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Abstract

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A NEW METHOD FOR DIRECT OBSERVATION OF THE STRUCTURE OF POLYMER SOLUTIONS IN THE ELECTRON MICROSCOPE

In recent years, new concepts have been formulated concerning the structure of amorphous polymers as ordered systems built from chains assembled into bundles ([1]). These concepts have been confirmed by direct studies of the structure of polymers in the glassy ([2–4]) and highly elastic ([5], [6]) states. However, up to the present time there have been no direct data on the supramolecular structure of polymers in solutions and melts. Nevertheless, on the basis of the considerations expressed ([1]), as well as the results of indirect methods of investigation, it may be concluded that the order found in solid polymers also exists in solutions and melts.

In this connection, the development of methods for the direct study of the structure of polymer solutions is undoubtedly of great interest. It may be thought that data obtained with the aid of such methods would make it possible to draw important conclusions about the nature and character of the order in amorphous polymers.

Naturally, for direct observation of large polymer chains and supramolecular structures, the high-resolution electron-microscopic method appears the most promising. However, because of the specific nature of electron-microscopic investigation, the known methods of specimen preparation, unfortunately, cannot be applied to the study of the structure of solutions of high-molecular-weight compounds. The necessity of preliminary complete removal of the solvent, and the complications inevitably arising in this process (concentration of solutions, structuring actions of surface-tension forces, etc.), do not allow us to draw conclusions about the actual structure of the polymers in solution.

In the present work an attempt has been made to develop a new method of preparation, free from the indicated shortcomings and, consequently, making it possible to investigate directly the structure of high-molecular-weight compounds in solution.

Fig. 2 and Fig. 1 micrographs

Figure 1: Fig. 2 and Fig. 1 micrographs

The principle of the proposed method is as follows. As the solvent for the system under study, a substance is taken which readily vitrifies on cooling and has a glass-transition temperature above room temperature. After complete dissolution of the polymer, the solution obtained is cooled below T_c. In this way a homogeneous glass is obtained in which the original structure of the polymer in solution is fixed, i.e., frozen. Brittle fractures are then made from the glass, the surface of which is studied by the replica method. In this way, obviously, it is possible to detect and evaluate the structure that the polymer had in the original solution. It is quite natural that a vitrifying substance must be used as the solvent; otherwise, as a result of crystallization of the solvent upon cooling, macrostratification of the system will take place. On the other hand, when using the replica method it is necessary that the T_c of the solution be above room temperature, since otherwise, because of the difficulty of obtaining low-temperature replicas, one must resort to a somewhat modified variant of the procedure, analogous to the well-known lyophilic drying ([7]).

In the present work, α-polybutylene with an intrinsic viscosity $[\eta] = 1.25$ was taken as the object of investigation. The solvent was purified rosin with a softening temperature of 70–80°. Preparation–

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Fig. 2

Fig. 1

Fig. 1. Replica from a fracture surface of vitrified pure rosin. 18 500×

Fig. 2. Solution of polybutylene in rosin at a concentration of 1% (A), at a concentration of 0.5% (B), at a concentration of 0.1% (C); A, B –17 000×, C –22 000×

The preparation of solutions and replicas was carried out as follows. A weighed portion of the polymer, together with the amount of rosin required for the given concentration, was heated in a bath or in a drying oven to 170–200° with constant stirring until the polymer was completely dissolved. The solution thus obtained was cooled to room temperature. With the aid of a sharp needle, thin flakes with an area of 1–1.5 cm^2 were made, from whose surface single-stage carbon replicas were obtained.

For preparing the initial solutions at lower temperatures, the following method was used. First, the weighed portion of polymer was dissolved in an organic solvent (benzene or toluene), and then the corresponding amount of rosin was added to the solution. After complete dissolution, the organic solvent was evaporated by heating at temperatures above room temperature.

It should be noted that both methods of preparing the solution give analogous results, although the second is more preferable because there is no need to heat the solution to high temperatures and because solutions can be obtained for a wider range of polymers.

By the methods described, solutions of polybutylene in rosin were prepared and studied at the following concentrations (weight percent): 1, 0.5, 0.25, 0.1, 0.07, 0.05, and 0.01.

The results are shown in Figs. 1 and 2; see inset p. 840. As is seen from Figs. 2 , , very ordered structures are formed in solutions of α-polybutylene, analogous to the bundles of molecules found in amorphous glasses ([2]-[4]). Such structures can be observed in solutions of α-polybutylene in rosin with concentrations of 0.5, 0.25, and 0.1%.

Figure 2 shows a micrograph obtained for a solution with a concentration of 1%. As is seen from this figure, at this polymer concentration large, relatively structureless formations are observed, which apparently indicates stratification of the system. With a further increase in the concentration of α-polybutylene, macrostratification proceeds up to the formation of a continuous polymer film. In the case when the solution concentration is below 0.1%, no relief is detected on the replicas. It may be assumed that, at these concentrations, the system passes into the region of a molecularly dispersed solution, and the high molecular weight of α-polybutylene (mol. wt. 180,000) does not make it possible to resolve individual macromolecules by means of replicas. One should note the unusually interesting, relatively sharp concentration dependence of the appearance of ordered structures in the α-polybutylene solutions studied. As a rule, for all the samples studied with a concentration below 0.1%, the replica is always without relief, and, beginning with a concentration of 0.1% and higher, up to stratification, clearly expressed bundles of molecules appear.

Thus, by using the method of vitrifying solutions, it is possible to record and study the structure of polymer solutions directly with the aid of an electron microscope. The preliminary results of the present investigation show that ordered supramolecular structures in the form of bundles of chains can form directly in a polymer solution.

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