INTRODUCTION

Study of phase transitions, owing to their fundamental theoretical importance and enormous practical significance, is one of the key problems in the physical chemistry of polymer systems. Many investigations, generalized in monographs and reviews [1–5], concern this topic. However, most of them consider phase transitions in systems unperturbed by an external field, e.g., a mechanical one. It is known that deformation causes significant changes in the structure of systems, and this fact is widely used in practice. Along with structural changes, one can also observe phase transitions that are not implemented at the same temperatures and concentrations under static conditions. A change in the thermodynamic stability of polymer solutions under their deformation, manifested in a displacement of the binodal and liquidus curves, was predicted by Frenkel [6]. The results of experimental and theoretical investigations of phase transition in polymer solutions under deformation are generalized in [5, 7–11]. As is presently established for solutions of polymers (mainly amorphous ones), mechanical stress is a parameter of state (like temperature and concentration) that determines the position of boundary curves. Depending on the deformation rate, concentration, and molecular mass of the polymer, as well as on the ratio of the polymer and solvent surface energies, the solubility of polymers in solutions subjected to deformation can either increase or decrease. This fact is manifested in the corresponding displacement of the binodal curves. A relationship between the displacement of binodal curves (a macroscopic phenomenon) and a change in the macromolecule size in the deforming systems (a microscopic phenomenon) is established. However, such investigations for solutions and blends of crystalline polymers were performed only in recent years. In this study, we generalize and analyze the results published during the last 10 years and concerning the effect of deformation on the phase and structural transitions in melts, blends, and solutions of crystallizing polymers. Most of the review is based on the results obtained by the author.

PHASE AND STRUCTURAL TRANSITIONS IN POLYMER MELTS UNDER DEFORMATION

The phenomenon of polymer crystallization under the action of applied mechanical stress is considered in monograph [7] and reviews [8–11], where the results of investigations conducted up to 1995 were generalized. It has been established [9] that mechanical action (tensile or shear deformation) increases the degree of orientation of macromolecular chains in melts. As a result, the period of induction decreases for crystallization, the crystallization temperature increases (by tens of degrees), the growth rate of nuclei becomes two to four orders of magnitude higher than before, the nucleation rate becomes one or two orders of magnitude higher, and the critical size of new-phase nuclei decreases. In recent years, crystallization in a shear field, along with the structure, has been studied for PP, PE, poly(ε-caprolactam), polybutene-1, poly(p-dioxanone), poly(ethylene-2,6-naphthalate), and PET. For PP, the methods of small-angle light and X-ray scattering, optical microscopy, polarized-light microscopy, phase contrast electron microscopy, atomic force microscopy, and DSC showed [12–18] that shear deformation promotes the appearance of anisotropic macromolecular conformations for fractions with a high molecular mass. The emerging fluctuations of orientation cause an increase in the nucleation and crystallization rates and
lead to the appearance of supramolecular formations that are elongated in the direction of deformation.

Significant structural changes resulting from deformation are also observed for polymers in the solid aggregation state. For example, the structure of PP and HDPE subjected to shear deformation at a pressure of 1 GPa on a Bridgman anvil was studied using X-ray diffraction analysis in [19]. As was shown for PP, shear deformation at high pressures causes the formation of three regions with different structures in the sample. The central part of the sample is characterized by the presence of fairly large (up to 15 nm) crystallites with monoclinic packing of chains and their slight orientation. In the intermediate region, active rearrangement of PP crystallites and a significant reduction of the crystalline regions take place. In the peripheral region, the dimensions of spherulites rapidly decrease and defects are accumulated in them until long-range order is completely lost; also, the polymer chains become oriented in the direction of the material flow. During shear deformation of HDPE, part of the rhombic crystallites, which are characteristic of it, pass into the monoclinic modification. Three regions are also observed in this case: the central region, where reorientation of crystallites is slight; the intermediate region, where the reorientation is notable; and the peripheral region, where active orientation of crystallites in the direction of flow takes place.

Using the methods of polarized-light microscopy and X-ray scattering, the authors of [20] showed that the melting temperature $T_m$ of PE remains virtually invariable at low shear rates $\dot{\gamma} = 0.5–5$ s$^{-1}$; however, a structure of the shish-kebab type, which is typical of deforming systems, is formed. The effect of flow on the morphology of PE was also observed in [21].

An increase in the crystallization and nucleation rates, as well as shortening of the period of induction and anisotropy of spherulites under the conditions of deformation, was found for poly(ethylene naphthalate) [22, 23], PET [24], and polybutene-1 [25].

For the biodegradable polyesters poly($p$-dioxanone) and $p$-dioxanone–glycolide copolymer, it was shown [26] that shear deformation does not affect the spherulite growth rate but significantly increases the nucleation frequency. These polymers pass into the crystalline state from a deformed melt more than twenty times faster than under static conditions.

Acceleration of crystallization during shear deformation was also observed for poly($\varepsilon$-caprolactone) [27, 28]. In this case, the exponent in the Avrami equation significantly increases, a result due to orientation of macromolecules, which causes an increase in the nucleation frequency and in the growth rate of nuclei of the new crystalline phase.

As is shown in [29], the crystallization temperature $T_{cr}$ of PEO with a fairly low (about $10^4$) molecular mass changes within 2 K under the conditions of deformation (in comparison with $T_{cr}$ of these samples under static conditions); i.e., the mechanical field has a minor influence on the crystallization process in these polymers. Similar results for poly(ethylene glycol) (PEG) with $M = 800$ and $2 \times 10^6$ are given in [30]. Deformation of PEO with $M = 3.5 \times 10^6$ at a shear rate of $30$ s$^{-1}$ has no effect on $T_{cr}$ either; however, in a shear field with $\dot{\gamma} = 150$ s$^{-1}$, the crystallization temperature of high-molecular-mass PEO becomes several tens of degrees higher. A significant increase in $T_{cr}$ in a shear field for PEO, PE, and other polymers with $M \sim 10^5–10^6$ was mentioned in [9, 31]. The increase in the temperatures of crystalline phase separation in polymer systems is associated [7–11] with orientational processes in them: unfolding of macromolecular coils and orientation of chains. As a result, the system entropy decreases and, consequently, since $T_m = \Delta H_m/\Delta S_m$ ($\Delta H_m$ and $\Delta S_m$ are the enthalpy and entropy of melting, respectively), the melting point increases. Orientation of macromolecules, which promotes crystallization, increases with the molecular mass of the polymer and with the shear rate; the $T_m$ and $T_{cr}$ values become higher as a result. The significant increase in the $T_{cr}$ value of high-molecular-mass PEO is also due to a notable increase in its melting enthalpy $\Delta H_m$; from 140 kJ/kg (under static conditions) to 320 kJ/kg (after shear deformation) [29]. A similar increase in the enthalpy of melting as a result of deformation was also observed for PE [32].

PHASE AND STRUCTURAL TRANSITIONS IN SOLUTIONS AND BLENDS OF CRYSTALLIZING POLYMERS SUBJECTED TO DEFORMATION

An increase in the crystallization temperatures of polymers has also been found for solutions under deformation. The authors of [33] showed that crystallization of polymers during flow of PET solutions in diphenyl ether takes place at a temperature 10 K higher than that under static conditions. The isolated polymer consisted of oblong crystallites, which are more thermally stable than spherulites formed upon phase separation of unperturbed solutions.

Malkin and Kulichikhin [34] performed the first investigations of the effect of the shear stress on the position of the liquidus curve for a polymer–solvent system with crystalline phase separation. Those authors showed that the boundary curve in a mechanical field shifts toward higher temperatures and changes its shape. The extent of curve displacement depends on the shear rate, and the reason for this shift is a decrease in the system entropy, an occurrence that is due to unfolding of macromolecules and their orientation during flow. Later, the phase separation temperatures $T_{ps}$ of solutions and the crystallization temperatures $T_{cr}$ of PE from its solutions in $p$-xylene and from a melt were determined in [35, 36] under static and dynamic condi-