ON THE DIFFERENCE BETWEEN THE SUPRAMOLECULAR STRUCTURES OF AMORPHOUS POLYARYLATES OBTAINED BY INTERFACIAL POLYCONDENSATION AND BY HIGH-TEMPERATURE POLYCONDENSATION IN A HOMOGENEOUS MEDIUM

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Abstract

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ON THE DIFFERENCE BETWEEN THE SUPRAMOLECULAR STRUCTURES OF AMORPHOUS POLYARYLATES OBTAINED BY INTERFACIAL POLYCONDENSATION AND BY HIGH-TEMPERATURE POLYCONDENSATION IN A HOMOGENEOUS MEDIUM

We have previously shown ([1]) the influence of synthesis conditions on the supramolecular structure and mechanical properties of polyarylate F-1 (the product of polycondensation of isophthalic acid chlorohydride and phenolphthalein). It was found that synthesis in a medium that dissolves the polymer leads predominantly to fibrillar structures of the polymer body and to improved mechanical properties in comparison with a polymer of the same chemical structure obtained by polycondensation in a medium that does not dissolve the polymer and possessing a globular structure.

In connection with this, it could be assumed that in the case of interfacial polycondensation, when formation of the polymer occurs at the boundary between two liquid phases and the polymer itself is insoluble in either of them, the supramolecular structure should be globular. In the case of homogeneous polycondensation in a dissolving medium, however, formation of a polymer of predominantly fibrillar structure should be expected. This assumption is also in good agreement with the known difference in the properties of polymers obtained by these two methods.

The corresponding electron-microscopic and mechanical studies were carried out on specially synthesized types of polyarylate F-7 (the product of polycondensation of terephthalic acid chlorohydride and phenolphthalein anilide).

Polyarylate F-7-M was synthesized by the method of interfacial polycondensation according to the procedure described earlier ([2]), using benzene as the organic solvent and Nekal as the emulsifier, and had a reduced viscosity (η_{red}) in tricresol of 1.0 dl/g.

Polyarylate F-7 was obtained by polycondensation in a homogeneous medium at elevated temperature, using α-chloronaphthalene as solvent (polymer concentration in solution 2 mol/l of solvent), and had $\eta_{\text{red}} = 0.80$ dl/g ([3]).

The objects were studied by the method of platinum-carbon replicas obtained from the fracture surfaces of monolithic specimens of the polyarylates. The preparations were observed with a UMB-100 electron microscope (electron-optical magnification 1500 and 20,000 times).

The results obtained fully confirmed the assumption stated above. As can be seen from Fig. 1A, the supramolecular structure of polyarylate F-7-M has a clearly expressed globular character. At still higher magnification (85,000×) it is seen that these globules, about 1000 Å in size, have a complex internal structure, being built mainly of very small globules (~ 50 Å) and, possibly, also of particles of other forms.

In contrast to polyarylate F-7-M, obtained by interfacial polycondensation, polyarylate F-7, synthesized in a homogeneous medium, has a completely different supramolecular structure, shown in Fig. 1B.

[Figure 1]

Fig. 1. Electron-microscopic images of the fracture surfaces of samples of the polyarylate of terephthalic acid and phenolphthalein anilide: synthesized by interfacial polycondensation (F-7-M) (**A**) and by homogeneous high-temperature polycondensation in an α-chloronaphthalene medium (F-7) (**B**)

Here fibrillar structures are clearly noticeable; among them (at a high magnification of 85 000×) only traces of a globular structure can be observed.

The mechanical properties of the polyarylates studied proved to be in full agreement with these structural data. From the data in Table 1 it is clear that polyarylate F-7 substantially surpasses polyarylate F-7-M in resistance to impact loading, in elongation at break, and in softening temperature. The latter circumstance is especially noteworthy, since it clearly shows that an amorphous polymer of one and the same chemical structure may have different softening temperatures depending on its supramolecular structure. It should be noted that the shift in softening temperatures is about 35°, and moreover in the case of an amorphous polymer already having a fairly high softening temperature.

Table 1

Basic properties of polyarylate F-7

Properties	Polyarylate F-7-M	Polyarylate F-7
Softening*, °C	280–285	315–320
Tensile strength, kg/cm^2	960	1000

Properties	Polyarylate F-7-M	Polyarylate F-7
Elongation at break, %	13	40–50
Specific impact toughness, kgf · cm/cm^2	~1	7–9

* The softening temperature is taken to be the temperature at which the stress in a monolithic specimen relaxes to zero (^{4}).

Analogous results were obtained by us both for other types of rigid-chain polyarylates and for polyarylates of phenolphthalein anilide obtained by homogeneous polycondensation at elevated temperatures in various media that dissolve the polymer.

The observed difference in the supramolecular structure of polyarylates obtained by interfacial and homogeneous polycondensation at elevated temperature explains the difference in the complex of mechanical properties of these polymers and undoubtedly opens paths toward the deliberate regulation of polymer properties through a rational choice of polycondensation conditions and methods.

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