The effect of deformation on the phase separation in the polycapramide–caprolactam system

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The phase state and phase transitions in melts and solutions of polycapramide (PCA) in caprolactam were studied by means of viscosimetry, optical interferometry, and polarization microscopy. It has been shown that the orientation of macromolecules of PCA in the flow zone results in the expansion of the area of immiscibility in the phase diagram. The isothermal crystallization was traced by the change of the length of the induction period by means of viscosimetry measurements. The dependence of the rate of isothermal crystallization on the rate of shear deformation is quite marked. The decrease of the rate of crystallization at high rates of shear is believed to be associated with the destruction of critical-size nuclei in a high velocity gradient stream.

INTRODUCTION

The phase diagrams of polymer solutions constitute the fundamental characteristics of a binary system. Great difficulties arise in constructing phase diagrams for solutions of crystallizing polymers, where the existence of two independent types of phase equilibria, namely amorphous and crystalline, are possible. An important factor, which is not taken into account in plotting phase diagrams and which is of general fundamental importance in industrial processes involving polymer melts and solutions, is deformation. Polymers in any of the physical states undergo shear or extension and large reversible deformations occur which in turn has a bearing on the change of the system. Naturally, this leads to a change in equilibrium conditions and to a shift of the temperatures of phase transitions[1–3]. However no systematic data characterizing the shift of phase curves during the orientation of a polymer in solution or melt are available in the literature.

The objective of the present work was to construct complete phase diagrams for the crystallizing polymer–solvent system and to investigate the effect of shear flow on the crystallization of the polymer from solution, over the entire range of concentrations, with the rate of deformation being widely varied.

EXPERIMENTAL

The material used for our investigation was polycapramide (PCA) obtained by the method of activated anionic polymerization. The specific viscosity of a 1% solution of the test sample in H_2SO_4 was 2.14. During the course of the experiment the polymer solution or melt was kept in an atmosphere of dry argon heated to the test temperature to prevent oxidation.

The phase state and phase transitions in solutions and melts of PCA, were investigated using the following methods: viscosimetry, optical interferometry, and polarization microscopy. The freezing of undeformed solutions and melts was determined from the jump of the intensity of the polarized light passing through the solution, which was cooled at a rate of 1–1.5 deg. $\min^{-1}$. The freezing point of the polymer upon deformation was determined by the onset of a sharp increase of the shear stress during the flow of the solution in a homogeneous stress field between the coaxial cylinders. An important factor observed in these experiments was the dependence of the moment when the stress began increasing, i.e. the duration of the induction period of crystallization on the rate of deformation. A similar dependence was displayed with some solutions of PCA in its lactam[1].

RESULTS AND DISCUSSION

The increase in shear stress after the completion of the induction period during the crystallization of the deformed polymer may be due to 2 factors—(1) the increase of the viscosity upon transition from a true solution to a suspension of crystallites and/or (2) increase of the rate of shear as a result of the deposition of the crystallizing polymer on the surface of the inner cylinder and the decrease in the gap between the outer and inner cylinders. Both these factors are connected with the crystallization process under study. When the polymer separated from solutions of low concentrations, it was possible to record the variation of the shear stress up to the completion of the crystallization; and in the case of concentrated solutions the crystallization in the bulk excluded the flow of the polymer.

At the point of amorphous-phase transition the viscosity of the solution sharply diminishes, which is accounted for by the deposition of the polymer and its removal from the working space of the viscometer.

The procedures used for conducting diffusion experiments and the treatment of interferograms were described earlier[4]. The measurements were carried out over a

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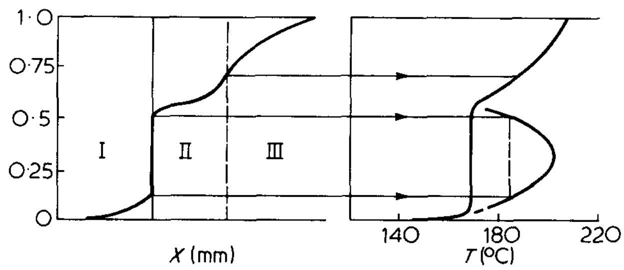

Figure 1 Plot of phase diagram on the basis of data provided by optical interferometry. I – region of a single phase solution; II – region of co-existence of two amorphous phases; III – region of retention of the crystalline phase

temperature range of 150°–200°C with stepwise increase in temperature.

The interference micro technique was at first intended for the determination of the amorphous-phase equilibrium in solutions of PCA in caprolactam. However, the incorporation of a polarizer and an analyser into the optical circuit of the interferometer enabled us not only to obtain in our diffusion experiment, information on the curve of concentration distribution near the phase curve of the mutual solubility of the components. but also to deduce the temperature and composition area on the distribution curve. Within the distribution curve there exists the crystalline phase of PCA, i.e. it allows determination of the position of the liquidus curve. *Figure 1* clearly shows the scheme of plotting of the phase points of the phase diagram for the PCA–caprolactam system.

The combined use of these various methods has allowed us to construct a complete phase diagram for the PCA–caprolactam system, which is presented in *Figure 2*. Deformation gives rise to crystal separation and this is reflected in the phase diagram as a region over which the transition temperature is dependent on shear rate.

The temperature at which the crystallization started, during the period of 2 to 5 hours after the onset of deformation, was assumed as the limiting value of the freezing point. The crystal-separation temperatures given are not thermodynamic equilibrium values because of the retarded crystallization processes, though they are close to such values due to the high rate of crystallization of PCA. With this reservation, the curves 2 and 3 in *Figure 2* may be regarded as the liquidus curves in the phase diagram for the undeformed and deformed PCA-caprolactam systems respectively. Certain differences in the region of cyrstal separation, which were observed in the use of viscometry and optical polarization microscopy, may be as a result of the possible overcooling of the solutions under the temperature–scanning conditions of measurement.

The experimental data presented in *Figure 2* are indicative of the shift of the liquidus curve under the influence of shearing deformation. Within the hatched area the freezing points of the solutions vary, depending on the flow conditions. Thus, when the course of the crystallization process was followed by means of the viscometric method, the polymer crystallized at higher temperatures than its freezing point under static conditions. For instance, the PCA melt was crystallized at a high speed at $T = 235°C$, which is higher than the equilibrium melting point of this polymer as determined by the various methods[5].

Just as the liquidus curve is shifted during the orientation of the dissolved polymer, the binodal curve of amorphous–phase separation may also be expected to be distorted. On the basis of the simplest relationships that determine the possibility of occurrence of a phase transition, it is possible to show that the phase–transition temperature for the oriented polymer is expressed as:

$$T_{or} = T_o \frac{\Delta\bar{S}_1}{\Delta\bar{S}_1^{or}} \tag{1}$$

where T_o is the phase-transition temperature for the unoriented polymer; $\Delta\bar{S}_1$ and $\Delta\bar{S}_1^{or}$ denote the change of the partial molar entropy of the phase transition for unoriented and oriented polymers, respectively.

For partially miscible polymer–solvent systems the following relationships between the thermodynamic parameters of dissolution are possible:

$$(a)\, \Delta\bar{H}_1 > 0; \Delta\bar{S}_1 > 0; |T\Delta\bar{S}_1| > |\Delta\bar{H}_1| \tag{2}$$

where $\Delta\bar{H}_1$ is the change of the partial molar enthalpy of the phase transition.

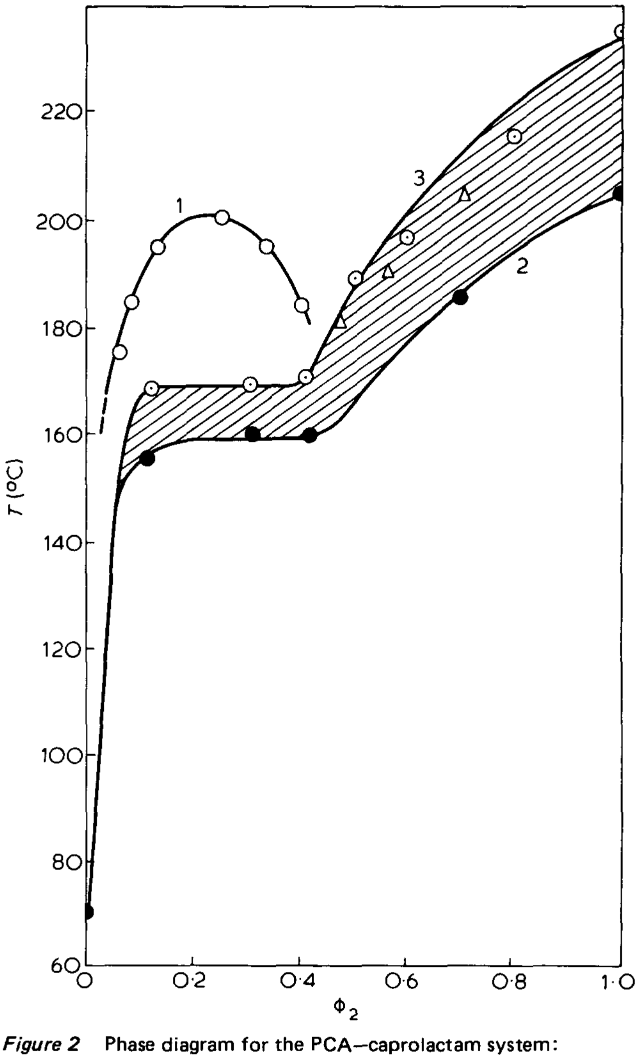

Figure 2 Phase diagram for the PCA–caprolactam system: 1 – binodal curve of amorphous-phase separation; 2,3 – liquidus curves for undeformed and deformed solutions, respectively (●, viscometric method; △, optical method)

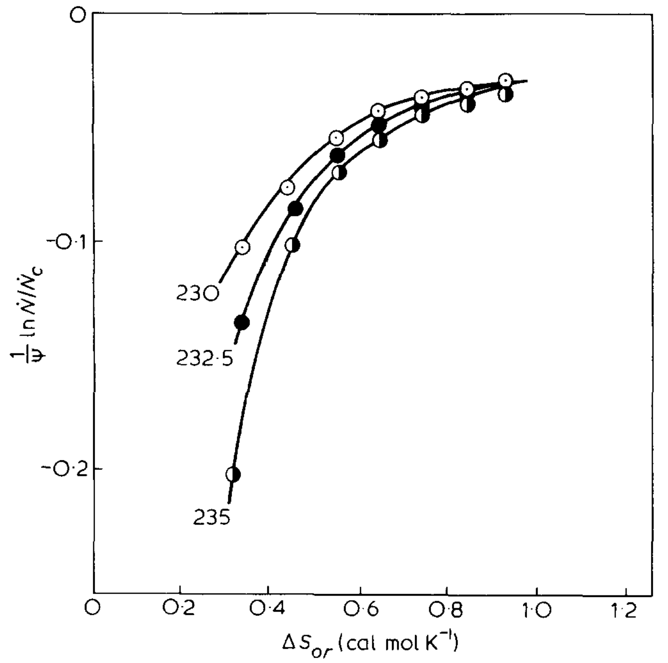

Figure 3 Variation in the equilibrium melting point and the rate of nucleation at various temperatures (indicated on the curves) *versus* the orientation of the PCA melt

In this case $\Delta\bar{S}_1^{or} < \Delta\bar{S}_1$ and, according to equation (1), the phase–separation temperature increases during the orientation of the polymer.

$$\text{(b)}\,\Delta\bar{H}_1 < 0;\ \Delta\bar{S}_1 < 0;\ |T\Delta\bar{S}_1| < |\Delta\bar{H}_1| \qquad (3)$$

With this variation in the thermodynamic parameters of dissolution $|\Delta S_1^{or}| > |\Delta\bar{S}_1|$ the phase–separation temperature on orientation of the dissolved polymer decreases. This corresponds to the existence of a lower critical shift temperature in the polymer–solvent system and a decrease in T_{or} leads also to the expansion of the immiscibility area in the phase diagram.

On the basis of analogous thermodynamic relations that determine a first-order phase transition the rate of nucleation of crystals of the oriented polymer near the melting point is expressed by the following ralation:

$$-\frac{1}{\psi}\ln\dot{N}/\dot{N}_c = \frac{\Delta H_m}{T[\Delta H_m - T(\Delta S_m - \Delta S_{or})]} \qquad (4)$$

where $\dot{N}$ is the rate of nucleation, ΔH_m and ΔS_m are the enthalpy and entropy of melting, respectively; ΔS_{or} is the change of the entropy of the polymer during the orientation; ψ and $\dot{N}_c$ are constants.

Using relation (4) and knowing the thermodynamic constants of melting of PCA[5], we can calculate the change in the rate of nucleation from the molecular orientation of the polymer (*Figure 3*). The rate of nucleation, which increases considerably at the initial stages of orientation, becomes only slightly dependent on the change of the entropy of the polymer, and at large deformation it is negligibly dependent on the freezing point. In this case, the orientation of macromolecules is so high that the change in the freezing point by several degrees is negligible when compared to the increase in extent of overcooling due to orientation.

The application of shear deformation to the crystallizing polymer or its solution does not lead to a monotanous increase in the equilibrium melting point (*Figure 4*), and the duration of the induction period of crystallization is influenced in a complex manner (*Figure 5*). The equilibrium melting points used to plot the graph shown in *Figure 4* were calculated from kinetic data, as was done earlier[1,2].

At low shear rates the rate of crystallization increases with increasing rate of shear ($\dot\gamma$) according approximately to the power dependence $t_u \sim \dot\gamma^{-n}$, the exponent increasing with rise in temperature (*Figure 5*). Here t_u is the duration of the period of induction before the crystallization can start. As a result, kinetic data in double logarithmic coordinates are a series of convergent straight lines, which on extrapolation intersect at a single point. This point corresponds to the conditions under which the rate of crystallization is almost no longer dependent on the temperature. This fact correlates well with the above theoretical analysis, from which the existence of such a region follows (*Figure 4*). In practice, this region is not attained since at high rates of shear the rate of crystallization begins to decrease. This effect is observed both during the crystallization of solutions of PCA in the lactam[1] and during the crystallization of the PCA melt. It may be assumed that this phenomenon is caused by the fact that the flow at a high rate of shear results in the

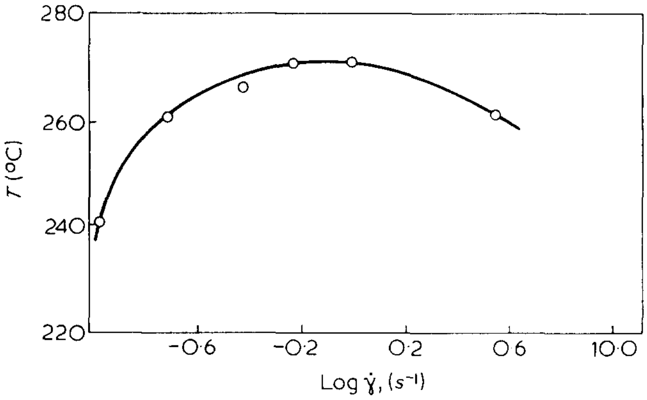

Figure 4 Dependence of the equilibrium melting point on the rate of shear $\dot\gamma$ during the flow of molten PCA

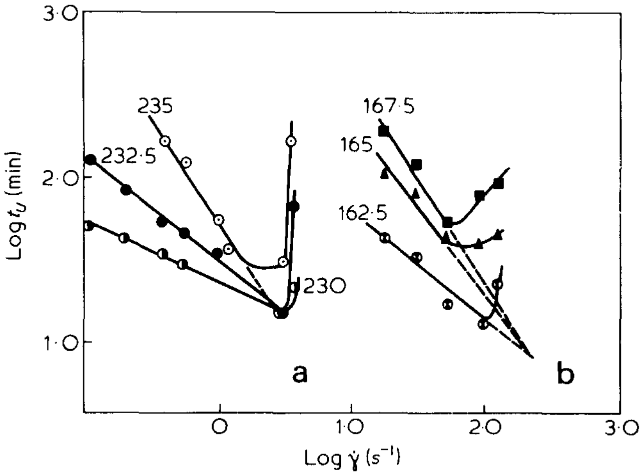

Figure 5 Dependence of the induction period of crystallization of PCA from a melt (A) and a 30% solution (B) at various temperatures (indicated on the curves)

destruction of nuclei of a critical size and a reduction in the time of contact between the macromolecules and the nuclei formed. Such a 'negative' effect of shear deformation on the kinetics of crystallization is most pronounced at high temperatures when the critical size of the nuclei and the rate of relaxation of macromolecules increases.

Thus, the flow of the polymeric solution results in the expansion of the immiscibility area in the phase diagram for the polymer–solvent system, the magnitude of this shift being dependent on the rate of deformation of the macromolecules. The deformation of the macromolecules and, hence, the change in the phase–separation temperature, attains a maximal value at a certain definite shear rate, exceeding of which leads to the weakening of this effect.

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