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Academician V. A. KARGIN, N. F. BAKEEV,

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Abstract

Full Text

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PHYSICAL CHEMISTRY

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AN ELECTRON-MICROSCOPIC METHOD FOR INVESTIGATING THE SUPRAMOLECULAR STRUCTURE OF POLYMERS IN SOLUTIONS

In a previously published work ([1]), the authors described a method proposed for the direct electron-microscopic investigation of the structure of polymers in solution. The essence of the method described consisted in studying replicas from the surface of a brittle fracture of glasses obtained by freezing the original solutions below T_c. In this way it proved possible to fix and study the structure of polymers in solution. The principal advantage of the proposed method lay in the absence of the need for preliminary removal of the solvent and of the complications associated with this (concentration of solutions, the structuring effect of surface-tension forces, and others).

In the present work a new method has been developed for preparing specimens for electron-microscopic investigation of polymer solutions, free from the shortcomings associated with evaporation of a liquid solvent ([2]) (Fig. 1).

The principle of this method is as follows. As the solvent for the system under investigation, substances with a low critical temperature are used (for example, propane, ethylene, etc.). The solvent is condensed into a capillary into which the polymer has previously been placed, and the capillary is sealed. In this process the filling of the capillary with the liquefied solvent is carried out in such a way that, during subsequent heating above T_k, no noticeable increase in the volume of the system occurs. The sealed glass capillary is heated in a specially designed furnace to 20–25° above the critical temperature. When the system is heated above T_k, we obtain a kind of solution of the polymer in a gaseous solvent. Then the end of the capillary is cut off and the polymer solution in the gaseous solvent, which was in the capillary at the critical pressure, is "shot out." Electron-microscope grids with a previously applied grid substrate serve as the "target."

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The entire operation is carried out under a protective hood, either at normal pressure or under reduced pressure, choosing, respectively, $T > T_k$ and the pressure under the hood in such a way that no condensation of the gaseous solvent occurs during the "shooting out." The object that reaches the substrates is then shadowed and examined in the electron microscope. With this method of preparation it is possible to avoid concentration of the solution and the structuring effects due to surface-tension forces, which always occur during evaporation of a liquid solvent ([3]).

In the present work, using the developed technique, two systems were investigated: a solution of poly-α-butylene in propane and a solution of atactic polypropylene in propane. The solutions were prepared as follows. Into a drawn-out glass capillary, sealed at one end, a definite volume of a solution of the polymers under investigation in benzene of known concentration was placed. Then the benzene was pumped off.

For the article by V. A. Kargin, N. F. Bakeev et al., p. 851

Fig. 1. Electron micrograph of a 0.2% solution of atactic polypropylene in benzene, obtained by the usual preparation method

Fig. 2. Electron micrograph of a suspension of carbon black in propane

Fig. 3. Electron micrograph of solutions of poly-α-butylene and atactic polypropylene in propane: a —poly-α-butylene at a concentration of 1.5%; b —the same at a concentration of 0.1%; c —atactic polypropylene at a concentration of 0.4%

This procedure was carried out for accurate dosing of the polymer sample. Next, the solvent was condensed into a capillary placed in a Dewar vessel with liquid nitrogen, and the capillary was sealed. Each system was first heated in a thermostat and the solubility was assessed visually ([4]).

The sealed capillary was inserted into a special furnace, which in turn was placed under the protective bell jar of a VUR-1 vacuum unit. After heating to a temperature of 115-125° (T_c of propane 96.8°) and evacuating the space under the bell jar to $\sim 10^{-4}$ mm Hg, "shooting" was carried out by the method described above. Grids with collodion film substrates were placed both in front of the capillary and throughout the space under the bell jar. Before examination in the electron microscope, the samples were shadowed with metallic palladium or tungsten oxide.

By the method described, solutions of poly-α-butene and atactic polypropylene at various concentrations (weight percent) from 3 to 0.05% were prepared and investigated.

Preliminary experiments were carried out on the study of suspensions of soot in propane, prepared in an analogous manner. It was found that, with the aid of the indicated technique, it is possible to "hit" the target and to achieve a relatively uniform distribution of soot particles on the substrate (Fig. 2).

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Figure 3 presents micrographs for solutions with concentrations of 1.5, 0.4, and 0.3%. As can be seen from the figure, for these concentrations, already in the solutions there is formation of ordered supramolecular structures similar to those found earlier ([1]). When the concentration is increased above 3%, complete dissolution of the polymer does not occur and, as a result, large formations are observed on the substrate, the structure of which is not resolved in the electron microscope. Reducing the concentration below 0.05 brings the system to a molecularly dispersed state; however, by electron microscopy it is not possible to determine reliably the shape and dimensions of individual molecules, especially since the molecular weight of the polymers studied is not very high (poly-α-butene $\sim 180\,000$, polypropylene $\sim 35\,000$).

Thus, the method described in this work for preparing objects for electron-microscopic study of polymer solutions using solvents with low critical temperatures makes it possible to assess the character of association of macromolecules directly in solution. For the systems studied—poly-α-butene in propane and atactic polypropylene in propane—it has been shown that, long before macrophase separation, aggregates of macromolecules arise directly in the solution.

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