LOCAL ORDER IN POLYMERS: A DESCRIPTION WITHIN THE FRAMEWORK OF THE MODEL OF IRREVERSIBLE COLLOIDAL AGGREGATION

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We propose to interpret the structure of amorphous glassy polymers as a set of clusters formed by diffusion-limited aggregation (Witten–Sander clusters). Within the framework of the investigation, we confirmed the existence of regions of local order in the structure of these polymers.

The processes of aggregation of colloidal particles have always been among the basic objects in studying the chemistry and physics of colloids, since they are of both theoretical and applied importance. In the past decade such investigations have attained a qualitatively new level due to the application of present-day methods of physics, namely, fractal analysis [1], the scaling approach [2], and models of irreversible aggregation developed by means of computer simulation [3-5]. The approaches indicated have been repeatedly applied with advantage to describe processes of colloidal aggregation of various actual systems [6-10].

In the present work the Witten–Sander model [3] of diffusion-limited aggregation (DLA) will be used to describe the structure of solid polymers by means of a cluster model representing the structure of the amorphous state of polymers [11, 12]. The model is based on concepts of local order suggested for the first time in [13].

Using two polymers (high-density polyethylene and polycarbonate) as an example, we will show a correspondence between the models of [3] and [11, 12], which implies the indispensable presence of a certain degree of local (short-range) order in the structure of solid polymers.

The required computational parameters for high-density polyethylene (HDPE) and polycarbonate (PC) are taken from the literature. They include the functionality of the regions of local order (the number of chains going out from such a region) F [11], the cross-sectional area of a macromolecule S [14], the distance between the regions of local order R_{loc} [11], the densities of the polymers in a crystalline state ρ_{cr} [15] and in a melt ρ_{melt} [16], and the value of the Poisson coefficient μ [17].

The model of [11, 12] presupposes that in the structure of the amorphous state of the polymers there are regions of local order of thermofluctuational origin that consist of several collinear close-packed segments of different macromolecules. In Fig. 1 a schematic representation of a region of local order is given, from which it follows that this region is an amorphous analog of a crystallite with elongated chains. Therefore the number of segments in such a region n_{loc} is taken to be equal to [12]

$$n_{loc} = F/2. \tag{1}$$

There are fairly many reasons for associating the structure of the amorphous state of the polymers with the Witten–Sander (WS) cluster and for assigning them to one class of universality. These reasons are considered in detail in [18]; here we shall mention three main ones. The first is the correspondence of the aggregation mechanism, which for the WS cluster will be the addition of individual particles to a growing cluster (aggregation of the particle-cluster type) [3, 9]. In the model of [11, 12] addition of a statistical segment to a region of local order is such a mechanism, with this act being equivalent to the "collapse" of the microcavity of a fluctuational free
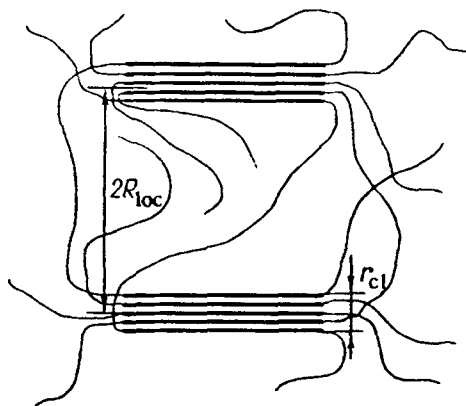

Fig. 1. Schematic representation of a region of local order in the model of [11, 12].

volume [11, 19]. The second reason stems from the first: by virtue of identical mechanisms of aggregation the structure of the amorphous state of the polymers and WS clusters have identical scaling indices, namely, the fractal (Hausdorff) dimensions d_f [20] and D [3], respectively. And, finally, it is well known [21, 22] that at the gelation point in the synthesis of polymers a change in the universality class occurs, namely, the cluster—cluster mechanism is replaced by a particle—cluster mechanism, with the latter resulting in the WS cluster.

For the WS cluster we can write the following relation, which characterizes the change in its density ρ_{WS} as a function of the cluster radius R_{WS} and the quantity D [6]:

$$\rho_{WS} = \rho_{cp} \left(\frac{R_{WS}}{\alpha}\right)^{D-d}, \tag{2}$$

where ρ_{cp} is the density of the substance of the WS cluster in the state of close packing; α is the lower limit of the fractal behavior of the WS cluster; d is the dimensionality of the Euclidean space in which the WS cluster is considered (it is evident in our case that $d = 3$).

Let us consider Eq. (2) at greater length. Since in the case of the WS cluster $D < d$ and $\rho_{WS} < \rho_{cp}$ (a change in the sign in these two inequalities to an equality sign means passage of the cluster to another class of universality, for example, passage to Eden's cluster [9]), then this fact determines the condition $\alpha < R_{WS}$. But since $\rho_{WS} \neq 0$ and $\rho_{cp} \neq 0$, then α cannot be equal to zero. Thus, at the center of the WS cluster a compact $(D \approx d)$ region of size α always exists, which for the structure of the amorphous state of the polymers is identified as a region of local order (see Fig. 1). This statement is one of the conditions for the existence of the WS cluster [23]. In this connection we should make two comments. First, it is easy to understand the reason for formation of a compact region in the first stages of formation of the WS cluster. The fractal nature of the WS cluster is determined by the screening effect of its "branches," which prevents access of particles to the internal regions of the cluster [23, 24]. But in the first stages of growth these "branches" are not well developed and their screening effect is small. Second, the structure of the polymers, just like any actual (physical) fractal, possesses fractal properties only in a certain range of linear scales [25]. It is shown experimentally for polymers [26] that this range extends from several angstroms to several tens of angstroms. This implies a certain gradient of the polymer density in the mentioned range of scales [25], which, in turn, presupposes alternation of clumps and rarefactions of the substance, which is also observed experimentally [27]. As follows from Fig. 1, the model of [11, 12] satisfies this condition, whereas Flory's "felt" model [28] of the structure of polymers, which assumes that the structure consists of interpenetrating macromolecular balls and has no the local order, cannot explain the experimentally observed fractal behavior [26].

Thus, the identification of the structure of the amorphous state of the polymers as the WS cluster (or, more precisely, as a set of such clusters) and the indispensable presence of compact regions in the latter presuppose the necessary existence of regions of local order in the amorphous state. To confirm this we compare the values of α
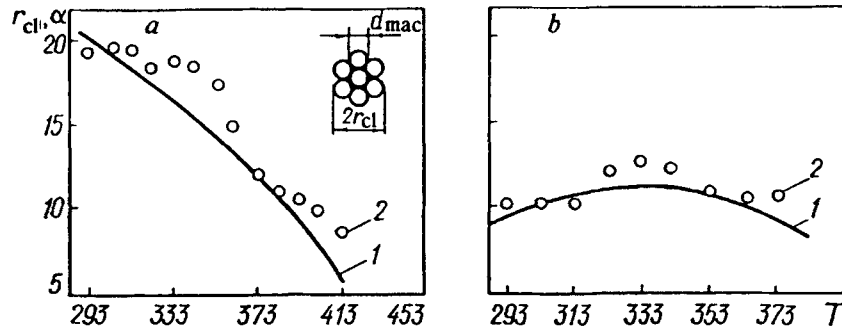
Fig. 2. Dependences of the dimensions of local-order regions r_{cl} (1) in the model of [11, 12] and compact regions α (2) in the model of [3, 23] on the temperature T for PC (a) and HDPE (b); the insert depicts schematically the cross section of a region of local order (Fig. 1) consisting of seven statistical segments (d_{mac} is the diameter of a polymer macromolecule). r_{cl}, α, Å.

obtained from Eq. (2) and the dimensions of the regions of local order r_{cl} (the inset in Fig. 2a). The quantity r_{cl} can be determined from the relation (on condition of close packing) [29]

$$r_{cl} = \left(\frac{n_{loc}S}{\pi\eta}\right)^{1/2}, \tag{3}$$

where η is the packing density, which for monodisperse circles is equal to 0.74 [29].

Figure 2 presents a comparison between the dimensions of the regions of local order r_{cl} in the model of [11, 12] and the compact regions α in the WS model [3, 23] as a function of the test temperature T for PC and HDPE, respectively. The density of the loosely packed matrix of the polymer is taken as ρ_{WS}, which coincides with the density of the polymer above the glass transition temperature [30], and the density of the crystal regions of PC and HDPE is taken as ρ_{cp}. Moreover, it is assumed in the calculations that $R_{WS} = R_{loc}$ and $D = d_f$. As follows from the figure, both the absolute values and the tendencies of the variation with T for the parameters r_{cl} and α are in good agreement. A certain spread in the values of α with respect to r_{cl} is caused by the error in the evaluation of d_f owing to the power-function dependence of α on $D = d_f$ (Eq. (2)), which exerts a significant influence on the accuracy of the comparison. The quantity d_f is determined from the relation [25]

$$d_f = (d - 1)(1 + \mu). \tag{4}$$

Thus, the results of the present work indicated the possibility of simulating the structure of the amorphous state of polymers within the framework of the diffusion-limited irreversible aggregation of colloid growth. In turn, this interpretation shows the obligatory existence of regions of local order in the structure of the indicated state of polymers.

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