# PHYSICAL CHEMISTRY

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## Abstract

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# MORPHOLOGY OF MOLECULAR PACKINGS IN LINEAR POLYESTERS

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Continuing our investigations of the packing of molecules in crystals of linear polyesters (1,2), we applied the methods of electron microscopy, electron diffraction, and small-angle X-ray scattering. Interest in the morphological structure of these objects arose in connection with the obtaining of small-angle X-ray patterns that indicated the presence of a very strict periodicity of the order of 100–200 Å. In addition, it was noted that the magnitude of the superperiod, in general, increases with the length of the chemical structural unit (see Table 1).* The X-ray patterns contained distinct reflections up to the fourth order. Usually, however, small-angle X-ray patterns of polymers contain a single order of diffraction. The only known case (ˆ3) in which four orders of reflections from a period of ~100 Å were obtained was in polyethylene; however, the latter was prepared by precipitation from solution under conditions of slow cooling, whereas the polyester samples were obtained from the melt without observing special thermal conditions during their solidification.

As is known (4-8), in recent years single-crystalline formations have been found in some linear polymers with a regular chain (polyethylene, gutta-percha, polyamides, isotactic polyolefins).** The same phenomenon has been discovered by us for the class of linear polyesters. Microphotographs show single crystals growing by spiral terraces, as well as individual single-crystalline layers (Fig. 1). Microdiffraction recording (Fig. 2) made it possible to establish the perpendicularity of the molecular axes to the plane of these monolayers. Study of the external shape of the single crystals, facilitated by knowledge of the crystal substructure (see Table 1), shows that the indices of the faces $\{+1,+1,0\}$ and $\{100\}$ can be assigned to the outer contours. These are precisely the planes in which neighboring chains are closely packed with one another and therefore are theoretically the most probable growth faces.

The very fact of the discovery of single-crystal growth in one more important class of polymers shows that, for polymers with a regular molecular chain, this phenomenon has a sufficiently general character. Study of the large number of electron-microscopic images at our disposal indicates a close connection of these structures with more complex morphological formations also observed in

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the electron microscope (see also (^9)).

Samples for study in the electron microscope were prepared by dissolving the polymer in hot ethyl alcohol or amyl acetate. Upon cooling under ordinary room conditions, single crystals precipitated from the ethyl alcohol solution, as a rule, in the form of hexagons, and from amyl acetate—in the form of rhombi, the process usually being readily reproducible. We believe that the extraordinary ease of crystallization is due—

* The magnitude of the indicated periodicity depends on the thermal regime of solidification. For example, a sample of decamethylene glycol and adipic acid, upon solidification in a jet of liquid-nitrogen vapor, gave a period of 151 Å, and after melting and slow cooling, 194 Å. However, all the substances listed in Table 1 were obtained under approximately identical conditions.

** The present investigation concerns crystalline polymers. As for amorphous polymers, geometrically regular forms have also been found in them (^13).

**Fig. 1.** *a, b* —monocrystalline formations in polyesters (samples obtained from solution); *c, d* —monocrystalline formations in polyesters—monolayers (from solution)

was determined both by the very nature of the objects and by their comparatively low molecular weight (2-3 thousand). With slow cooling of the solution, crystals several tens of microns in size grew. On the contrary, under less equilibrium conditions, the creation of which sometimes required special measures, intermediate forms transitional to spherulites were obtained. In a number of photographs it is evident that a structure consisting of individual single-crystal layers superposed on one another continuously passes into "bundles," which, as is known, are the embryonic form of spherulites.

**Fig. 2.** Diffraction pattern from a monolayer shown in Fig. 1 *g*

The height of steps on spiral terraces deserves special consideration. It is known that in crystals of normal paraffins the direction of the molecular axes either coincides with the normal to the crystal plane or makes a small angle with it, and the thickness of the steps corresponds to the length of the molecule (10). In polyethylene the axes of the chains are normal to the layers; the layer thickness (11) corresponds to the "fold period" (the term was introduced by Keller), i.e., to the distance between two successive folds of the molecular chain, usually equal to 100-120 Å; however, the physical nature of chain folding with the

Fig. 3

Figure 3: Fig. 3

observance of the unusually strict periodicity of the indicated magnitude has not yet been revealed. The structure of the polyester chain differs from polyethylene in that ester groups are regularly arranged along it. The period of the chemical structural unit for the objects studied of the decamethylene glycol series is 17-30 Å, and for the eicosamethylene glycol series 30-43 Å.* Measurements of the height of steps and of individual monolayers from electron-microscopic photographs gave values lying within 15-35 Å for objects of the decamethylene glycol series and 40-70 Å for the eicosamethylene glycol series. Comparison of these figures gives some grounds for believing that in packings of polyester molecules we encounter a new phenomenon, when the fold period is determined by the length of the chemical structural unit. We hope later to verify this fact more thoroughly. All three cases mentioned above are shown schematically in Fig. 3. Analysis of a large number of microphotographs makes it possible to suppose that the height of steps in single crystals is not a completely stable quantity. This conclusion is confirmed by X-ray photography at small and large angles of a specimen deposited from a solution of the same concentration as that used in electron microscopy. The X-ray diffraction patterns contained only the diffraction pattern of the subcell; but the superstructural periodicity (~100-200 Å), as well as the periodicity due to the oxygen atoms of the C=O groups (~10-15 Å), disappeared completely. No periodicity corresponding to the thickness of the crystalline layers (~20-30 Å for specimens of the decamethylene glycol series) was detected either.

**Fig. 3.** Thickness of the crystalline layer (schematic). Methyl and ether groups are denoted by a bold dot. *a* –*n*-paraffins, *b* –polyethylene, *c* –polyesters

In the microphotographs, many other varied morphological forms were also recorded. By varying the conditions of preparation of the objects, one can obtain large dendritic formations consisting of fused single crystals, spiral growth of unlimited monolayers, globules twisted into a spiral, dendrites in the form of a monolayer with folds in the middle, fibrils, etc. Sometimes 2-3 different forms can be observed in one field of view.

* If the chain is regarded as a flat zigzag with period $c_0 = 2.5$ Å and the doubling of the period associated with chain symmetry is not taken into account for some members of the homologous series.

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Fig. 4. **a** –dendritic formations (from the melt); **b** –fragment of a ribbon consisting of several threads. 140 000×

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Fig. 1. Debyegrams of beryllosodalite (**A**) and sodalite (**B**)

Searches for a correlation between small-angle periodicity (100–200 Å) and the electron-microscopic pattern led us to examine, in an electron microscope, samples crystallizing from the melt. In order for them to be transparent to the electron beam, they were first prepared by the method described above, deposited on a support, and then subjected to melting followed by solidification under specified thermal conditions. The resulting picture, reproduced in Fig. 4, reveals monolayers in the form of dendrites with folds in the middle, consisting of a row of parallel threads. The same threads sometimes lie separately on the support, combining several at a time to form ribbons, which in turn gradually pass into monolayers. In those places where the ribbons consist of threads lying in a single row on the support, it can be established that the width of the individual threads composing it is $\sim 130$ Å, and the height is $\sim 30$ Å. Let us note that the first number has the same order of magnitude as the periodicity detected in the small-angle camera, while the second approximately coincides with the height of a step in single crystals. Thus, despite the fact that the cross section of an individual thread is very small and exceeds the cross-sectional dimensions of one molecule by only two orders of magnitude, this gives no grounds for considering it to be a bundle of extended parallel molecules. On the contrary, our data are in better agreement with the data of ([12]), according to which the axes of the molecules are more likely perpendicular than parallel to the axis of the thread.

Finally, it is important that from the melt there were obtained photographs of "sheaves" gradually passing into monocrystalline layers, completely analogous to those obtained from samples prepared from solution, while from solution there were obtained dendrites, ribbons, and threads coinciding in appearance with those shown in Fig. 4, the threads having the same width. In addition, in Fig. 4a one can note the appearance of crystalline faceting of monolayers for a sample obtained from the melt.

**Table 1**

| Sample | Length of the chemical structural unit*, Å | Greatest interplanar distance due to C=O groups, Å | Large periods, Å | Large periods, number of diffraction orders | Parameters of the R-subcell, Å, $a_0$ | Parameters of the R-subcell, Å, $b_0$ | Parameters of the R-subcell, Å, $c_0$ |
|---|---|---|---|---|---|---|---|
| Polyester of decamethylene glycol and oxalic acid | 17.5 | 13.2 | 104 | 2 | 6.90 | 5.24 | (?) |
| Polyester of decamethylene glycol and succinic acid | 20.0 | 13.0 | 142 | 3 | 7.30 | 5.04 | 2.47–2.51 |
| Polyester of decamethylene glycol and glutaric acid | 21.2 | 18.9 | 162 | 3 | 7.36 | 4.96 | 2.46 |

| Sample | Length of the chemical structural unit*, Å | Greatest interplanar distance due to C=O groups, Å | Large periods, Å | Large periods, number of diffraction orders | Parameters of the R-subcell, Å, $a_0$ | Parameters of the R-subcell, Å, $b_0$ | Parameters of the R-subcell, Å, $c_0$ |
|---|---|---|---|---|---|---|---|
| Polyester of decamethylene glycol and adipic acid | 22.5 | 10.6 | 182 | 4 | 7.40 | 5.01 | 2.48 |
| Polyester of decamethylene glycol and azelaic acid | 26.2 | 18.3 (?); 9.5 | 208 | 4 | 7.45 | 4.98 | 2.48 |
| Polyester of decamethylene glycol and sebacic acid | 27.5 | 12.2 | 180 | 4 | 7.41 | 4.96 | 2.47 |

* See footnote on p. 1134.

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