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ESTIMATION OF THE FLEXIBILITY OF POLYBUTYLENE CHAINS FROM SORPTION DATA

Earlier, in studying the sorption properties of polyethylene over a wide temperature range above and below the melting temperature of its crystals, it was shown that this polymer, the simplest representative of the polyolefin series, has chains of sufficiently great flexibility, which accounts for its crystallinity (^1). The present work is devoted to a study of the sorption properties of crystalline polybutylene in order to obtain data for estimating the flexibility of its chains. This polymer is of considerable interest, since, along with a crystalline structure, it also possesses the properties of elastomers. As the object of investigation we used a sample of polybutylene whose intrinsic viscosity, determined in decalin at 90°, was 1.14. Observation under a polarizing microscope established that the sample melts over the temperature interval from 94.3 to 104.8°.

Using spring balances placed in a high-temperature air thermostat, sorption isotherms of *n*-octane by polybutylene were obtained at temperatures from 50 to 115° (Fig. 1). As is seen from Fig. 1, the magnitude of sorption increases regularly with increasing temperature. The exception is the isotherm obtained at 50°, which up to a relative vapor pressure of the adsorbate equal to 0.45 lies above the isotherm obtained at 60°. This somewhat unexpected result is possibly associated with a looser packing of the chains at 50°, which leads to a larger sorption value. At higher values of the relative vapor pressure, when, owing to the plasticizing action of the solvent, the flexibility of the chains increases, the density of molecular packing increases and the sorption value becomes smaller than at 60°.

On detailed examination of the entire series of curves, attention is drawn to the fact that the sorption isotherm at 85° intersects the isotherm obtained at 94° (the melting temperature of the crystals) and then rises rather sharply upward. Such a course of the curve suggests that, in the premelting region at large values of the relative vapor pressure, the mobility of the chains increases so much that favorable conditions are created for the formation of larger ordered

Fig. 1. Sorption isotherms of n-octane by polybutylene: a –at 50°, b –60°, c –70°, d –75°, e –85°, f –94°, zh –104°, z –115°

Figure 1: Fig. 1. Sorption isotherms of n-octane by polybutylene: a –at 50°, b –60°, c –70°, d –75°, e –85°, f –94°, zh –104°, z –115°

structures, which is accompanied by an increase in the distances between the latter. If these distances are sufficiently large, then capillary condensation of the adsorbate vapor may occur in the gaps formed between the structures. It is interesting to note that the sorption isotherm obtained at 75°, when extrapolated to higher values of the relative vapor pressure, intersects the isotherm obtained at the melting temperature of the polybutylene crystals; i.e., in this case as well, capillary condensation of vapors should occur.

If the supposition made is correct, one can tentatively estimate the dimensions of the pores arising in the premelting region of the polymer, in which capillary condensation occurs. Such an estimate can be made, for example, by determining the diameter of the capillaries from the Kelvin equation (⌒2). The onset of capillary condensation was taken to be that region of relative–

vapor pressure, in which the isotherm rises sharply upward. In this way the diameters of the capillaries condensing the adsorbate vapors were calculated; their order of magnitude is estimated at approximately 100-1000 Å.

The results obtained are also confirmed by data from direct observation of structure-formation processes in polybutylene occurring upon heating. In work (⌒3), using an electron-microscopic method, the formation of large ordered structural entities was found; these are a system consisting of compacted elements and pores, whose dimensions also reach 100-1000 Å.

Fig. 1. Sorption isotherms of *n*-octane by polybutylene: **a** –at 50°, **b** –60°, **c** –70°, **d** –75°, **e** –85°, **zh** –104°, **z** –115°.

It should also be noted that in a number of studies on the investigation of polymer structures (^{4}-6) there are indications of the possibility of spontaneous crystallization in the premelting region, which also confirms the validity of the assumption made above. As for the sorption isotherms obtained at 104 and 115°, within the limits of experimental error they coincide with the isotherm at 94°.

On the basis of the sorption data, a calculation was made of the thermodynamic segment characterizing the flexibility of the chains, i.e., an effective quantity describing the behavior of the polymer in the melt (⌒7). It turned out that the segment consists of approximately 60 carbon atoms. However, taking into account that the main-valence chain of polybutylene is twice as short because of the lateral ethyl groups, the flexibility of its chains should be estimated by a smaller segment, on the order of 30 carbon atoms, which agrees well with the segment length of typical rubbers, equal to 20-40 carbon atoms.

Thus, the study of crystalline polybutylene has shown that this polymer is characterized by very flexible chains, with their flexibility corresponding to that of the chains of rubber-like polymers.

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References

1. T. V. Gatovskaya, G. M. Pavlyuchenko, V. A. Berestnev, V. A. Kargin, DAN, **143**, No. 3, 590 (1962).
2. A. V. Kiselev, *Usp. khim.*, **14**, 367 (1945).
3. V. G. Zhuravleva, Z. Ya. Berestneva, V. A. Kargin, DAN, **146**, No. 2 (1962).
4. M. Dole, *Fortsch. Hochpolymerenforsch.*, **2**, No. 2, 221 (1960); *Khim. i tekhnol. polimerov*, No. 1, 3 (1962).
5. A. Müller, R. Pflüger, *Kunststoffe*, **50**, No. 4, 203 (1960); *Khim. i tekhnol. polimerov*, No. 1, 67 (1961).
6. Proceedings of the American Chemical Society Conference in Cleveland, April 1960; *Khim. i tekhnol. polimerov*, No. 1, 143 (1961).
7. V. A. Kargin, T. L. Slonimskii, *Brief Essays on the Physical Chemistry of Polymers*, Moscow, 1960, p. 32; A. A. Tager, V. A. Kargin, *Koll. zhurn.*, **10**, 455 (1948).

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