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Abstract

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ON THE QUESTION OF THE MECHANISM OF ACTION OF NUCLEATING AGENTS IN CRYSTALLIZING POLYMERS

As we have shown earlier ([1,2]), the introduction into polymers of certain high-melting substances can initiate the process of crystallization of polymers; we have called such substances nucleating agents, and the centers of polymer crystallization that arise on their surface—surface nuclei. The centers of polymer crystallization that arise not on the surface of the introduced crystals we have called bulk nuclei.

It was of interest to determine whether all solid particles introduced into a polymer can be nucleating agents, irrespective of their chemical nature.

Isotactic polystyrene was chosen as the object of study.

As nucleating agents, substances of different chemical nature were introduced: metal oxides and high-melting organic substances of various classes (in an amount of 2% by weight).

It turned out that the chemical nature of the introduced crystals has a substantial influence on their nucleating action in crystallizing polymers. Hydrophilic inorganic oxides (quartz, zinc oxide, alumina, vanadium oxide, titanium oxide) are not nucleating agents in polystyrene. At the same time, these oxides act as nucleating agents in hydrophilic polymers, for example in capron ([3,4]). On the other hand, crystals of organic nature (indigo, quinacridone, alizarin, 1,5-dinitroanthraquinone) prove to be active nucleating agents in isotactic polystyrene. Evidently, this is connected with better wetting of the surfaces of these crystals by polystyrene. The role of wetting of the nucleating-agent surface by the polymer is confirmed in the following experiment: hydrophilic cotton fibers do not act in polystyrene as active nucleating agents (Fig. 1a). After hydrophobization of the surface with zinc stearate ([5]), cotton fibers become active nucleating agents (Fig. 1b; see insert to p. 1153).

From these data it may be concluded that good wetting of the surface of foreign crystals by a polymer promotes their nucleating action in this polymer.

Until recently, the question remained open whether a geometrical correspondence of the crystal lattices of a foreign crystal and a polymer is necessary in order for this crystal to play the role of a nucleating agent. By analogy with

Figure 1

Figure 1: Figure 1

Figure 4

Figure 2: Figure 4

low-molecular-weight substances, one could suppose that, in the process of crystallization, oriented growth of the polymer crystal occurs on a foreign matrix having two lattice parameters close to the lattice parameters of the polymer (epitaxy) ([6]). However, verification of this assumption on the systems used in the present work showed that correlation of the parameters of the crystal lattices of the nucleating agent and of the polymer is evidently not required. As an illustration, Table 1 gives literature data on the types and parameters of the crystal lattices of isotactic polystyrene and of nucleating agents that act effectively in polystyrene.

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Fig. 1. Microphotographs of films of isotactic polystyrene crystallized in the presence of cotton fibers. Melt temperature 285°, crystallization temperature 165°, crystallization time 1 h. **a**—initial cotton fiber; **b**—cotton fiber after hydrophobization

Figure 2 Figure 3

Fig. 2. Microphotographs of films of isotactic polystyrene crystallized in the presence of large indigo crystals. Melt temperature: **a**—235°, **b**—252°, **c**—275°; crystallization temperature 202°; crystallization time 3 h

Fig. 3. Microphotographs of films of isotactic polystyrene crystallized in the presence of large indigo crystals. Melt temperature 295°, crystallization temperature: **a**—210°; **b**—195°; crystallization time 3 h

Fig. 4. Microphotographs of films of isotactic polystyrene crystallized in the presence of small indigo crystals. Melt temperature 295°, crystallization: **a** —202°; **b**—165°; **c**—the same film of the initial polystyrene, melt temperature 295°, crystallization temperature 165°; crystallization time for **a**, **b**, **c**—3 h

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The absence of a need for correlation between the parameters of the crystal lattices of the nucleating agent and of polystyrene gives grounds to suppose that the introduced foreign crystals are not ready-made nuclei of polymer crystallization, and that their role, evidently, is reduced to initiating the formation of a polymer nucleus on their surface. This conclusion is supported by the data of work (4), in which it was shown that isotactic polystyrene acts as a nucleating agent in polypropylene, independently of the phase state of the polystyrene.

Table 1

Parameters of the crystal lattices of nucleating agents that act effectively in isotactic polystyrene

Object	Type of crystal lattice	a	b	c	β
Isotactic polystyrene	Rhombic	22.08	22.08	6.626	
Indigo	Monoclinic	9.23	5.74	12.25	116°30′
Alizarin	Rhombic	21.0	77.4	3.75	
Indanthrone	Monoclinic	30.83	3.833	7.845	91°55′

To clarify in greater detail the mechanism of formation of surface polymer nuclei, we studied the crystallization of isotactic polystyrene in the presence of the same large indigo crystals, varying over wide limits the melt temperature and the crystallization temperature.

Samples for the study were prepared by slow evaporation of a chloroform solution of polystyrene containing a suspension of indigo crystals; in this process many bulk crystallization centers arose and fine-spherulitic films were formed. In the film an indigo crystal of definite geometric shape was selected, and in the region of this crystal the regularities of growth of crystalline formations of polystyrene were followed under different temperature regimes of crystallization.

In the first series of experiments crystallization was carried out at 200°* for 3 hours, varying the melt temperature: 235°, 252°, 275°; the samples were held at the melt temperature for 2 min.

In the case when the melt temperature exceeds the melting temperature of crystalline polystyrene (m.p. 226°) by only a few degrees, fine-spherulitic films are formed as a result of crystallization (Fig. 2a), which is associated with preservation of a large number of bulk heterogeneous centers. The specificity of the action of the nucleating agent under this crystallization regime is not detected (see Fig. 2 in the insert to p. 1153).

When the melt temperature is raised to 252°, the number of spherulites arising not on the surface of the indigo crystal sharply decreases, and the spherulites themselves become coarser (Fig. 2b). This indicates the destruction of a large number of bulk centers. At the same time, the crystallization centers located on the surface of the indigo crystal are preserved (the entire surface of the indigo crystal is covered with crystalline formations of polystyrene).

Finally, in the case of a melt temperature of 275° spherulites do not arise at all at bulk centers (Fig. 2c), which indicates complete destruction of the bulk centers; however, the greater part of the surface of the indigo crystal remains covered with spherulitic formations of polystyrene. Consequently, in the polymer melt on the indigo surface there remains a high-

* The crystallization temperature was chosen close to the melting temperature of polystyrene, since under these conditions the rate of formation of bulk homogeneous centers is very small, and crystallization occurs only on the bulk heterogeneous centers and surface centers preserved in the melt.

some ordering of the elements of the polymer structure at such temperatures, when in the bulk it disappears completely. It may be assumed that this is connected with adsorption of elements of the polymer structure on the foreign surface.

The decrease in the number of surface crystallization centers as the melt temperature is raised indicates that the effectiveness of the nucleating action of foreign crystals decreases somewhat with increasing melt temperature.

It is of interest to determine how the effectiveness of the nucleating action of the indigo surface can be increased when high melt temperatures are used.

It turned out that this can be achieved by lowering the crystallization temperature. The corresponding data are given in Fig. 3 (see insert to p. 1153).

In the series of microphotographs in Fig. 3 there is shown a large indigo crystal, in the presence of which the crystallization of polystyrene was carried out, using a melt temperature of 295° and varying the crystallization temperature (duration of crystallization 3 hours). As is seen from Fig. 3a, at 210° only a small part of the indigo surface initiates crystallization of polystyrene; lowering the crystallization temperature to 202° leads to an increase in the number of surface centers, as evidenced by the increase in the number of polystyrene spherulites on the indigo surface.

Finally, at a crystallization temperature of 195° the entire surface of the indigo crystal is covered with spherulitic formations of polystyrene (Fig. 3b), while at the same time an extremely small number of spherulites arises in the bulk of the polymer; a further lowering of the crystallization temperature (for example, to 165°) increases still more the number of nuclei of polystyrene crystallization on the surface of the indigo crystal.

Consequently, the effectiveness of the nucleating action of a foreign surface increases as the crystallization temperature is lowered.

It was of considerable interest to determine whether the size of the introduced foreign crystals affects the effectiveness of their nucleating action. It turned out that increasing the indigo crystals up to macroscopic dimensions does not affect the effectiveness of their action as nucleating agents in polystyrene, i.e., there is no upper limit to the size of nucleating-agent crystals. In contrast to this, the experiment showed that, for each temperature, there exists a lower size limit for indigo crystals actively acting as nucleating agents in polystyrene. For example, indigo crystals with a linear size of about 1 μ do not initiate crystallization of polystyrene at 202° (Fig. 4a), whereas on larger indigo crystals at this temperature a noticeable number of polystyrene spherulites forms (Fig. 3b) (Fig. 4 see insert to p. 1153).

It was found, however, that the same indigo crystals of size 1 μ, which did not exert a nucleating action at 202°, are active nucleating agents at 165°, and in their presence completely crystallized fine-spherulitic films of polystyrene arise (Fig. 4b); in the absence of indigo at this temperature only sparsely distributed large spherulites form in the film (Fig. 4c). However, indigo crystals of smaller size (approximately 0.1 μ, according to electron-microscopic data) do not act as nucleating agents even at 165°.

Thus, the lower critical size of nucleating-agent crystals depends on the crystallization temperature and decreases with increasing supercooling; the lower the crystallization temperature, the smaller the foreign crystals that are already nucleating agents.

···nucleating agents. It should be noted that the temperature dependence of the critical size of the nucleating-agent crystal is similar to the temperature dependence of the size of the critical polymer nucleus*.

From the totality of the experimental material presented, it may be concluded that foreign crystals in polymers are not true nuclei of **crystallization****, but nuclei of **structure formation**, which do not cause crystallization but rather the ordering of bundles of polymer chains at their surface and thereby facilitate the onset of polymer crystallization and the formation of a polymer nucleus. Therefore, at small supercoolings, when the rate of formation of polymer crystallization centers is very low, the activity of artificial nucleating agents is minimal.

It is obvious that the minimum size of nucleating-agent crystals must be in a definite correspondence with the size of the critical polymer nucleus at a given crystallization temperature, which is also confirmed by the experimental results presented in micrographs 4.

Thus, we have shown that the effectiveness of the nucleating action of foreign crystals in isotactic polystyrene is not connected with the isomorphism of the crystal lattices of the nucleating agent and polystyrene, but depends on the wetting of the foreign crystal by the polymer, the size of the foreign crystal, and the crystallization regime.

It follows from the experimental material presented that there are two possible ways of making most effective use of the surface of a foreign crystal for initiating polymer crystallization: 1) lowering the crystallization temperature at a given melt temperature, and 2) lowering the melt temperature of the polymer at a given crystallization temperature. This makes it possible to vary, over wide limits, the conditions of polymer crystallization in the presence of nucleating agents, which is necessary for processing polymers into articles and expands the possibilities for obtaining materials with improved properties.

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* To each crystallization temperature there corresponds, strictly determined by thermodynamic considerations, a critical size of the stable nucleus, which decreases as the crystallization temperature is lowered.

** According to Tamman' s classical work on the crystallization of low-molecular liquids, true crystallization nuclei are crystals isomorphic with the crystallizing substance and causing in it a phase transition of the first order.

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