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Abstract

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STRUCTURE FORMATION IN PLASTICIZED CRYSTALLINE POLYSTYRENE

A study of the supramolecular structure of the original unplasticized isotactic polystyrene showed (1) that, during its crystallization in the temperature range 110—215°C, secondary formations arise, consisting of aggregated spherulites of various sizes and shapes in the form of "ribbons," plates, and individual spherulites. It was important to determine the character of the secondary structures and how the crystallization process proceeds in a polymer containing a plasticizer.

For this purpose, studies were carried out of the mechanical and optical properties of crystalline polystyrene in order to examine the influence of various plasticizers on its structure and to establish the relationship between the nature of the secondary supramolecular structures and the change in the mechanical properties of the polymer upon its plasticization. Observations of the process of structure formation in crystalline plasticized polystyrene were made by the method described in (1), at temperatures of 120°, 145°, and 175° for 10—150 min. Even preliminary observations showed that, during crystallization of plasticized polystyrene, individual spherulites mainly arise, while secondary structures of the "ribbon" and plate type are formed in considerably smaller amounts.

It became evident that plasticization of crystalline polystyrene changes the conditions for the formation of such structures. Therefore our studies were directed toward establishing the cause of this phenomenon. For this purpose, first of all, the influence of various plasticizers on the growth rate of spherulites, their sizes, and the conditions of their aggregation into ribbons was studied.

Table 1

Sizes of spherulites (in microns) of crystalline polystyrene

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Duration of crystallization, min	Original polystyrene	Dimethyl phthalate, 15 vol.%	Dimethyl phthalate, 25 vol.%	Ethyl chloride, 8 vol.%	Ethyl chloride, 20 vol.%	Dibutyl sebacate, 12 vol.%	Dibutyl sebacate, 18 vol.%	Dibutyl sebacate, 31 vol.%
10	4	10	15	13	11	15	–	10
30	8	35	35	60	55	50	50	38
60	17	70	67	110	92	70	–	65
150	40	260	190	300	230	220	–	170

Microphotographs are shown in Fig. 1, illustrating the change in the sizes of spherically symmetrical particles (of the spherulite type) in the original polystyrene and in polystyrene plasticized with 25 vol.% dimethyl phthalate, crystallization of which took place at 145° for 60 and 150 min. Experimental data on the influence of other plasticizers and of crystallization duration on spherulite sizes, given in Table 1, show that all the plasticizers we used significantly increase the sizes of spherulites. It is interesting to note that this phenomenon occurs even at small concentrations of plasticizer. For example, the presence of 8.0%

Fig. 1. Spherulites formed during crystallization of the original polystyrene. Crystallization temperature 145°, crystallization time: **a** –60 min., **b** –150 min. 200×. Spherulites formed during crystallization of polystyrene plasticized with 25 wt.% dimethyl phthalate. Crystallization temperature 145°, crystallization time: **c** –60 min., **d** –150 min. 200×.

Fig. 2. Microphotographs of secondary "ribbon"-type structures in polystyrene: **a** –original, **b** –plasticized with 25 wt.% dimethyl phthalate. Crystallization temperature 120°. Crystallization time 20 min. 200×.

ethyl chloride in crystalline polystyrene increases the size of the spherulites formed from 17 to 110 μ (crystallization time 30 min). A study of the crystallization process of the original and plasticized isotactic polystyrene at 120° showed that in this case as well the presence of a plasticizer considerably increases the growth rate of secondary structures of the spherulite type.

Fig. 3. Dependence of spherulite sizes on the content of plasticizers in volume percent: a —ethyl chloride, b —dimethyl phthalate, c —dibutyl sebacate

Figure 3: Fig. 3. Dependence of spherulite sizes on the content of plasticizers in volume percent: a —ethyl chloride, b —dimethyl phthalate, c —dibutyl sebacate

Fig. 4. Change in the strength of crystalline polystyrene upon its plasticization: a —ethyl chloride, b —dimethyl phthalate, c —dibutyl sebacate

Figure 4: Fig. 4. Change in the strength of crystalline polystyrene upon its plasticization: a —ethyl chloride, b —dimethyl phthalate, c —dibutyl sebacate

If structure-formation processes are carried out at higher temperatures, then in the range from 175 to 215° no such effective action of the plasticizer on spherulite growth is observed, since under these conditions, even in the absence of a plasticizer, the growth rate and the size of the spherulites are sufficiently large. Moreover, when structure formation takes place at considerable concentrations of plasticizer, even a decrease in the size of the spherulites is observed, owing to dissolution of the crystalline structures being formed.

Fig. 3. Dependence of spherulite sizes on the content of plasticizers in volume percent: *a* —ethyl chloride, *b* —dimethyl phthalate, *c* —dibutyl sebacate

Fig. 4. Change in the strength of crystalline polystyrene upon its plasticization: *a* —ethyl chloride, *b* —dimethyl phthalate, *c* —dibutyl sebacate

It should also be noted that at temperatures of 145-215° supramolecular structures are formed mainly in the form of separate large spherulites, whereas at lower temperatures (120°), among a large number of spherulites, sparsely arranged "ribbons" arise which do not form continuous plates. However, the transverse dimensions of these ribbons are greater than the dimensions of the ribbons observed in unplasticized polystyrene (Fig. 2).

This change in the character of the secondary structures is clearly associated with a change in the conditions of growth and aggregation of spherulites into ribbons and plates. The experimental data obtained by us (Fig. 1) show that in plasticized polystyrene the growth rate and size of the spherulites increase considerably. From Fig. 3, which expresses the dependence of the spherulite sizes on the content of plasticizers in the polymer, it is clearly seen that small additions of plasticizers considerably increase the sizes of the spherulites formed. In addition, the presence of a plasticizer also creates additional obstacles to aggregation into ribbons and plates.

Thus, plasticization of crystalline polystyrene leads to a sharp change in the structure of the secondary formations. By considerably increasing the growth rate of spherically symmetrical structures of the spherulite type and hindering their aggregation into ribbons or plates, the plasticizer promotes spherulitic crystallization of polystyrene (i.e., crystallization that ends with the formation of large and spherically symmetrical particles). If we now consider the change in mechanical properties

of crystalline polystyrene,* it is clearly seen that, in the concentration range below 10% plasticizer, there is a sharp decrease in strength (Fig. 4). This change in strength cannot be explained by a change in the primary crystalline structure of the polymer, since the X-ray diffraction patterns of the original and plasticized polystyrene differ little from one another. Consequently, the effect of the plasticizer on strength is associated with changes in supramolecular structures occurring in this same concentration range. It should be noted that the strength of crystalline polystyrene, whose supramolecular structure is determined by the presence of small spherulites joined into ribbons and then into plates, must naturally be higher than the strength of plasticized polystyrene, whose structural elements are mainly spherulites separated by the plasticizer.

It is quite clear that fracture of the plasticized system will occur along the boundaries between spherulites, thereby significantly reducing the strength of the polymer.

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* The mechanical properties of the original and plasticized crystalline polystyrene were measured in identical phase states at a temperature 25°C above their glass-transition temperatures (2).

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

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