mixed crystal-solvates of the PPTA with the two different solvents. Along with the reduction in melting point of the anisotropic solution, its viscosity is also considerably reduced (Fig. 4). A possible reason for this is the decrease in viscosity of the mixed solvent because of the lower viscosity of CSA as compared with that of sulfuric acid.

In contrast to CSA, the use of MSA on introduction in the amount of 5-15% by wt. in the main solvent leads to an increase in the melting point of the liquid-crystal systems (Fig. 3). The significant increase in viscosity of copolymer solutions on addition of MSA to a sulfuric acid solution proved unexpected; by itself it is less viscous than sulfuric acid (Fig. 4). It is known that MSA is a "good" solvent for PPTA [5]; in the presence of it the degree of structure formation in the solution should not be increased. It is true that, if we judge from the intrinsic viscosity values, which vary in the series CSA > MSA > H2SO4 [5], CSA is more efficient as a solvent for PPTA than MSA. Therefore the viscosity of a concentrated solution of PPTA in CSA should be less, as is observed in experience with small additions of these solvents.

CONCLUSIONS

The temperature regions of fusion and viscosity of mixed liquid-crystals based on PPTA have been investigated.

On appropriate selection of the copolymers, mixtures of polymers, or mixed solvents, it is possible to vary the temperature of transition of these systems from the solid state to the liquid one over a wide range.

LITERATURE CITED

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ACTION OF THE H3PO4–H2O–POLYETHYLENE GLYCOL SYSTEM IN THE SYNTHESIS OF POLYCAPROAMIDE

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A specific feature of the caprolactam (CL) polyamidation process in the presence of the ternary activating system H3PO4–H2O–polyethylene glycol (PEG) is a rapid attainment of a stationary growing chain concentration and the occurrence of further reaction mainly via a condensation-hydrolytic mechanism involving ammonium and amidinium ions [1]. In the present article we describe the technological possibilities of this system.

In conformity with the concepts developed in [1, 2], we have

\[-d[CL]/dt = k[H2O][H3PO4][CL]([CL] - [CL_eq]) \]

(1)

\[P = \sqrt{\frac{K[H3PO4][CL_eq]}{[H2O]}} = \frac{K[H2O]}{[H3PO4]} \]

(2)

at

\[\beta = \frac{[\text{PEG}]-[\text{NH}]+[\text{H2O}]}{2[H3PO4]} = 0.247 + 0.155 [\text{PEG}] [\text{H2O}][\text{H3PO4}] \]

(3)

where $\bar{P}$ is the equilibrium degree of polymerization; $k$ and $K$ are the rate constants for chain growth and amide equilibrium; $[H_2O]_0$, $[H_3PO_4]_0$, and $[PEG]_0$ are the initial concentrations of water, phosphoric acid, and polyethylene glycol, respectively; $[\equiv NH^+]_0$ is the steady-state concentration of amidinium ions; and $T$ is temperature.

Fig. 1. Relationship between $\bar{P}$ and $\tau_m$ at water contents of 0.08 (a) and 0.05% (b) by wt. in the melt and at various temperatures (in °C): 1) 280; 2) 270; 3) 260; 4) 250.

\[
\lg (h/T) = 3.467 - 3897/T
\]

To illustrate the technological possibilities of the ternary activating system in the synthesis of fibre-forming PCA in continuous polymerization apparatus (CPA), we utilized these relationships and calculated the maximum $\bar{P}$ values which can be attained at various reaction times if the flow regime of the melt is laminar ($\tau_m = 2\tau_{min}$)* and the degree of approach to the ring–chain equilibrium is 95%.

From the data shown in Fig. 1, it follows that, at a moisture content of the melt of 0.05-0.08% by wt. and a temperature of 250-280°C, during a time of not over 40-45 h a PCA having a $\bar{P}$ of about 250 can be synthesized. Meanwhile, for the polymer with $\bar{P} = 150$, which is ordinarily used for spinning textile fibres, the reaction time may be varied within the range 13-33 h; and for the polymer with $\bar{P} = 200$, which is used in forming technical fibres, it may be varied within the range 25-45 h.

However, it should be stressed that the reaction time may be considerably shortened (almost by a factor of two) on transition from an apparatus of the column type, with predominant movement of the reaction mixture from above downward, to horizontal apparatus of the extruder type [3], as a result of eliminating the parabolic distribution of the rates of movement of melt layers over the cross-section of the apparatus.†

Since an important quality characteristic of fibre-forming PCA is stability of the molecular weight of the polymer under fibre-spinning conditions, in selecting the technological conditions for polymer synthesis one should obviously start not only, as it may be, not so much as, from an attempt to attain the maximum apparatus productivity as from requiring minimization of the rate of further polycondensation of the polymer in the spinning assembly.

The driving force for this reaction is the difference in the temperature-moisture content regime in polyamidation of CL and in polymer processing [4], which is expressed by the difference:

\[
\Delta = \frac{[H_2O]_0}{K_{sp}} - \frac{[H_2O]_s}{K_s} = ([\equiv NH\text{eq}-\text{COOH\text{eq}}]_0 - ([\equiv NH\text{eq}-\text{COOH\text{eq}}]_s) \times (5)
\]

where $K_{sp}$, $K_s$, $[H_2O]_0$, and $[H_2O]_s$ are the amide equilibrium and melt equilibrium moisture constants under the conditions of spinning and synthesis; and $[\equiv NH\text{eq}$] and $[\equiv COOH\text{eq}]$ are the equilibrium end-group concentrations.

*$\tau_m$ and $\tau_{min}$ are the mean and minimum residence times of the melt in the CPA.

†Since there is no need to degas the melt during the CL polyamidation process when the initiating systems under consideration are used, the transition to such apparatus is rational, particularly in the case of making PCA which is characterized by very high $\bar{P}$ values and high melt viscosity.