PROPERTIES OF SOLUTIONS OF POLY-(p-PHENYLENEBENZOBISTHIAZOLE)
IN POLYPHOSPHORIC ACIDS OF DIFFERENT COMPOSITION

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The possibility of hydrolytic degradation of an oligomeric solvent — polyphosphoric acid — in finished spinning solution was established. The viscosity of the polymer solution can be decreased by decreasing the proportion of phosphoric anhydride in the solvent with a small change in the concentration of polymer in the solution; the properties of the fibre fabricated from such a solution do not worsen. When the degree of polymerization of the polyphosphoric acid decreases (up to its conversion to orthophosphoric acid), poly-(p-phenylenebenzobisthiazole) crystal solvates are crystallized into single crystals hundreds of micrometers in size.

Poly-[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl]-1,4-phenylene, or poly-(p-phenylenebenzobisthiazole) (PPBT), is a very promising polymer with respect to its physicomechanical indexes (strength, modulus, thermal stability). Polyphosphoric acid (PPA), which can be used as reaction medium for synthesis of PPBT from 2,5-diamino-1,4-dimercaptobenzene (DADMB) and terephthalic acid (TPA), is used as the solvent for this polymer.

The conditions of synthesis of PPBT from DADMB and TPA [1] require creating a dehydrating medium for binding the water of polycondensation. PPA with the corresponding phosphoric anhydride (PA) content fully satisfies this condition. The dehydrating properties (and water capacity) of PPA increase proportionally to the PA content [2]. An important drawback of PPA with a high PA content is the high dynamic viscosity in a relatively wide temperature range (Fig. 1).

Processing of solutions of PPBT in PPA of a composition corresponding to the conditions of synthesis of the industrially acceptable concentration of 13-14 wt. % requires increasing the temperature of the spinning solution to 180-190°C, which combined with the chemical aggressiveness of PPA, creates certain equipment difficulties.

The formation of solvates in dissolution in proton-donor solvents, which include PPA, is a major characteristic of polymers with trivalent nitrogen in the polymer chain (azo, azoxy, thiazole, amide, and other groups). As a result of protonation, trivalent nitrogen equimolarly binds some of the solvent up to a certain temperature. For this reason, the molar ratio of trivalent nitrogen groups in the polymer and the molar concentration of solvent become especially important for these solutions. For a molar ratio close to unity, the solution is a solid or highly viscous body in a relatively wide temperature range. Decreasing this ratio allows obtaining a fluid solution of solvated polymer in unbound solvent in the acceptable temperature range. We investigated the properties of solutions of PPBT in PPA of varying composition. The concentration of PA was decreased by adding water to the solution.

Previously prepared solutions with a polymer content of 14.1-13.9 wt. % in PPA with 85% PA were used to prepare the solutions of PPBT in PPA with a different PA content. A calculated amount of water was added to the mixture of solutions of this composition at the softening point to reduce the PA content to the required content. It was arbitrarily assumed that during storage of the solutions, no more than 2% of the mass of PPA would be uncontrollably absorbed from atmospheric water. This 2% would be taken into account in changing the composition of PPA.

The simplest calculation shows that changing the composition of the solvent by decreasing the PA content from 85 to 77% by addition of water decreases the concentration of the polymer to only 13%, so that a change in the concentration of polymer in the solutions was considered unimportant and was not taken into consideration in examining the results.

The viscosity of the solutions was determined on a PIRSP-31 unit using a cone—plate working unit with a 2° gap in conditions of sinusoidal loading with an amplitude at 1°. Determination of the mechanical loss modulus (G") with consideration...
of the loading frequency ($\phi = 0.1 \text{ sec}^{-1}$) allows finding the viscosity of the solution ($\eta$, Pa·sec) [3] using the equality $\eta = \frac{G''}{\phi}$. This method of determining the viscosity, in contrast to shear flow, perturbs the structure of the solutions to a smaller degree.

The behavior of 13-14\% solutions of PPBT in PPA with a different PA content when the temperature changes is shown in Fig. 2. In the examined temperature range (up to 180°C, inclusively), only the solution with an approximately 83\% PA content in the solvent has no right ascending branch, while the others have two branches — left descending and right ascending.

The left branch characterizes the change in the viscosity as a function of the temperature in dissolution of the solid crystal solvate in solvent (PPA) not bound with the polymer.

The equimolar concentration of nitrogen is approximately 1 mole/kg of solution for a 13\% solution of PPBT with a base-mole molecular weight of 266 having two trivalent nitrogen atoms per base-mole in the chain. The molarity of the solvent in such a solution for PPA with a PA content of 83\% will be approximately 3.07 moles, while it is approximately 6.18 moles for PPA with 77\% PA (table in [4]). The concentration of free solvent is 2.07 mole/kg of solution in the first case and 5.18 mole/kg in the second case, i.e., it is 2.5 times higher.

Increasing the molar concentration of solvent in the solution and decreasing its viscosity not only decreases the viscosity of the solvated polymer solution. Dissolution of the solid crystal solvate begins at a lower temperature and as the temperature increases, the amount of solid phase (crystal solvate) decreases until it totally disappears. When the crystal solvate is totally dissolved, the shape of the temperature—viscosity curve changes sharply — a left break appears on the curve.