Polymer Bulletin 1, 275–279 (1979)

Polymer Bulletin

Method of Determining the Kinetics of Spherulite Primary Nucleation from the Truncation of Spherulites

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It is often assumed, for the sake of simplicity, that primary nucleation of spherulites takes place entirely at the beginning of the crystalization process and has a heterogenous character (e.g. (ISHIKAWA, STEIN 1976 and MISHURA et al. 1974). In such a case all spherulites arise simultaneously and are randomly distributed over the entire sample; their boundaries form broken straight lines. For each two adjacent spherulite centers the border line will be halfway between them. The situation is more complex in the case of thermal nucleation: the boundaries are not straight and the positions of border lines between adjacent spherulite centers depend on the time lags in the nucleation of subsequent spherulites. The picture is even more complicated if two types of crystals growing with different rates are nucleated, as can happen in the case of polypropylene (PADDEN, KEITH 1959 and LOVINGER et al.1977).

In this study a general equation describing the boundaries between two growing structures is derived assuming time lag of subsequent nucleation occurences and different growth rates. Moreover, a method of calculating the number of arising nuclei vs. time based on the shape of spherulites is elaborated. The findings were tested using real samples.

Experimental

Spherulite shape and size was studied using polyoxymethylene (POM) Delrin 500 (Du Pont de Nemours). Two samples were prepared on glass supports by coating a glass plate with a 1 µm film of POM from 5% solution in dimethylformamide. The films were melted at 200°C and then crystallized isothermally at 151°C or 118°C. Crystallization was stopped after the entire area had been covered with spherulites. The spherulites were examined using a polarizing microscope.

Results and discussion

Let us condider two spherulites one of which is nucleated by an inteval Δt earlier than the other and growing with a different rate. In the course of isothermal crystallization they meet each other

0170-0839/79/0001/0275/$01.00

causing truncation. A schematic view of mutual spherulitic truncation is shown in Figure 1.

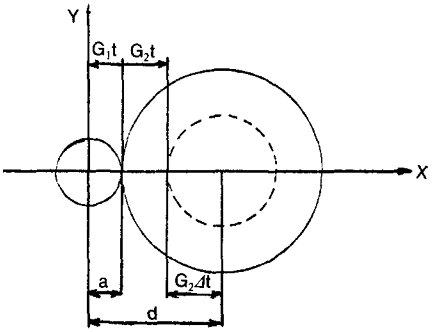

Fig.1. Scheme of the positions of two coinciding spherulites.

The growing spherulites can be described in polar coordinates by means of the following equations :

$$\rho_1=G_1t$$

$$\rho_2^2-2\rho_2 d\cos\Theta + d^2=G_2^2(t+\Delta t)^2 \tag{1}$$

where ρ_1, ρ_2 and Θ are polar coordinates, centered on the second nucleus to beformed, G_1 and G_2 are the growth rates of the spherulites, t is the time and d is the distance between the centers of the spherulites. The equations (1) resembele circles which will truncate each other in the course of growth. According to Figure 1 the distance a measured from same origin where the spherulites meet is given by the following formula:

$$a = \frac{d-G_2\ t}{1+\frac{G_2}{G_1}} \tag{2}$$

Eqs. (1) and (2) fully describe the boundary between the spherulites in general.

In the case of crystallization of a sample containing spherulities of one type Eqs. (1) and (2) lead to a form resembling a hyperbola or a straight line for the boundary of two adjacent spherulites:

$$\rho = \frac{d^2-G^2\Delta t^2}{2(d\ \cos\Theta+G\Delta t)} \tag{3}$$

where d is the distance between the centers (Fig.1), Δt is the time lag of nucleation of the smaller spherulite and G is the growth rate.

Whenever the time lag between two spherulites exists the truncation line resembles a hyperbola; otherwise it is a staight line. That observation may serve as a very sensitive test for the occurence of thermal or athermal nucleation. Moreover, from formula (3) one can find the time lag for each pair of neighbouring spherulites:

$$\Delta t = \frac{d-2a}{G} \tag{4}$$

If so, it is possibile to reconstruct the succesion of each occurence of nucleation from spherulite shapes and sizes even in the case of fully spherulitic samples. Taking one spherulite as reference one can establish whether the neighbouring spherulite arose earlier or later in relative units of time. Repeating that procedure for a chain of pairs of neighbouring spherulites one obtains a time distribution of primary nucleation. Calibration of the time axis is made by direct measurement of the growth rate G. The time lags between spherulites were calculated for two polyoxymethylene samples crystallized at 118°C and 151°C (Fig. 2a and 2b) leading directly to a time distribution of primary nucleations in the samples. Figures 2a and 2b show the dependences of the number of nucleations on crystallization time for those samples.

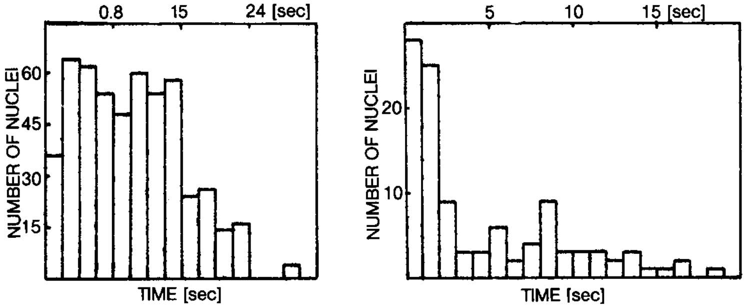

Fig.2. Time distribution of primary nucleations as calculated from spherulite shapes for polyoxymethylene crystallized a. at 118° and b. 151°C.

The number of neighbouring spherulites taken for calculation was 265 and 115 respecively; the area covered was 1 mm^2.

In both cases primary nucleation occured during the time comparable with the total crystallization time. One can distinguish a peak at the beginning of crystallization and the rest having a thermal character (see WUNDERLICH 1976). For low degree of supercooling (T_c=151°C) only a small number of spherulites arise by thermal nucleation extending over a long period of time while for high degree of supercooling thermal nucleaction yields many nuclei in a short period of time. The number of athermal nuclei is approximately the same for both samples. Therefore, changing the crystallization temperature one can change the proportion of thermal and athermal nucleation. This leads immediately to changes in spherulite size distribution. The spherulite size distributions for POM films crystallized at 118°C and 151°C are shown in Fig.3a and 3b. They were determined by integrating the area of each spherulite and calculating the mean size from formula:

$2R=(4S/\Pi)^{\frac{1}{2}}$ where S is the area of a spherulite. At 151°C, where the athermal nucleation prevails, the

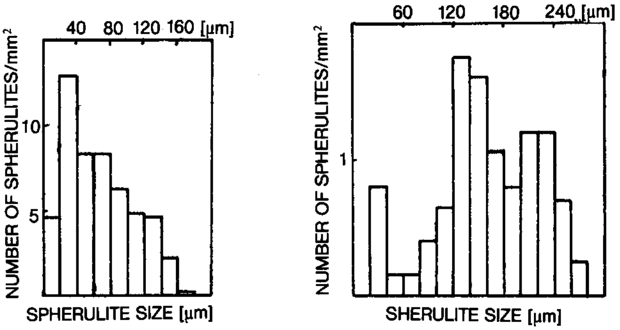

Fig.3. Spherulite size distribution of polyoxymethylene samples crystallized a. at 118°C and b. at 151°C.

spherulites have large diameters, while at 118°C, where thermal nucleation dominates (see Fig.4b), there is a relatively large number of small spherulites. The latter effect was also observed in low density polyethylene using the small angle light scattering technique (PAKULA et al. 1976).

The equations presented are also correct for three - dimensional spherulites if one considers the calculated shapes as figures of revolution around an axis passing through the spherulite centers. Therefore using the principles of stereology one can calculate the kinetics of primary nucleaction of spherulites for samples of any choice. This is of special interest because primary nucleaction determines spherulite shape and size distribution. The method of calculating the time distribution of primary nucleation from spherulite shapes will be helpful in the cases when nucleation occurs too often to be counted in the course of crystallization or when the only evidence are micrographs.

Synopsis

An attempt is made to describe mutual truncation between two coinciding spherulites. It is shown that if in a sample the borderlines between spherulites are not straight lines, the spherulites did not arise simultaneously. Using a mathematical approach it is possible to determine the time distribution of primary nucleation from the shapes of truncated spherulites. This was done for polyoxymethylene samples at two different crystallization temperatures. The superiority of thermal over athermal type of nucleation depends on the crystallization temperature which lead to different spherulite size distributions.

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Received November 23, 1978