SYNTHESIS OF THERMOTROPIC AROMATIC POLYESTERS HAVING A HETEROCYCLE IN THE MACROMOLECULAR CHAIN


In recent years the problem of preparing liquid-crystal systems, particularly high-molecular aromatic polyesters, has been attracting the attention of researchers. The interest displayed in such polymers is caused both by the high physico-mechanical properties of fibres based on them and also by the very economical method of spinning fibres from the melt. However, most aromatic polyesters have a very high melting point, which often limits, or even completely eliminates, the possibility of processing them from the melt, and the lack of a solvent for them does not allow them to be processed by other methods.

The object of the research described in the present article was to prepare thermotropic aromatic polyesters with a reduced melting point and increased solubility. This objective has been attained by introducing various heterocycles into the polymer macromolecule.

The polymer synthesis was carried out by melt polycondensation of the diacetyl derivatives of diols containing a heterocycle [1, 2], for example:

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\begin{align*}
\text{H}_2\text{COCO}-\text{C}&\text{N} &\text{N} \\
&\text{C} &\text{C} \\
&\text{C} &\text{N} \\
&\text{C} &\text{O} \\
&\text{OCOCH}_3
\end{align*}
\]

(which were also used in a mixture with other aromatic diols) and dicarboxylic acids (terephthalic, isophthalic, or 2,6-naphthalenedicarboxylic acid). In some cases, the reaction was carried out with 4-acetoxybenzoic acid as one of the reagents.

As a result of these studies, some principles of the reaction were established, specifically the effect of the temperature regime of synthesis, ratio of monomers, and process catalyst on the extent of reaction and the viscosity of the polyester. In Figs. 1-3 we show these principles as applicable to the preparation of a copolyester based on 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole, terephthalic, 2,6-naphthalenedicarboxylic, and 4-hydroxybenzoic acid having a proportion of the corresponding units of 0.2:0.1:0.1:0.6. These principles are also characteristic of other copolymers containing heterocycles, but in other temperature ranges. The completeness of reaction was judged from the amount of acetic acid evolved and from the change in effective viscosity of the polycondensation melt. As is evident from Fig. 1, the polycondensation process can be separated into two stages.

The first stage is transesterification and formation of oligomers, as is indicated by the low effective viscosity figures and the low inherent viscosity values of the product obtained in this stage (η\text{inh} = 0.3 dl/g). Regardless of the temperature (280 or 300°C), 50-60 min after the start of reaction approximately 80-85% of the theoretically calculated amount of acetic acid has been distilled off. The reaction rate decreases sharply on further heating.

In the second stage of the process, at a residual pressure of 0.133-0.266 kPa, a sharp increase in melt viscosity is observed, which is probably connected not only with an increase in the molecular weight of the polymer, but also with elimination of the plasticizing action of the acetic acid evolved from the melt.

As a result of the determination of the reaction kinetics, it is advisable to carry out the reaction stage for 2 h. It is well known that for equilibrium polycondensation it...
is necessary to observe the rule of nonequivalence of functional groups. However, because of the volatility of the heterocyclic diols, they were taken in an excess of 5-10% by wt., which compensated for carry-off of diol during the reaction process. A number of transesterification and polycondensation catalysts were tested for the preparation of polyesters. The most active one proved to be a mixture of antimony trioxide and zinc acetate, taken in an amount of 0.1% of the dicarboxylic acid content. All of the synthesized polymers were soluble in o-chlorophenyl; their inherent viscosities in this solvent were 1.1-1.6 dl/g.

Additional polycondensation is possible at a pressure of 0.0133-0.00133 Pa to increase the molecular weight of the polymer after carrying out the main stage of reaction. The dependence of polymer $\eta_{inh}$ on the degree of vacuum (Fig. 2) indicates that, with decrease in pressure from 0.0133 to 0.0067 Pa, the rate of final polycondensation rises, but a further reduction in pressure to 0.00133 Pa shows up only slightly in the rate of reaction.

The final polycondensation reaction temperature exerts the greatest effect on molecular weight. In Fig. 3 it is shown that with increase in temperature from 270 to 300° a significant increase in reaction rate takes place. On further increase in temperature, apparently the proportion of side reactions increases, as is indicated by the loss of polymer solubility.

Fig. 1. Curves for polycondensation kinetics of a copolyester based on 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole at synthesis temperatures of 300°C (1, 3) and 280°C (2, 4): 1, 2) by evolution of acetic acid (AA); 3, 4) from change in effective melt viscosity.

Fig. 2. Dependence of $\eta_{inh}$ on degree of vacuum (in kPa) used in final polycondensation of copolyester based on 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole at 300°C: 1) 0.00133; 2) 0.0066; 3) 0.0133.

Fig. 3. Dependence of $\eta_{inh}$ on final polycondensation temperature of copolyester based on 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole under a vacuum of 0.0066 kPa at temperatures of 270 (1); 280 (2), and 300°C (3).