Physical Chemistry

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1964

SovietRxiv

Abstract

Full Text

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FIBROUS STRUCTURES AND THE FORMATION OF A GEL OF ISOTACTIC POLYSTYRENE

As studies of recent years have shown, the mechanical properties of crystalline polymers, just like the mechanical properties of metals, depend on their supramolecular structure $^{(1-3)}$. The question of the connection between the mechanical properties of amorphous polymers and their structure has been studied to a considerably lesser extent. In this connection it seemed of interest to us to study the mechanical properties of amorphous films of isotactic polystyrene obtained from various solvents, since electron-microscopic investigations have shown that, depending on the nature of the solvent, amorphous films of isotactic polystyrene of different structure can be obtained $^{(4)}$.

In the present work chloroform and decalin were used as solvents. Films 20–30 μ thick for mechanical tests were prepared by evaporating the solvents from 2% polystyrene solutions at 25°. Evaporation of chloroform at atmospheric pressure proceeded over 30–40 min; in this case an amorphous structureless polystyrene film was formed. Evaporation of decalin at atmospheric pressure proceeded for 40 days, and a crystalline polystyrene film was formed. The slowness of decalin evaporation is connected, first, with its low vapor pressure at 25°, and second, with the fact that freshly prepared 2% solutions of isotactic polystyrene in decalin gelled within 16–20 h, which reduced the rate of evaporation still further. Therefore amorphous films of isotactic polystyrene from decalin solutions were obtained by evaporating freshly prepared 2% solutions in vacuum at a residual pressure of 5 mm. In this case film formation took 4–5 h; traces of decalin were removed in high vacuum to constant film weight.

Table 1

Stretching temperature, °C	Polystyrene from decalin	Polystyrene from decalin	Polystyrene from decalin	Polystyrene from chloroform	Polystyrene from chloroform	Polystyrene from chloroform
	σ_{break}, kg/cm^2	ε, %	$\sigma_{\varepsilon=20\%}$, kg/cm^2	σ_{break}, kg/cm^2	ε, %	$\sigma_{\varepsilon=20\%}$, kg/cm^2
20	380	5	–	400	5	–
120	85	100	30	55	260	16

In view of the fact that the process of gelation of the solution proceeds the faster, the higher the concentration of polystyrene in the solution (for example, 5% solutions gel in as little as 70 min), while during evaporation of decalin the concentration of the solution gradually increases, it is evident that even in vacuum, under certain—

at a certain concentration the solution gels and the polystyrene film is formed not from the solution in decalin, but from the gel.

The films obtained were subjected to mechanical tests on a Schopper dynamometer for elementary fibers at temperatures of 20 and 120°. The test results are given in Table 1.

As can be seen from the data in Table 1, below T_{st} the films have practically the same breaking strength, whereas above T_{st} the films obtained from decalin solutions prove to be considerably stronger, stiffer, and less deformable than the films from chloroform. The angle of inclination to the abscissa axis of the stretching curves for specimens obtained from decalin, at temperatures above T_{st}, is considerably greater than the angle of inclination of the stretching curves for specimens from chloroform. As an example, Table 1 gives the stresses required for a 20% elongation at 120° for both types of specimens.

The difference, manifested in the high-elastic state, between the breaking stresses and the stresses required for 20% elongation of specimens obtained from decalin and from chloroform solutions indicates a difference in the structure of these specimens. A weaker difference in structure is already apparent when the films are examined in a polarizing microscope with crossed nicols. The sharpest difference in structure can be observed in an electron-microscope study. Specimens for electron-microscopic studies were prepared under the same conditions as the specimens for mechanical tests, so that the only parameter varied was the film thickness. Electron micrographs of the structure of films obtained from chloroform and decalin are presented in Fig. 1a, b. As can be seen from Fig. 1a, the film obtained under these conditions from a chloroform solution is empty in the electron microscope, whereas that isolated from a solution in decalin (Fig. 1b) consists of fibrous formations, the electron-diffraction study of which indicates their amorphous phase state.

The fibrous formations apparently exert a micro-reinforcing effect on polystyrene films, increasing their strength and stiffness—this is the so-called self-reinforcement effect, which was first observed in polycarbonates (^{5}).

The appearance of fibrous formations in the decalin solution of isotactic polystyrene is evidently the cause of gelation of these solutions. The gel formed melts reversibly at 80°. The rate of gel formation depends on the concentration of the initial solution, the duration and temperature of dissolution of polystyrene in decalin, and the storage temperature of the solutions.

The structure of the gel, as revealed in the electron microscope, is presented

Figure 1: Electron micrographs of amorphous isotactic polystyrene isolated from chloroform solution (a), from decalin solution (0.02 g of isotactic polystyrene in 100 ml of decalin) (b), and from a gel in decalin (2 g of isotactic polystyrene in 100 ml of decalin) (c).

Figure 1: Figure 1: Electron micrographs of amorphous isotactic polystyrene isolated from chloroform solution (a), from decalin solution (0.02 g of isotactic polystyrene in 100 ml of decalin) (b), and from a gel in decalin (2 g of isotactic polystyrene in 100 ml of decalin) (c).

in Fig. 1c. As can be seen from Fig. 1c, the gel consists of entangled fibrous formations 0.04 μ in diameter, analogous to those presented in Fig. 1b. As electron-microscopic studies have shown, melting of the gel is associated with the disappearance of the fibrous formations, since upon rapid evaporation of a drop of molten gel on a hot substrate a structureless film is formed.

From the standpoint of the modern theory of gel structure, the process of gel formation is associated with the appearance of sufficiently strong local intermolecular bonds formed between polar groups of individual polymer chains (6, 7). This leads to the construction of a molecular network permeating the entire volume of the solution. We have succeeded in showing that, in the case of isotactic polystyrene, the structural element of the spatial network of the gel is not individual molecular chains, but supramolecular formations—aggregates of molecular chains arranged in fibrous structures 0.04 μ thick.

The presence of a spatial framework constructed from fibrous structures is the cause of the formation of a gel of isotactic polystyrene in decalin.

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Fig. 1. Electron micrographs of amorphous isotactic polystyrene isolated from chloroform solution (a), from decalin solution (0.02 g of isotactic polystyrene in 100 ml of decalin) (b), and from a gel in decalin (2 g of isotactic polystyrene in 100 ml of decalin) (c)

Thus, we have obtained amorphous films of isotactic polystyrene possessing different supramolecular structures, and the difference in their mechanical properties has been shown.

Gels of isotactic polystyrene have been obtained, and it has been established for the first time that the structural element of the spatial network of the gel of a polymer body is a fibrous supramolecular formation.

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Received

29 XII 1963

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