that bright spots would appear on the dark background of the micrographs, these representing ordered regions in which the axes of the macromolecules were perpendicular to the radius of the chosen segment of the diffraction maximum[109]. Dark-field micrographs of thin films (< 500 Å[109]) of poly(ethylene terephthalate)[103], polystyrene, and natural rubber[108] (Fig. 6*b*) exhibit discrete bright spots respectively 75, 27 ± 13, and 20 Å (30 Å[109]) in size. Bright-field (unshadowed) micrographs of poly(ethylene terephthalate) films revealed a nodular structure of the same dimensions[103,109], those of polystyrene showed little contrast, and with films of natural rubber aggregates of grains of diameter 100–150 Å were probably observed after shadowing with platinum[108]. A more definite tendency for grains to aggregate into superdomains was traced by another novel method—decoration with gold—in poly(ethylene terephthalate) during uniaxial and biaxial orientation[104]: the primary grains of 60–100 Å were aggregated into coarser superdomains of minimum size 300–500 Å, which behaved as individual entities during orientation. We can now recall the studies by Schoon[59,60] discussed already, in which the application of various methods for intensifying contrast also revealed in polystyrene, poly(methyl methacrylate), and butadiene–styrene copolymer films grains and their aggregates respectively 40–70 and 200–900 Å in size (Fig. 6*c*).

The granular morphology of amorphous films has been observed many times on bright-field micrographs even without any intensification of contrast—in the films of collodion[44,109] and polyvinyl formal resin[109] used as supports, in thin films of poly(ethylene terephthalate)[103] and poly(methyl methacrylate)[111], and also in thin amorphous inorganic specimens of silicon dioxide[112,113] and germanium dioxide[114]. In general it was clear that phase contrast is not the final factor in establishing such a morphology on the micrographs, and such effects have usually been regarded rather as undesirable phenomena[44,109].

A recent publication[115] traces in greater detail the influence of phase contrast on formation of the electron-microscopic image in work with amorphous subjects in the range of limiting magnifications. The authors consider[115] that phase contrast can and must be converted from an interfering factor into an effective new procedure in electron microscopy applied to polymeric subjects, as it was[116] when the structure of inorganic materials was examined at limiting resolutions. The main conclusion from the experimental work[115] was that phase contrast is able to reveal in amorphous poly(methyl methacrylate)

films (100–150 Å thick) grain-like structures of diameter 15–30 Å and their linear aggregation with a periodicity of 15–40 Å extending for 100–200 Å (Fig. 6*d*).

Such an abundance of well founded electron-microscopic data on nodal structures in amorphous polymers led to the model of the latter described in detail by Yeh[107], shown diagrammatically in Fig. 4*b* with his lettering. The actual grains observed on bright-field micrographs are usually G = 40–100 Å in size. The central portion of the grain OD = 20–40 Å comprises more or less parallel and almost equidistant chain segments, and is revealed in dark-field electron microscopy. The boundary regions of the grains, 10–20 Å thick, include folds, chain ends, and individual bent chains. The intergranular regions, of size 10–50 Å, consist of intermediate portions of chains of individual molecules (probably oligomeric) and free space. The refinement of this model by Klement and Geil[104] involves merely introducing a supergranular structure (supernodes, superdomains), within which intergranular bonds are assumed to be denser than those between grains in different superdomains; however, these authors do not indicate the reason for such differentiation of intergranular bonds. It was assumed[107] that the grains should have directional properties; polymer chains may enter and leave the ends of grains, so that the latter should be linked as in a string of beads. Nevertheless, the possibility that they could be linked into a three-dimensional lattice is not denied.

The "electron-microscopic" and "diffraction" structural models of the amorphous state of polymers (suggested independently though not simultaneously) are clearly very similar (Figs. 4*b* and 4*a*). Such similarity is evidently due to the use of essentially the same experimental diffraction evidence of order in the arrangement of chain segments in the amorphous state. The contribution of electron microscopy to further development of the model was to detect boundaries between regions of nematic order and disorder, and to establish more detailed size characteristics independently of diffraction estimates. The authors of the electron-microscopic model could cite no experimental evidence for the underlying hypothesis that macromolecules had a predominantly folded conformation in the ordered regions. They considered that the hypothetical chain folding in grains was supported by the facts that the crystallisation of poly(ethylene terephthalate) involves the conversion of grains of size 75 Å into isometric crystallites of size 140 Å, in which the chains probably have a folded conformation[104], that polycoumarin grains of size 60–110 Å coalesce during prolonged annealing at the glass point to form platelike crystals, chain folding in which has been proved by electron diffraction[105], and that the nodal morphology of natural rubber films of size 100–150 Å is transformed on cooling into a lamellar morphology with plates 55 Å thick in the direction of the chain[106].

V. OTHER PHYSICAL METHODS OF INVESTIGATION

The low degree of order in the arrangement of segments of macromolecules in amorphous polymers and the small size of the ordered regions make it necessary to use the widest possible range of physical methods to study structural details of the amorphous state. Definite progress has already been made in this direction, and several interesting facts have been discovered concerning the supermolecular organisation of amorphous polymers. Simple density measurements on an amorphous polymer, e.g. poly(methyl methacrylate)[117,118], showing a decrease on quenching from the rubberlike elastic state and a continuous increase during annealing below the glass point, have already indicated the occurrence and the reversibility of ordering in the amorphous state, while the proportionality of the density of oriented specimens of the same polymer to the double refraction[118] indicates quite clearly the character of the ordering.

However, this method is not always sufficiently sensitive: in the case of polystyrene, for example, the density remains constant after it has been stretched 50 times[119], although the double refraction and the infrared dichroism definitely record a certain degree of molecular orientation[120]. It is noteworthy that oriented amorphous preparations have seldom been chosen as subjects for structural investigations. The above examples may be supplemented by the observation of a long period (150–250 Å) on the equator of the small-angle X-ray diffraction pattern of slightly oriented poly(vinyl acetate)[121]. Furthermore, application of X-ray diffraction and physicomechanical study of oriented amorphous fibres of polyaminoacids has shown[41] that the modulus of elasticity calculated from the change in the repeat distance along the chain under the influence of tension is several times larger than the macroscopic value for the specimen as a whole. By analogy with the corresponding phenomenon in crystalline polymers, which has been studied thoroughly, this result may indicate an alternation along the texture axis of regions differing in degree of order.

More comprehensive information has been obtained for isotropic specimens. Thermographic study has shown that ordering processes, unconnected with crystallisation, the effects of which appear separately[125–127], occur in the amorphous phase of poly(ethylene terephthalate)[117], poly(vinyl chloride), and copolymers of the latter[122–124] during annealing. Interesting attempts have been made to apply nuclear magnetic resonance to polyethylene in concentrated solutions and in the melt[128]. The distortion of the form of the resonance line observed in the spectra of these preparations were interpreted as due to the superposition of two components, narrow and wide, which they assigned to disordered and ordered regions respectively. The amorphous phase of polyethylene was similarly divided into two components on analysis of the n.m.r. spectrum obtained by rotation at the "magic" angle[129], although the numerical ratios found[129] for the two components differ from the values obtained by other workers[128]. The development of order in amorphous polymers is apparent in the infrared spectra[130]: the splitting of the carbonyl vibrational band is similar in character when amorphous poly(methyl methacrylate) is precipitated from solution or from a polymerisation product and when poly-ϵ-caprolactone is crystallised from the melt. The type of splitting indicates the presence of mutually oriented molecular structures in poly(methyl methacrylate).

The scattering of light has recently been used to examine the structure of amorphous polymers. With poly(methyl methacrylate)[39], polystyrene[131], and polycarbonate[39] the observed intensity of vertically polarised scattering exceeded the calculated value, which may be due to the presence of scattering centres of 1000–2000 Å.[39] The intensity of this scattering increases with rise in temperature, but the monotonic character of the dependence does not change on passing through the glass point[131], as might have been expected from the electron-microscopic observations[102,109]. The horizontally polarised component of the scattered light was independent both of temperature and of angle of scattering[39,131]. This was

regarded[39,131] as implying that the internal structure of the scattering centres is isotropic: i.e. the method of light scattering reveals no anisotropy in the molecular packing at dimensions exceeding 1000 Å.

Another approach to solving the problem of the scattering of light on poly(methyl methacrylate) is to replace the latter by a model consisting of spheres having different refractive indices[132]. The histograms ultimately obtained (which showed the relative contents of hypothetical spheres having various refractive indices) were even sensitive to annealing and quenching of the specimen. Nevertheless, attempts to confer a real physical meaning on absolute values of the density calculated from the refractive indices obtained are hardly soundly based. Indeed, the values found[132]—a content of ~ 40% of spheres of density $\rho_{calc} = 1.29$ g cm^{-3}—appear very high in comparison with $\rho_{amorph} = 1.19$ and $\rho_{cryst} = 1.22$–1.23 g cm^{-3},[5] especially in view of results obtained by application of small-angle X-ray scattering to amorphous materials.

Theory indicates[133] that the intensity of the scattering of X-rays at very small angles by a material exhibiting density fluctuations extending over the range 10–10^4 Å is directly proportional to the square of the density difference between "particle" and medium and to the number of inhomogeneities, and is related exponentially to their radius of gyration. For a long time, therefore, it was expected that papers would appear on the application of such scattering to the study of amorphous polymers, in order to obtain experimental estimates of the density difference between domains and interdomainal space. The very low intensity of small-angle scattering by amorphous polymers was already emphasised in the first few papers[117,134]. Within the limits of the moderate resolving power of the apparatus used ($2\theta \geqslant 8.5'$) the experimental curves for poly(ethylene terephthalate) were well reproduced by Guinier's approximation[133] with a radius of gyration of the inhomogeneous regions of 15–20 Å.[134,135] This was half the radius of domains found from electron-microscopic measurements[56,109]. It was noted that annealing at a temperature below the glass point tends to increase the product of the number of scattering centres and the square of the density difference. A study by small-angle X-ray scattering of the crystallisation of the same polymer has revealed[136] a decrease in density of uncrystallised regions from 1.337 to 1.31 g cm^{-3} (by 1.5%) with increase in the degree of crystallinity to its maximum value.

Lin and Kramer[137] were probably the first to attempt to estimate the density difference between domains and interdomainal space directly from absolute measurements of the intensity of small-angle X-ray scattering: for polycarbonate they found the radius of gyration of inhomogeneities to be 130 Å, and the density difference to be 1.6–1.8% (it is noteworthy that $\rho_{cryst} - \rho_{amorph} = 21\%$). Polycarbonate was soon examined with small-angle apparatus of ultrahigh resolution[138] ($2\theta_{min} = 10''$). The intensity of scattering at moderately small angles ($2\theta > 20'$) was almost constant, and consistent with the theoretical scattering on density fluctuations in a homogeneous liquid. At angles approaching the smallest possible with the given apparatus the intensity of scattering increased sharply, and could not be described in Guinier coordinates by a single radius of gyration. Hence it is not possible to calculate both the density difference and the concentration of scattering centres from the experimental data. If the density of the domains is taken to be ρ_{cryst}, their dimensions will lie in the range 50–3000 Å, while the volume fraction is ~ 0.04%. This most likely comprises dust particles, catalyst residues, etc. If, however, the volume fraction and the dimensions are taken from electron-microscopic data (~ 50% and 50–100 Å respectively), the density of the domains should be very close to that of the matrix. Similar results have been obtained for poly(methyl methacrylate)[39] and for polyglycol ethers[101]. Thus the results of small-angle X-ray scattering indicate a very insignificant difference ($\leqslant 1.5\%$) in the density of inhomogeneities in the structure of amorphous polymers.

A new page in research on the structure of amorphous polymers was opened by Krigbaum and Goodwin[139], who used small-angle scattering by specially prepared specimens to determine the size of single macromolecules in the block state. They studied the scattering of X-rays by a 5% solid solution in ordinary polystyrene of polystyrene molecules weighted at the ends with silver atoms. The calculated root mean square distance between the silver atoms, i.e. between the ends of the chain, was 269 Å, which exceeded by 24% the unperturbed dimensions of macromolecules of the given molecular mass (217 Å for $M = 87\,000$) according to Flory[140].

Polymer*	$10^{-3}M_w$	R_w(bl), Å	$R_w(\theta)^{135}_{calc}$, Å	$\frac{R_w(bl)-R_w(\theta)}{R_w(\theta)}$, %	$\frac{R_w(bl)}{M_w^{1/2}}$
ps	7.1	30[142]	23.1	21.2	0.33
ps	21	40[143]	39.7	0.8	0.28
ps	57	80[143]	65.3	22.5	0.34
ps	90	100[143]	82.1	21.8	0.30
ps	97	90[145]	85.1	5.4	0.29
ps	112	115[143]	91.5	25.7	0.35
ps	325	200[143]	156	28.2	0.35
ps	390	280[145]	258	8.5	0.30
pmma	250	116—130[146—148]	109[146]	16—19	—
pe	81	126[39]	123[39]	24.4	—

* ps = polystyrene; pmma = poly(methyl methacrylate); pe = polyethylene.

The small-angle scattering of neutrons by solid solutions comprising a low concentration of deuterated molecules dissolved in the usual substance, or conversely, has become more widely used during recent years. Most of the investigations have been made on polystyrene[141–145], as well as on poly(methyl methacrylate)[146–148] and molten polyethylene[39]. The radius of gyration of the macromolecules in the block R_w(bl) was in all cases comparable with values for solutions in a θ solvent $R_w(\theta)$, but nevertheless usually exceeded it on the average by 20%, as is evident from the Table. The latter shows clearly for polystyrene the proportionality of the size of macromolecules in the block to the square root of the molecular mass: $R_w(bl) = \frac{1}{3}M_w^{1/2}$. A similar dependence has been found also for poly(methyl methacrylate)[148].

The possibility of obtaining quantitative information on the dimensions of macromolecules in the block, demonstrated in the above publications, is undoubtedly one of the greatest achievements of polymer science during recent years. Nevertheless, the conclusions reached by the authors and sustained by such authorities as Fischer[39] and Flory[162], on the correspondence of the conformation of macromolecules in the block and in solution, which were based merely on the correspondence of their external dimensions, are too categorical in the Reviewer's opinion.

In the search for ways of resolving the apparent contradiction between many facts on the development of order in the packing of macromolecules and their coiled form several authors sought to deepen the analogy between amorphous and crystalline structures: it was suggested that macromolecules are folded in vitreous polymers. This hypothesis was probably first put forward by Robertson[149], the immediate occasion being his comparison of experimental density ratios for several polymers in crystalline and amorphous states with those calculated for various angles between neighbouring chain segments. The best agreement was observed if divergence of the segments from parallelism did not exceed 5–15° for different polymers. However, Robertson's calculations on the density of packing of molecules with skew contacts have recently been subjected to serious criticism. According to Fischer et al.[39] the density of packing of polyethylene calculated on the assumption of a random distribution of angles of contact between neighbouring segments is 0.687, whereas experimental values for the molten and vitreous states are respectively 0.625 and 0.645.

Despite the controversial character of the initial premise, the hypothesis of chain folding in the amorphous state gained wide popularity. Details were filled in by Privalko et al.,[150] who suggested a formula for calculating the length of a fold from experimental values of the molecular mass, the steric factor of restricted internal rotation, and the cross-section of the molecules. An active search is being made for experimental evidence of the folding of chains in the amorphous state. Thus small-angle meridional reflections have been observed in several crystallisable polymers even when, according to large-angle X-ray diffraction, crystallisation has not yet taken place[151]. Petermann and Gleiter[152] observed that, if a single crystal of polyethylene in which the axes of folded chains are parallel to the electron beam is melted directly in the electron microscope, the diffuse ring of period 2.55 Å is absent from the resulting electron-diffraction pattern. This means that even after fusion the axes of the macromolecules retain their previous orientation perpendicular to the plane of the specimen, and hence have a folded conformation as before. In the study of polyethylene it was also observed[153] that increase in molecular mass is accompanied by a sharp increase in diamagnetic susceptibility in the region of transition from alkane crystals having straightened chains to polyethylene crystals with a folded conformation, reaching and even somewhat exceeding the values corresponding to liquid alkanes. It was then found that in the same region the diamagnetic susceptibility of molten polyethylene also increases, to a value typical of gaseous alkanes. Comparison of experimental data on the optical anisotropy of macromolecules, the root mean square distances between the ends of a chain, and several other similar characteristics of polyethylene with values calculated for models of chains containing straightened segments of various lengths showed[154] that most satisfactory agreement is obtained with lengths of 10–20 monomer units. Investigation of the dependence of the density and the surface tension of narrow polyoxyethylene fractions on molecular mass revealed a minimum in the range of values of this last factor (~ 3000) at which chain folding began on crystallisation. Similar types of relations were obtained with non-crystallising oligomers of diethylene glycol adipate[155,156].

In concluding this survey of experimental results of the application of structural methods to amorphous polymers we must also remark that the repeatedly noted ambiguity and sometimes even inconsistency of the direct structural information, the very wide range of highly specialised methods of investigation and the consequent great dispersion of literature sources among the pages of several dozen different periodicals, and several other similar factors led to the appearance of a number of models of the amorphous state arising from the need for a logical explanation of anomalies in the macroscopic properties of polymers—the molecular-domain model to describe rheological phenomena and mechanical breakdown[157], the folded-fibrillar model to explain anomalies in the recovery from forced elastic deformation[158], its cluster modification[159], the dislocation model for viscous flow[160], the associative model to explain dynamic mechanical data[161], etc. A distinguishing feature of such models is unnecessary detail, structural evidence for which is at present completely lacking.

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Several important characteristics of the structure of amorphous polymers have been reliably established by the broad application of the traditional and the most recent resources of physical experiment to its analysis.

Firstly mention must be made of determination of the dimensions of individual macromolecules in isotropic block specimens (root mean square distance between ends of chain and weight-average radius of gyration) from data on the small-angle scattering mainly of neutrons. The principal result of these investigations is that the size of macromolecules is proportional to the square root of their molecular mass, and exceeds the size of a Gaussian coil by ~ 20%.

The next important conclusion, based on the diffraction of X-rays and electrons at large scattering angles, is that segments of chains are folded roughly in parallel in microregions of dimensions 20–50 Å. The scattering of X-rays at small angles indicates further that the density of such microregions differs very little from that of portions with skew contacts between chain segments (by 1.5% or less).

Despite the slight differences in density, these inhomogeneities in the packing of macromolecules could be visualised by the correct application of various procedures in electron microscopy (contrast enhancement, etching, dark-field technique, phase contrast effects).

The hypothesis of chain folding in the formation of ordered microregions in amorphous polymers has gained great popularity. It is based on certain theoretical arguments and several experimental analogies with the phenomena of chain folding in single crystals of polymers. Nevertheless, it must be borne in mind that all experimental results relating to chain folding have been obtained for the amorphous state of crystallisable polymers.

Of the large number of schematic models of the structure of amorphous polymers in the unoriented state (on the scale up to ~ 100–200 Å) those of Vainshtein and of Yeh and Geil, which differ merely in whether folding of macromolecules is essential, correspond most completely to the above characteristics.

Structural data at present available for dimensions of the next scale (200–9000 Å) are few and contradictory. Reliable data on the structure of the oriented state of amorphous polymers are almost completely lacking, and it is here that important advances in our knowledge of the fine structure of amorphous polymers must be expected in the very near future.

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