Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964, Volume 156, No. 4

PHYSICAL CHEMISTRY

G. L. SLONIMSKII, Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK,
S. V. VINOGRADOVA, A. I. KITAIGORODSKII, A. A. ASKADSKII,
S. N. SALAZKIN, E. M. BELAVTSEVA

PHYSICOCHEMICAL WAYS OF REGULATING THE SUPRAMOLECULAR STRUCTURES AND MECHANICAL PROPERTIES OF AMORPHOUS POLYARYLATE F-1

Polyarylate F-1, formed on the basis of phenolphthalein and isophthalic acid, is a transparent glassy body (glass-transition temperature about 240°) possessing a number of valuable properties ([1]), which have determined its use in the national economy. However, the very high brittleness of this polymer proves to be a serious drawback.

In light of the most recent ideas on the role of supramolecular structures in the formation of the complex of mechanical properties of polymers ([2–5]), it was supposed that the high brittleness of polyarylate is due to its supramolecular structure, rather than to the chemical structure of the macromolecules. In this case one could expect that changing the type of supramolecular structure would affect the complex of mechanical properties of polyarylate and make it possible to improve them. An electron-microscopic study of the structure of a polyarylate film (Fig. 1a) showed that this glassy transparent polymer is formed from not entirely regular spherical particles (of the order of 1000 Å in size), which in turn consist of still smaller, likewise almost spherical particles (30–40 Å in size).

Electron-microscopic and light-optical images of the fracture surface of an F-1 specimen (Fig. 2, Ia and IIa) show the presence of numerous small cracks, which indicates weak cohesion of the spherical particles of which it consists.

All the above convinced us that one of the causes of the high brittleness of glassy polyarylate F-1 is the globular type of its supramolecular structure.

Since the chemical structure of the F-1 macromolecules indicated their high rigidity, and also since all attempts to change the type of supramolecular structure by forming F-1 films from its solutions in various solvents gave no positive results, the natural conclusion was that these macromolecules have stable, rigid,

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

coiled conformations, the consequence of which is the development of globular supramolecular structures. Thus, in order to obtain another type of supramolecular structure, it proved necessary to intervene in the process of polyarylate synthesis, directing it toward the formation of extended rigid polyarylate macromolecules.

In the previously described ([1]) reaction for the synthesis of polyarylate F-1, ditolylmethane was chosen as the medium in which the polymer was formed. However, ditolylmethane is not a solvent for polyarylate F-1, and therefore the free energy of formation of coiled macromolecules should be lower than the free energy of formation of extended macromolecules (a coiled macromolecule has fewer contacts with the nonsolvent).

This difference in the free energies of formation of coiled and extended macromolecules undoubtedly led to the selection (during synthesis) of globular forms of macromolecules, which accordingly also determined the globular type of supramolecular structures.

To the article by G. L. Slonimskii, V. V. Korshak et al., p. 924

Fig. 1. Surface of a film of polyarylate F-1 synthesized in ditolylmethane (a) and in α-chloronaphthalene (b)

Fig. 2. Fracture surface of a sample of polyarylate F-1 synthesized in ditolylmethane (a) and in α-chloronaphthalene (b). I —electron-microscopic image, II —light-optical image.

On the basis of these considerations, we carried out the synthesis of polyarylate F-1 in a specially selected medium (in α-chloronaphthalene, which dissolves this polymer well). It could be expected that in this case extended (stretched) macromolecules would be synthesized predominantly, as a result of which corresponding bundles of macromolecules and other fibrillar supramolecular structures would arise. A polyarylate with such a structure should, of course, be less brittle.

The results of the synthesis carried out and of the investigation of the structure and properties of the two above-mentioned types of polyarylate F-1 of identical molecular weight (28,000; determined by the light-scattering method) fully confirmed these ideas.

In the film of the new polyarylate F-1, fibrillar structures took the place of globular structures (Fig. 1b), and the fracture surface shows no cracks (Fig. 2,

Ib). When the fracture surfaces are examined with an optical microscope (Fig. 2, II), the sharp difference between the fracture patterns of polyarylates with globular and fibrillar structures is also clearly visible.

In accordance with the structure, the set of mechanical properties also changed: the elongation at break increased from 10-20% to 50-80%, the strength from 640 to 740 kg/cm^2, and the specific impact toughness increased from 2-3 to 6-10 kg $\cdot$ cm/cm^2. Thus, the most important shortcoming of the polyarylate—brittleness—was eliminated; it decreased by approximately a factor of four. (It is interesting to note that at a molecular weight of about 50,000 the elongation at break of the fibrillar polyarylate reaches 130%, and the specific impact toughness 20 kg $\cdot$ cm/cm^2.)

The new results obtained by us clearly show the importance of supramolecular structures in the formation of the properties of a polymer body not only in the crystalline state, but also in the glassy state. At the same time it became obvious that, in the synthesis of polymers with rigid macromolecules, it is necessary to select the reaction medium with allowance for its influence on the selection of particular conformations of macromolecules during the synthesis process itself. Thus, the set of mechanical properties of any polymers with rigid macromolecules can and should be regulated not only by chemical changes in the macromolecules, but also by the physical conditions of interaction of the growing macromolecule with the medium surrounding it.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
2 III 1964

REFERENCES

1. V. V. Korshak, S. V. Vinogradova, S. N. Salazkin, *Vysokomolek. soed.*, **4**, No. 3, 339 (1962).

2. V. A. Kargin, A. I. Kitaigorodskii, G. L. Slonimskii, *Koll. zhurn.*, **19**, 131 (1957).

3. T. I. Sogolova, Doctoral dissertation, L. Ya. Karpov Physicochemical Institute, 1963.

4. V. A. Kargin, T. I. Sogolova, G. Sh. Talypov, *Vysokomolek. soed.*, **5**, No. 12, 1809 (1963).

5. V. A. Kargin, T. I. Sogolova, L. I. Nadareishvili, *Vysokomolek. soed.*, **6**, No. 1, 165, 169 (1964).

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