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Abstract

Full Text

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TRICLINIC MODIFICATION OF POLYETHYLENE

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1. Molecules of the paraffin type can crystallize in one of three modifications –triclinic (T), monoclinic (M), or orthorhombic (R) ([1]). Two of them have been found experimentally ([2,3]). Triclinic subcells have been found in normal paraffins with an even number of carbon atoms from C_{18} to C_{26} and in some normal fatty acids; orthorhombic subcells have been found in polyethylene, in odd *n*-paraffins, in even *n*-paraffins from C_{28} and higher, in some normal fatty acids, etc. Substances with monoclinic subcells have not yet been found, which is readily explained, since packing of this type is low-symmetry and less dense than the two preceding ones.

The difference in free energy between the R and T packings is small. This follows at least from the circumstance that a few percent of impurities of neighboring homologs convert the triclinic structure of an *n*-paraffin into an orthorhombic one. Of all possible packing types, the packing in the T-subcell has the greatest density; however, the R-subcell has higher symmetry. On the basis of an analysis of the packing of long-chain molecules, the probable existence of a triclinic modification of polyethylene was previously indicated ([4]).

2. Since the T-subcell has a high density of molecular packing, it could be assumed that it can be realized only in polyethylene specimens that are most perfect from the structural point of view, i.e., the purest and possessing a minimal number of lateral branches. Therefore the objects of investigation were: low-pressure polyethylene (provided by V. Kabanov), polyethylene obtained at a pressure of 100 atm with tributylboron as catalyst (provided by G. S. Kolesnikov and T. A. Soboleva), and polyethylene synthesized from diazomethane (supplied by V. A. Sergeev).

Powder-type X-ray photographs, obtained using monochromatized reflection from a crystal of CuK_α radiation, showed that the polyethylene samples studied had a pattern characteristic of a two-phase R + T system. The triclinic modification was present in a smaller amount than the orthorhombic one, as followed from comparison of the reflection intensities. We had previously observed an analogous two-phase pattern in studying the phase diagrams of *n*-paraffins ([5]).

In Fig. 1, both X-ray photographs are given for comparison. Measurement of

Fig. 1

Figure 1: Fig. 1

the interplanar spacings and comparison of intensities definitively confirmed the existence, under ordinary conditions, of the triclinic modification of polyethylene. The corresponding data are given in Table 1.

Comparison of X-ray photographs of various polyethylene samples shows that the reflections corresponding to the triclinic modification of polyethylene are relatively more intense in those cases in which the crystalline pattern as a whole possesses greater perfection (a larger number of sharp lines, absence of amorphous scattering).

Finally, let us compare our data with data from an X-ray study of *n*-paraffin C_{30} under high pressure (S. S. Kabalkina and L. F. Vere-

Fig. 1. A –One of the X-ray diffraction photographs of polythene containing both the rhombic and the triclinic modification. (The lines of the R-cell are indexed; for the T-cell, the interplanar spacings are indicated in the photographs by arrows.) **B** –X-ray diffraction photograph of 94% C_{18} + 6% C_{19} (shown for comparison). Two-phase region $R + T$.

Table 1

Interplanar spacings for the most intense reflections

Modification	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å
T-subcell n-C_{20}	4.54		3.79	3.58; 3.46	2.58
R-subcell n-C_{30}		4.12 (110)	3.73 (200)		
Polyethylene (R + T) of low pressure	4.55 (T)	4.12 (R)	3.71 (R)	3.47* (T)	2.58 (T)
Polyethylene from diazomethane (R + T)	4.55 (T)	4.14 (R)	3.72 (R)	3.53* (T)	2.58 (T)

Modification	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å	Interplanar spacings, Å
n-C_{30} under high pressure (R+T)	4.39 (T)	3.98 (R)	3.58 (R)		

Note. The interplanar spacings marked with an asterisk were measured approximately because of the proximity of the intense reflection (200), belonging to the R-cell.

Shagin, personal communication). In n-C_{30} under high pressure, the appearance, along with the rhombic phase, of another phase is also observed (see Table 1). Since under high pressure the crystal lattice is compressed, the interplanar spacings decrease by $\sim 3\%$. Multiplying them by the corresponding coefficient, we obtain $d_1 = 4.55$ Å; $d_2 = 4.12$ Å; $d_3 = 3.71$ Å. Whereas d_2 and d_3 belong to the R-subcell, d_1 coincides with the interplanar spacing of the strongest reflection of the triclinic modification of paraffins and polyethylene.

The character of the arrangement of molecules of the type under consideration in the triclinic subcell was established by us earlier ([1,6]). It may be assumed that the packing of triclinic polyethylene does not differ from the lateral packing of molecular chains in triclinic n-paraffins.

Thus, the present work confirms the prediction of the existence of a triclinic modification of polyethylene, made by us earlier*.

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CITED LITERATURE

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* When this article had already been typeset, we had the opportunity to become acquainted with the work of P. W. Teare, D. R. Holmes, *J. Polymer Sci.*, **24**, 496 (1957). The authors also experimentally detected the triclinic modification of polyethylene. The conclusion drawn on the basis of the theory of packing of chain molecules received new independent proof.

Note: Figure translations are in progress. See original paper for figures.