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Abstract

Full Text

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ESTIMATION OF THE FLEXIBILITY OF POLYETHYLENE CHAINS FROM SORPTION DATA

From general considerations it is assumed that crystalline polymers must have flexible chains, since rigid chains cannot pack with sufficient regularity to form a crystalline lattice. To estimate the flexibility of molecules of amorphous polymers it is convenient to use sorption data obtained at room temperature ([1]). However, the flexibility of the chains of crystalline polymers cannot be determined in this way, since in a crystalline structure under these conditions the entire set of conformations characteristic of the given polymer cannot be realized. It should be determined in the melt, where realization of all conformations possible for the given polymer is not hindered by the presence of crystalline regions.

The present article is devoted to the study of the sorption properties of the simplest crystalline polymer—polyethylene—over a wide temperature range, above and below the melting temperature of its crystals. The polyethylene sample had a regular structure and a molecular weight of about 1 million. The melting temperature was determined with a polarizing microscope. It was found that at t = 131-136° spherulites disappear, and at 164° droplets appear. The sorption isotherms were obtained by means of spring balances placed in a high-temperature air thermostat.

Fig. 1. Sorption isotherms of *n*-dodecane by polyethylene:
1–75°, 2–100°, 3–110°, 4–120°, 5–125°,
6–127°, 7–130°, 8–140°, 9–150°, 10–200°

The obtained sorption isotherms, shown in Fig. 1, indicate that the magnitude of sorption in the temperature interval from 75 to 130° gradually increases. Upon further heating to 140, 150, and 200°, the sorption isotherms coincide with the isotherm at 130°. This means that already at the melting temperature of the spherulites the sorption reaches its maximum value. It is interesting to

Fig. 2. Dependence of the value of the polyethylene segment on the relative vapor pressure of *n*-dodecane. Symbols as in Fig. 1

Figure 2: Fig. 2. Dependence of the value of the polyethylene segment on the relative vapor pressure of *n*-dodecane. Symbols as in Fig. 1

Fig. 3. Dependence of the reduced value of the segment on temperature

Figure 3: Fig. 3. Dependence of the reduced value of the segment on temperature

note that the sorption isotherm obtained at 125° differs in appearance from the other isotherms: at approximately 60% relative,

vapor pressure it rises sharply upward, merging with the isotherm at 130°. Apparently, owing to the plasticizing action of *n*-dodecane, the polymer begins to melt at a lower temperature. This effect is still more pronounced for the sorption isotherm obtained at 127°. Here the curve up to 20% relative vapor pressure lies below the isotherm at 130°, and thereafter merges with it.

For estimating the flexibility of polymer chains on the basis of sorption data, the value of the thermodynamic segment was calculated ([2]).

In Fig. 2 are presented plots of the change in the value of the segment as a function of the relative vapor pressure of *n*-dodecane at different temperatures. The results obtained indicate that the value of the segment is affected by the presence of a low-molecular component in the system. Therefore the true value of the segment can be obtained by extrapolating the curves shown in Fig. 2 to zero adsorbate content. The dependence of this reduced value of the segment on temperature is shown in Fig. 3. At 75° the segment consists of approximately 600 carbon atoms.

Fig. 2. Dependence of the value of the polyethylene segment on the relative vapor pressure of *n*-dodecane. Symbols as in Fig. 1

Fig. 3. Dependence of the reduced value of the segment on temperature

The gradual decrease in the value of the segment indicates that, with increasing temperature, the flexibility of the chains increases and the possibility of realizing an ever larger number of conformations is enhanced. Finally, upon melting, the flexibility increases sharply; the entire conformational set inherent in polyethylene is realized, and the segment reaches the minimum and true value of 60 carbon atoms, which is only five times greater than the length of the adsorbate molecule. Apparently, such flexibility is optimal for crystallization to occur.

Indeed, on the one hand, rubbers and rubber-like polymers have chains of very great flexibility, 20–40 carbon atoms in a segment, and crystallize poorly because of the large difference between the entropy values of the crystalline and amorphous states. On the other hand, polymers with rigid chains do not crystallize

at all, which is due to considerable kinetic difficulties.

Thus, for crystallization to occur, polymer chains must possess some intermediate flexibility between that of rubber-like polymers and hard plastics.

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