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Phase transitions in polymer solutions induced by mechanical fields

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Abstract. The review summarises and analyses recent results of studies into phase transitions in polymer solutions induced by mechanical fields. Processes of dynamic structure formation preceding phase transitions in shearing and longitudinal fields are described. The effect of molecular weight, chain flexibility, and concentration of the polymer, shear stress (rate), and surface energies of components on the phase separation of polymer solutions in a mechanical field is considered. The theoretical concepts of phase transitions in polymer solutions under mechan ical stress are analysed. The bibliography includes 186 references.

I. Introduction

The study of phase transitions in polymer systems is a task of current interest, since phase transitions largely govern the structure, and hence, the properties of systems.

Processes leading to the formation of new phases play an important role in polymerisation and polycondensation, microencapsulation, adsorption from solution, and in the production of fibres, films, and membranes. Studies of phase equilibria are necessary for the development of the solution theory and for experimental verification of the existing theoretical assumptions. It is therefore natural that phase equilibria draw much attention.[1–8]

Polymeric systems are exposed to various mechanical effects (shearing, stretching, compressing, and other deformations) during exploitation and processing. Directed mechanical stress is the main method for the orientation of polymers aimed at enhancement of their mechanical properties. For example, molecular orientation implemented by deformation of melts or solutions and arrested by a phase transition (crystallisation) has opened the possibility of manufacturing high-module fibres.

A considerable number of publications on the effect of mechanical stress on the phase transitions in polymer systems have appeared over recent years; some have been reviewed.[9,10] Undoubtedly, mechanical stress can play a role of an independent thermodynamic factor determining the positions of the boundary curves, *viz*., binodals and liquidus curves, on phase diagrams. According to Frenkel,[8] mechanical stress should lead to a shift of these boundary curves. However, the theory of phase transitions in polymeric systems induced by mechanical fields † is still under development.

The accumulated body of data on the effect of a mechanical field on the liquid and crystalline phase separation, as well as on the gel formation in polymer solutions are summarised and analysed in this work. Phase transitions in polymer mixtures are not considered.

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II. Dynamic structure formation in polymer solutions

Changes in viscosity, optical, thermodynamic, and other properties are observed in polymer solutions well below phase separation temperatures (T_{ph}) (on approaching T_{ph}).[7,11–15] This implies a continuous reorganisation of the solutions: concentration fluctuations increase abruptly, and the size of light-scattering particles, which are nuclei of the new phase, increases.

In addition to temperature, concentration, and chemical structure of the components, the structure of polymer solutions is much affected by the external mechanical field. Its action can cause uncoiling of macromolecules, their orientation resulting in the formation of supramolecular structures, and decomposition of the structures already present.

Polymer flow can be caused by both stretching and shearing deformations. The shearing field causes the rotation of macromolecules, and the direction of deformation is reversed before a high degree of stretching is attained. Under uniaxial stretching conditions, the component of rotational movement is absent, and molecule stretching is determined by the $\varepsilon\tau$ product, where ε is the deformation rate and τ is the maximum time of molecule relaxation in which it returns to the coil conformation. Since τ is proportional to the molecular weight ($M^{1.5-2.0}$), considerable stretching of a macromolecule with high M can be reached even at very low polymer concentrations ($c \simeq 10^{-2}$ g dl^{-1}).[16] A small fraction of molecules with molecular weight 15 times higher than the average are deformed 100 times more strongly.[17] For this reason, at moderate stretching stress in a flux, the majority of short molecules only move, while long molecules present in small quantities stretch almost completely and can form nuclei of a new phase.

The transition from a coil to a stretched chain was considered theoretically in a series of papers.[18–25] It was shown within the

† Mechanical field signifies a field of vectors of stresses (forces) that appear in a system when it is deformed.

scope of nonequilibrium thermodynamics [19] that in a longitudinal hydrodynamic field (under uniaxial stretching), full uncoiling of macromolecules occurs, which is accompanied by an increase in energy dissipation by the flowing solution. It was shown [19] that in the case of unpermeable macromolecular coils, the transition of chains to the stretched state on changing the velocity gradient occurs as a first-order phase transition and is accompanied by an abrupt change in the conformational entropy of the chain. When the molecular weight of a polymer decreases, the transition behaviour becomes uniform.

The theoretical conclusions are confirmed by the experimental data for dilute solutions of carboxymethylcellulose, methylcellulose, nitrocellulose and a number of other polymers.[19] The fact that a transition of polystyrene molecules in xylene solutions from coiled to strongly stretched state does occur was confirmed experimentally.[26, 27] The transition, detected by the appearance of strong birefrigence, was observed at shear rates (γ) above a certain critical value (γ_{cr}). The correlation $\gamma_{cr} \simeq N^n$, where N is the degree of polymerisation and $n = 1.47 \pm 0.08$, has been established for the polystyrene – toluene system.[28] The phenomenon of chain uncoiling was also observed in polymer melts. It was found [29] that the mean stretching of polyethylene molecules under shear deformations can be as high as 50%.

A number of papers [20 – 26] present a theoretical consideration of macromolecule uncoiling in a longitudinal hydrodynamic field and analyse the changes in the friction coefficient of macromolecules and in the chain conformational microstructure under stretching. These processes change the environment of macromolecules to anisotropic.[30] Such induced anisotropy is determined by the orientation of macromolecules and manifests itself as experimentally observed birefrigence of solutions, Weissenberg effect, flow swelling, *etc*.[16, 31]

The degree of macromolecule uncoiling in a shearing field is much smaller than that in a stretching field.[32] For example, 100% uncoiling of polyethylene molecules requires a *ca*. 10^3 times higher deformation rate in the shearing field than in the stretching field. Uncoiling and orientation of macromolecules leading to their association have been observed for solutions of poly(ethylene oxide) and polyacrylamide (PAA),[33] polyacrylic acid,[34] and poly(octyl methacrylate).[35]

The increase in concentration fluctuations in the course of flowing has been observed for polystyrene solutions.[36 – 38] The formation of supramolecular particles in such processes was considered in Refs 39 and 40. It was shown that, depending on γ, a sharp increase in concentration fluctuations can lead to the phase separation of the system. In solutions of polymer mixtures, the dependence of the magnitude of concentration fluctuations on the shearing rate passes through a maximum at medium γ values. The micellar structure formation in aqueous surfactant solutions depends on γ in a similar way.[41, 42]

It was found for the poly(vinyl alcohol) – water,[41 – 46] poly(ethylene oxide) – water,[47, 48] polyethylene – xylene,[49, 50] and poly-

Table 1. Effect of mechanical field on the properties of polymer solutions.

System	Shear rate, s^{-1}	Type of deformation	Result of exposure	Ref.
Polymethacrylic acid – water	10	shear	irreversible structure formation	60
PAA – water	1000	"	formation of gel-like particles	61
PMMA – chlorinated biphenyl	20	"	irreversible structure formation	62
PVAL – water	1000	"	formation of molecular aggregates	63
		stretching field	orientation solidification	64
PS – dioctyl phthalate	20	shear	formation of gel-like particles	61
PS – chlorinated biphenyl	150	"	reversible structure formation	65
PS – cyclohexanone	400	"	irreversible structure formation	66
PS – dioctyl phthalate	100	"	reversible phase separation	67
PS – decalin	100	"	the same	67
PS – *tert*-butyl acetate		"	"	68
PS – dioctyl phthalate		"	"	69
		"	structure formation	70
PE – xylene	–	"	crystallisation	71, 72
PVAL – water	200	"	irreversible structure formation	73
		"	irreversible phase separation	74
		stirring	structure formation	46, 75
Tobacco mosaic virus – water	14 400	shear	irreversible structure formation	76
Albumin – water	290	"	reversible structure formation	76
Polyesters and epoxide resins in toluene and ethylbenzene		"	abrupt viscosity change	77
PE – xylene	150 rpm	"	irreversible separation	78
	2000	stretching flow	crystallisation	79
PE – diphenyl ether	2000	the same	"	79
PE – octadecane		shear	"	51
PEO – chlorinated biphenyl	100	"	irreversible structure formation	80
PEO – water	1000 – 10 000	"	the same	47
		turbulent flow	structure formation	81, 82
Polycaproamide – caprolactam		shear	crystallisation	83
PAA – water		stirring	irreversible structure formation	52
		stretching flow	structure formation	54

ethylene–octadecane [51] systems that structure formation resulting in phase separation occurs in the solutions exposed to mechanical stress (stirring, flowing). Analogous effects were observed for polyacrylamide–water,[52–54] polystyrene (PS)–dioctyl phthalate,[55] poly(methyl methacrylate)–chlorinated biphenyl,[56] polystyrene–decalin [57] and polystyrene–cyclohexane [58] systems. It was found that dynamic structure formation is most pronounced in solutions of medium concentration.[59] Table 1 displays data on the effect of mechanical field on the properties of a number of polymeric systems.

Structure formation occurs in rheometer parts of various shapes: cone–plane, coaxial cylinders, capillary. The effect of deformation on solubility does not depend on the type of deformation. For example, similar results were obtained [69] in a study of changes in T_{ph} of solutions for a laminar Poiseuille-type flow through a capillary and for a torsion flow geometry in a gap between a cone and a plate. This is a common phenomenon for solutions of polar and nonpolar polymers with high molecular weight in a wide range of concentrations at any temperatures and in any solvents.

Thus, a study of the structure of polymer solutions showed that, first, uncoiling of macromolecules, their orientation and association leading to phase separation occur in a hydrodynamic field; second, depending on the shear rate and the polymer concentration, the effect of a mechanical field on the solution structure has a dependence passing through an extremum; third, as the molecular weight of a polymer and concentration increase, structure formation starts at lower shear rates; and fourth, a solid phase with new morphology, which is completely stable with respect to re-dissolution, is sometimes isolated from the solution.

III. Phase transitions in polymer solutions induced by mechanical fields

1. Systems with crystalline phase separation

The effect of mechanical field on crystallisation has been studied most thoroughly for polymer melts.[84–98] The phenomenon of stress-induced crystallisation was discovered in 1805 by Gough.[87] Later, this problem was studied by Katz,[88] Flory,[89] Krigbaum and Roe,[90] Vinogradov and Malkin,[91] Haas and Maxwell,[92] Southern and Porter,[93] Fritzsche and Price,[94] Baranov,[95] Hoffman,[96] and Lindenmeyer.[97] This phenomenon has been covered in detail in a monograph [9] and in a review.[98]

Crystallisation of polymers from solutions and melts induced by mechanical stress has been observed in a number of studies.[99–121] For example, crystallisation of *cis*-1,4-polyisoprene, *trans*-1,4-polybutadiene, poly(ethylene terephthalate), poly(vinylcarbazole), and poly(vinyl chloride) due to stretching has been observed by birefrigence and small-angle light-scattering methods.[99] The formation of rod-shaped crystalline structures upon shearing and stretching has been found for melts [100, 101] and solutions [102] of poly(ethylene terephthalate) in *m*-cresol and diphenyl ether. The crystallisation of isotactic polystyrene,[119] polyethylene,[95, 122] and poly(ethylene oxide) [96, 114, 123] melts in a shearing field has been studied.

It has been found for melts that mechanical stress (stretching or shearing deformation) increases the degree of orientation of macromolecular chains so that the induction period of crystallisation decreases, the crystallisation temperature increases (by tens of degrees), the rate of nuclei growth increases by two to four orders of magnitude, the nucleation rate increases by one to two orders of magnitude, and the critical size of the new phase nuclei decreases.

An increase in the crystallisation temperature has also been found for polymer solutions. It was shown [102] that crystallisation of poly(ethylene terephthalate) under flowing conditions occurs at a temperature 10 K higher than that on cooling under static conditions. The polymer that formed consisted of elongated crystals, which were more thermally stable than the spherulites obtained upon phase separation of unperturbed solutions.

Pennings *et al.*[78, 108, 116] have carried out systematic studies of polyethylene crystallisation from flowing solutions. They found that flowing causes a 15–20 K increase in the crystallisation temperature, while the crystallisation rate increases by a factor of several thousand. Similar dependences for polymer solutions were observed in other studies.[103–107, 111] It should be noted that experimental data are in good agreement with those calculated using the theory of polymer crystallisation from melts under deformation.[103, 108] Acceleration of crystallisation under flow conditions has been found in solutions of polypropylene, poly(ethylene oxide),[104] and poly(*p*-phenylene terephthalimide).[104]

In a study of polycapramide crystallisation in caprolactam,[123, 124] it was found that an increase in shear rate to 50 s^{-1} decreases the induction period of crystallisation, but starting from 130 s^{-1}, the flow slows down the crystallisation, *i.e.* inversion occurs. It is assumed [95, 123, 124] that this phenomenon is caused by the destruction of crystallisation nuclei at high shear rates.

Thus, it has been shown experimentally that uncoiling of macromolecules in the flow and orientation of chains favour the formation of nuclei of a new phase and phase separation. A detailed study of the effect of shear stress on the position of the boundary curve in the crystal separation of phases has been first carried out by Malkin and Kulichikhin.[124] They have shown that the mechanical field causes the boundary curve to shift to higher temperatures. This shift depends on the shear rate and is caused by a decrease in the entropy of the system due to processes of uncoiling and orientation of molecules in the flow.

Later, the T_{ph} of solutions and the melting points (m.p.) of polyethylene under static and dynamic conditions (Fig. 1) were determined by Vshivkov *et al.*[48, 125, 126] It was found that application of a mechanical field results not only in an increase in T_{ph} and m.p., but also in a change in the boundary curve shape. It was only in the case of dilute solutions ($c < 1$ mass %) that no change in T_{ph} within the γ range studied was observed. In concentrated solutions, an increase in the shear rate results in a 10–30 K increase in T_{ph}. For solutions with $c = 30$ mass % and 40 mass %, the $T_{ph}-\gamma$ function is a curve with a maximum; this indicates that the dependence of the crystallisation rate on the rate of the solution deformation has an extremal form. A similar correlation was observed by other authors. [123] These data and the data given below prove that this phenomenon is of general character and results from two oppositely directed processes, namely, uncoiling of macromolecules, their orientation in the flow, and destruction of nuclei of a new phase by the mechanical field at high γ values. The first process favours the crystallisation and the second one impedes phase separation.

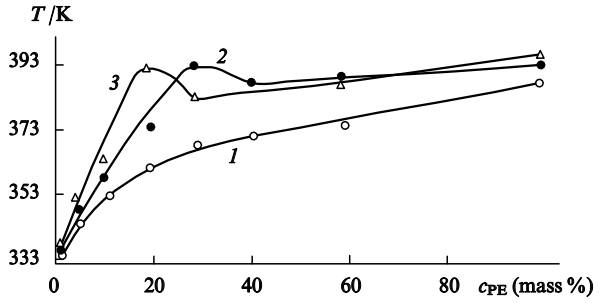


Figure 1. Boundary curves for the PE ($\bar{M}_\eta = 2.3 \times 10^5$)–xylene system. γ /s^{-1}: (*1*) 0, (*2*) 47, (*3*) 246.

From analysis of data on crystallisation of polyethylene from flowing solutions it was assumed [127] that the formation of amorphous gel-like phases precedes the formation of polyethylene fibrils. It was concluded that the phase diagram of solutions of a polymer that undergoes crystallisation can be changed both quantitatively and qualitatively under flowing conditions. In

fact, a shearing field can cause a qualitative change in the boundary curve (see Fig. 1). A maximum appears, the position of which is shifted towards low concentrations of the polymer on increasing the shear rate. Such curves are typical of systems where both liquid and crystal phase separation occurs simultaneously. However, we did not observe liquid phase separation in this system; the shearing field caused only a decrease in the degree of crystallinity of polyethylene precipitated from solutions.

2. Systems with liquid – liquid phase separation

Winsor [128] was the first to mention the effect of mechanical stress on stratification of liquids. He found that turbid systems, such as water – cyclohexanol – alkyl ethers of poly(ethylene glycol), lauryl alcohol – sulfodioctyl succinate – benzene – ethylene glycol and others, become transparent on vigorous shaking and return to the original state after a few minutes of rest.

Silberberg and Kuhn [129–131] studied a polystyrene – ethylcellulose – benzene ternary system, which became turbid on cooling. They showed that the solution was turbid under quiescent conditions but became transparent on flowing at a certain critical shear rate and stratified again at a lower temperature, *i.e.*, the solubility of the components increased on flowing. In this case, the difference in phase separation temperatures under dynamic and static conditions (ΔT) was defined by the equation $\Delta T = -(\gamma_{cr}/\alpha)$, where $\alpha = 3.6 \times 10^6$ mol^{-1} litre. As can be seen from this equation, significant changes in T_{ph} under flow should occur for polymers with high molecular weight ($10^6 - 10^7$).

The enhancement of miscibility in the flow has also been observed for other ternary systems, such as polystyrene – polypropylene – decalin,[132] polystyrene – polypropylene – toluene,[133] legumin – sodium chloride – water [134] and polystyrene – polybutadiene – dioctyl phthalate.[135, 136]

The observed phenomenon was explained [129–131] by the fact that the mechanical field destroys drops of a new phase. This is possible if the interfacial surface energy is low ($\sigma \simeq 10^{-6}$ J m^{-2}). In this case, the energy of the hydrodynamic field may be sufficient to compensate the free energy gain due to the destruction of drops. The drops are destroyed until their volume reaches V

$$V = \left(\frac{0.74\sigma}{\eta\gamma}\right)^3,$$

where η is the viscosity of the medium.[137]

Homogenisation in the flow of a polystyrene – polybutadiene – dioctyl phthalate ternary system, which stratifies on cooling, was studied using small-angle light scattering.[136–138] It was found that the decrease in T_{ph} depends on the shear rate within its 6 – 1300 s^{-1} range according to the equation

$$\frac{\Delta T_{cr}}{T_{cr}} = (2.6 \pm 0.6) \times 10^{-3} \gamma^{0.50 + 0.02}.$$

The enhancement of solubility of the components is explained by the fact that a mechanical field suppresses the concentration fluctuations and destroys the nuclei of a new phase. Similar results were obtained using low-angle scattering of neutrons.[137]

In a study of the optical properties of a polystyrene – toluene system, a decrease in the miscibility of components in the flow was observed.[139] A beam of light was passed parallel to the capillary walls, and it was found that the layer of the solution which scatters light decreased on flowing.

The effect of changes in mutual solubility of components in the flow on the shape of the phase diagram was first studied by Ver Strate and Philippoff.[67] They showed that T_{ph} for solutions of polystyrene in dioctyl phthalate and decalin increases in the flow from 284 to 313 K and from 289 to 302 K, respectively.

Later, the shift of boundary curves in shearing field was observed for polystyrene – cyclohexane, poly(methyl methacrylate) – butanol and poly(ethylene oxide) – water [47] systems. The observed increase in the higher critical solution temperature (UCST) and decrease in the lower critical solution temperature

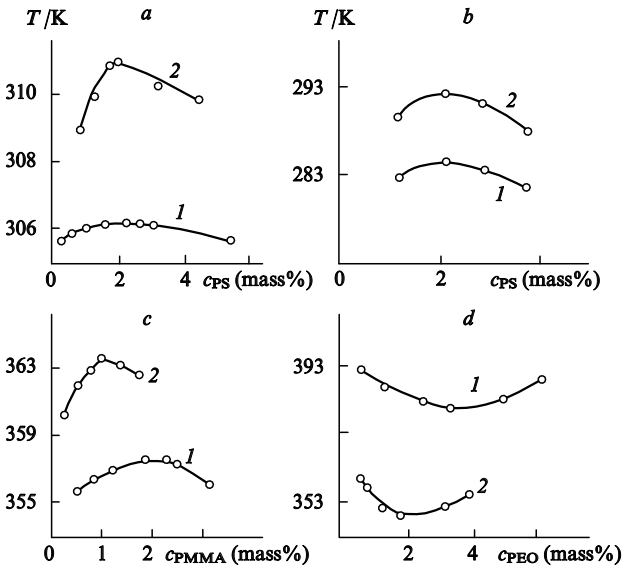


Figure 2. Boundary curves for PS – cyclohexane (*a*), PS – di(2-ethylhexyl) phthalate (*b*), PMMA – butanol (*c*), and PEO – water (*d*) systems under static (*1*) and dynamic (*2*) conditions.

(LCST) (Fig. 2) means a decrease in solubility of the components and formation of stable associates of polymer macromolecules in solution at temperatures at which none are formed under static conditions. The observed phenomenon is explained [47, 67] by uncoiling of macromolecular coils in the mechanical field and by the orientation of chains along the flow, which increases the number of contacts between the macromolecules, *i.e.* increases the degree of association. This assumption has been confirmed experimentally.[54, 58, 70, 84, 140, 141]

The decrease in the solubility of components, which manifests itself as changes in the T_{ph} of flowing solutions, has also been observed for poly(vinyl acetate) – ethanol,[142] poly(methyl methacrylate) – dimethylformamide,[143] polystyrene – cyclohexanone – ethanol,[144] polybutadiene – toluene – ethanol, [144] and poly-(dimethylsiloxane) – ethyl methyl ketone [145] systems.

It was shown [145] for the poly(propylene glycol) – water, polyacrylic acid – dioxane, and poly-*p*-chlorostyrene – isobutyl acetate systems [145] that mechanical stress does not necessarily result in shifting of the boundary curves if uncoiling of macromolecular coils and the orientation of chains in the flow are hindered. In this case, insignificant uncoiling of macromolecules is explained by the low molecular weight of poly(propylene glycol) (1000) and by the high stability of polyacrylic acid globules near T_{ph} due to intramolecular hydrogen bonds.[146] The orientation of poly-*p*-chlorostyrene molecules is hindered by thermal motion (LCST = 423 K). Thus, the orientation effects in all the three systems are small and can be compensated by the destruction of nuclei of new phases in the mechanical field; as a result, the position of the boundary curves remains unchanged.[147]

Wolf *et al.*[148–154] have systematically studied the liquid phase separation of polymer solutions initiated by mechanical field. Using solutions of polystyrene in decalin, *tert*-butyl acetate, and dioctyl phthalate, they showed that both stratification and homogenisation of a system in the flow can be expected, depending on the concentration and the molecular weight of the polymer and the γ value. For example, for polystyrene with $M = 10^5$, mechanical field does not affect the T_{ph} of the solutions; for the sample with $M = 6 \times 10^5$, flowing results in an increase in miscibility, which manifests itself as a decrease in T_{ph}; for the sample with $M = 2 \times 10^6$, flowing decreases the solubility. For solutions with $M = 1.2 \times 10^6$, $\Delta T = 0$ at low shear rates, T_{ph} becomes negative (the solubility increases) with an increase in γ, and $\Delta T > 0$ at high shear rates ($\gamma = 3000$ s^{-1}).

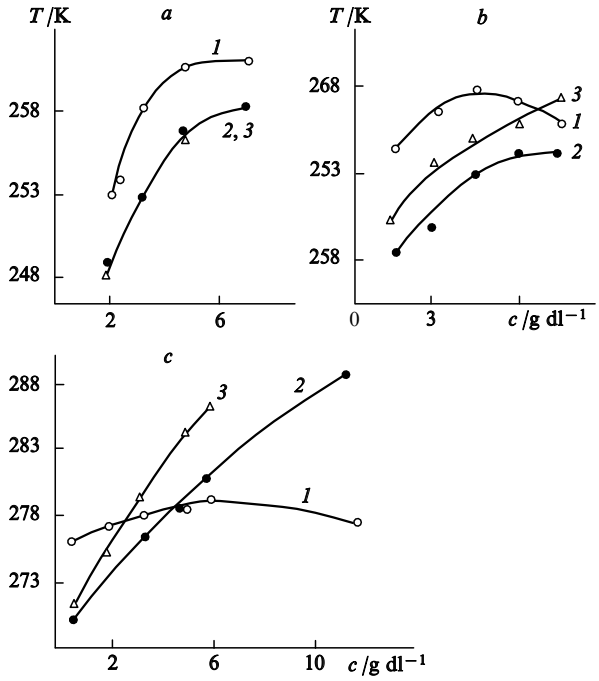


Figure 3. Boundary curves for a PS–di(2-ethylhexyl) phthalate system. $\bar{M}_\eta = 5.7 \times 10^4$ (*a*), 1.6×10^5 (*b*), 2.5×10^5 (*c*); γ /s^{-1}: (*1*) 0, (*2*) 24, (*3*) 118.

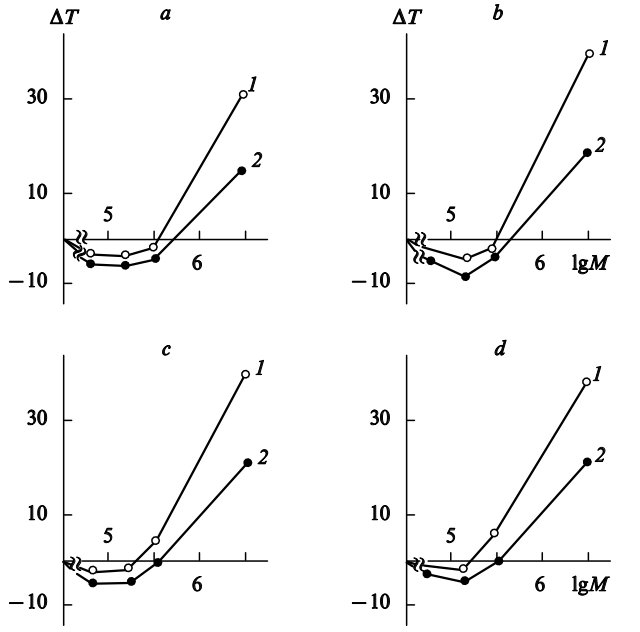


Figure 4. Dependence of ΔT on lg M for the PS–di(2-ethylhexyl) phthalate system.
c_{PS} /g dl^{-1}: (*a*) 1.51, (*b*) 3.06, (*c*) 4.26, (*d*) 5.00; γ /dl^{-1}: (*1*) 118, (*2*) 24.

A different dependence was found for a polystyrene–cyclohexanone–ethanol system.[144] For the polystyrene samples with $M < 10^4$, the mechanical field did not affect T_{ph}, whereas at $M \simeq 10^6$, the ΔT–γ dependence was described by a curve with a maximum. This is explained by the effect of two opposite processes occurring in the system, *viz*., the orientation of macromolecules due to flowing and the destruction of new phase nuclei by the mechanical field. The first process favours phase separation and the second one prevents it. It was shown that the decrease in miscibility in the flow in the case of solutions of polystyrene, poly(vinyl acetate), and polybutadiene can be described by one curve in the ΔT–τ coordinates (where τ is the shear stress). The enhancement of solubility of the components (decrease in ΔT) starts from different τ for each polymer.

A systematic study of the effect of the polymer molecular weight and concentration on liquid phase separation under the action of mechanical field has been carried out for a polystyrene–di(2-ethylhexyl) phthalate system (Figs 2–4).[155, 156] An increase in γ leads to a shift of the boundary curve towards higher temperatures, *i.e*. to a decrease in the solubility of a high-molecular polystyrene sample. A more complicated effect of mechanical field was observed for solutions of polystyrene with lower molecular weight. An increase in the solubility of the components, which manifested itself in a decrease in T_{ph}, was observed for a sample with $\bar{M}_\eta = 5.7 \times 10^4$. These data indicate an inversion of the effect of the mechanical field on liquid phase separation: the mutual solubility of the components increases in the flow in dilute and moderately concentrated solutions ($\Delta T < 0$) and decreases in concentrated solutions ($\Delta T > 0$). The higher the molecular weight of the polymer and the higher γ, the lower the concentration of the inversion point (c_i). It should be noted that c_i is close to the concentration c^* at which macromolecular coils begin to overlap. According to Debye, it equals $c^* = [\eta]^{-1}$, where $[\eta]$ is the characteristic viscosity. One may assume that in solutions with $c < c^*$, the shear field can destroy associates of fluctuation origin that form macromolecular coils in solution upon decrease in the quality of the solvent. The dependences of ΔT on the molecular weight of polystyrene for equiconcentrated solutions are described by curves with minima. In this case, the critical molecular weight (M_{cr}), which marks the limit where ΔT becomes positive, decreases with an increase in the polymer concentration and shear rate. The mutual solubility of the components in the shear field increases for solutions of polystyrene with $M < M_{cr}$.

In the opinion of Barham and Keller,[143] flowing of solutions results in adsorption of macromolecules on the capillary walls. They classify the adsorption-entanglement layers according to their thickness: (1) layers several microns thick formed upon adsorption from solutions in good solvents at small γ (the existence of such layers has been discussed in a monograph[157]); (2) layers formed in poor solvents at large γ that can be several millimetres thick and block the capillary, which increases τ. In these cases, the formation of gel-like particles is referred to. An attempt was made[158] to distinguish processes of liquid phase separation and the formation of adsorption-entanglement layers using oscillating flow. Periodic changes in the flow direction hinder the growth of adsorption layers but do not prevent liquid phase separation, which is determined by the magnitude of shear stress rather than by its direction. Four types of flow behaviour of solutions of poly(methyl methacrylate) in dimethyl phthalate were found: (1) usual flowing, which is not disturbed either by adsorption or by phase separation, at small rates of rotor oscillation (less than 2×10^{-5} rad s^{-1}); (2) flowing where τ increases with time to a constant value (at 2×10^{-5}–10^{-2} rad s^{-1}), which is related to the formation of adsorption-entanglement layers of interpenetrating chains; (3) flowing where τ increases continuously (at 10^{-2}–2 rad s^{-1}) due to the formation of adsorption-entanglement layers followed by liquid phase separation according to the nucleation and growth mechanism in which the role of nuclei is played by adsorption layers; (4) flowing characterised by large unstable τ oscillations. At rates above 3 rad s^{-1}, solutions become turbid due to liquid phase separation according to the spinodal mechanism. Thus, transition from behaviour type 3 to type 4 corresponds to crossing a spinodal, while transition from behaviour type 2 to type 3 corresponds to crossing a binodal. Using these rheological criteria, Barham and Keller[158] have determined the binodals and spinodals and showed that boundary curves and UCST shift to higher temperatures as τ increases. The results of the analysis performed by these and other authors are presented in Table 2.

Table 2. Polymer – solvent systems displaying anomalies on flowing.

System	Geometry of the measuring cell	Type of behaviour	Ref.
PS – toluene	capillary	formation of adsorption layers	56, 62, 158
PS – decalin	"	the same	158, 159
PS – chloroform	"	"	160
PS – dimethyl phthalate	cone – plane	spinodal separation	161
PS – dioctyl phthalate	coaxial cylinders	phase separation according to nucleation-growth mechanism or spinodal separation	67
	capillary	phase separation according to nucleation-growth mechanism	67
PE – xylene	coaxial cylinders	the same	162
PE – decalin	the same	spinodal separation	163
	capillary	phase separation according to nucleation-growth mechanism	164
PAA – water	"	formation of adsorption layers	165
Proteins – water	oscillating plate	spinodal separation	166
PVAL – water	coaxial cylinders	the same	162
PMMA – dimethyl phthalate	cone – plane	phase separation according to nucleation-growth mechanism or spinodal separation	161
	coaxial cylinders	phase separation according to nucleation-growth mechanism	62
	capillary	the same	62
PMMA – chloronaphthalene	cone – plane	"	167
	coaxial cylinders	"	62
PMMA – xylene	the same	"	62

The effect of mechanical field on phase transitions in solutions in which both liquid and crystal phase separation occurs was first studied for the polyethylene glycol (PEG) – poly(propylene glycol) (PPG) and PEG – glycerol – water systems.[168–170] In the former system, a combination of liquid phase separation and crystal phase separation on cooling is observed; in the latter, liquid phase separation on heating and crystal phase separation on cooling occur. In the PEG – PPG system, the shearing field considerably increases the crystallisation temperatures ($\Delta T \simeq 10-16$ K) and almost does not affect liquid phase separation. The absence of a noticeable effect of the hydrodynamic field on the liquid phase separation of PEG solutions is caused by the low molecular weight of PEG. A similar dependence was found for the PEG – glycerol – water system: the change in crystallisation temperatures in the flow was an order of magnitude greater than the change in liquid phase separation temperatures. In both systems, the solubility of the components decreases under flowing conditions.

3. Gel-forming systems

It was found [171] for a polymethacrylic acid – water system that gel formation leading to a sharp increase in viscosity is observed in the shearing field. The time dependence of viscosity (at γ = const) is described by a curve with a maximum the position of which shifts to smaller times with increasing γ. The decrease in viscosity is explained by macroscopic destruction of the gel that formed. It is assumed that the aggregation of polymethacrylic acid molecules results from the deformation and orientation of the polymer chains.

It was shown [169] that the increase in viscosity upon shear can be described by the Avrami equation, which is generally used for the description of polymer crystallisation. Gel formation under flowing conditions has been found for aqueous solutions of poly(vinyl alcohol),[172] gelatine,[126] hydroxypropylguar,[173] and for a poly(dimethylsiloxane) – ethyl methyl ketone system.[174]

An opposite phenomenon has been observed for a cellulose diacetate – acetone – water system, which forms a gel on cooling:[125, 170] applying mechanical field results in a decrease in gelation temperatures, *i.e.* widening of the homogeneous region. This phenomenon is probably caused by the fact that cellulose diacetate has high kinetic rigidity, thus no considerable additional uncoiling of macromolecules should be observed in the flow. Hence, the role of the hydrodynamic field is reduced mainly to the destruction of nuclei of a new phase, which enhances the mutual solubility of the components. It was found that under deformation with $\gamma \simeq 10^2$ s^{-1}, solutions containing a 1.4 – 2 times higher concentration of the polymer can exist than in the absence of flow.

IV. Theoretical background of the phase separation of solutions exposed to mechanical fields

1. Liquid separation

At present, several approaches to the description of the effect of mechanical field on the miscibility of components in polymeric systems are known. For example, Di Marcio and Guttman [175] assume that the polymolecular nature of polymers is the reason for the stratification of the flowing solutions. Since the distance between the mass centres of particles and the capillary walls cannot be smaller than the radii of the particles, larger molecules will be closer to the capillary centre and will thus move at a higher velocity, which results in phase separation. However, this concept has not been developed further, as it did not explain the shift of boundary curves for monomolecular polymer solutions and low-molecular-weight compounds.

Other scientists [67, 126, 127, 149, 154] suggest that the free energy of solution mixing in mechanical field (ΔG_γ) should be represented by a sum of the free energies of solution mixing under static conditions (ΔG) and the energy the solution can store while it flows (G_s),

$$\Delta G_\gamma = \Delta G + G_s \,.$$

The free energy of solution mixing under static conditions is calculated according to the Flory – Huggins theory

$$\Delta G = RT(n_1 \ln\varphi_1 + n_2 \ln\varphi_2 + \chi n_1 \varphi_2) \,,$$

where n and φ with indices 1 and 2 are the mole number and the volume fraction of the solvent (1) and the polymer (2), respectively, and χ is the parameter describing the interaction of the solvent (1) with the polymer (2). The free energy G_s accumulated by the flowing solution due to uncoiling and orientation of macromolecules can be determined according to the equation [67, 148]

$$G_s = \tau^2 I \,,$$

where τ is the shear stress and I is the compliance caused by the first difference of normal stresses, which equals

$$I = 0.4 \frac{M_2}{c_2 RT} \left(1 - \frac{\eta_0}{\eta}\right)^2$$

for Newtonian solutions, where M_2 is the molecular weight of the polymer, c_2 is the polymer concentration, and η_0 and η are the solvent and solution viscosities, respectively.

The first calculations of the stored energy at temperatures near T_{ph} were performed by Ver Strate and Philippoff[67] for the polystyrene–decalin system. It was shown that at $\Delta T \simeq 5$ K, $\tau = 3 \times 10^3$ dyn s^{-1}, $I \simeq 10^{-3}$ cm^3 dyn^{-1}, $\chi = 0.5$, and $\varphi_2 = 0.03$, the stored energy G_s is 2×10^{-4} cal cm^{-3}. The magnitude of G_s is of the same order as the change in the energy of mixing ($\Delta G'$) required for the given change in the solution T_{ph} ($\Delta G' \simeq 5 \times 10^{-4}$ cal cm^{-3}). The concentration dependences of G_s and $\Delta G'$ corresponding to the change in T_{ph} in a polystyrene–di(2-ethylhexyl) phthalate system in the flow were calculated.[155] The calculated values coincided. Hence, the change in the solubility of components in a mechanical field can actually be caused by the energy stored by solutions in the flow.

It was found for a polystyrene–dioctyl phthalate system[69] that the dependence of normal stress, which determines G_s, on the polymer concentration at a constant τ is described by a curve containing a maximum. The pure solvent behaves as a Newtonian liquid, hence the normal stresses are equal to zero. The addition of the polymer imparts elastic properties to the solution, leading to the development of normal strains upon shear deformations. At high polymer concentrations, the fluctuation entanglement network hinders the elastic deformation of chains in the shearing field, which results in a decrease in normal stresses. It is the extremal character of the $G_s - c$ dependence that explains the extremum observed on the $\Delta T - c$ dependence.[69]

Using the Marrucci and Sarti relationship[176] between the solution elasticity and G_s, an equation relating the system parameters for the critical point in a shearing field was found[69]

$$-\frac{1}{(1-\varphi_2)^2} + 2\chi - \frac{a\bar{V}_1}{RT} = 0\,,$$

where a is a coefficient relating G_s to the volume fraction of the polymer and $\bar{V}_1$ is the partial molar volume of the solvent.

By comparing this equation with the known equation for $\gamma = 0$

$$-\frac{1}{(1-\varphi_2)^2} + 2\chi_0 = 0\,,$$

it is possible to find a parameter of interaction between the components in a flowing solution

$$\chi = \chi_0 + \frac{a\bar{V}_1}{2RT}.$$

Presumably, the polymer concentration in the critical point of a system is not changed in the flow,[69] but the interaction parameter is 'shifted' by $\Delta\chi = a\bar{V}_1/2RT$. Hence, boundary curves for a system under mechanical stress should be shifted along the χ (or T) axis and remain parallel to the boundary curves for the undisturbed system. The ΔT values determined experimentally for solutions of polystyrene in dioctyl phthalate at 3–28 K coincided with those predicted[69] to within ±3 K. However, it should be noted that experimental boundary curves are shifted along the T axis with an increase in τ but are not parallel to those for the undisturbed system.

The concept of stored energy was used[149, 154] to calculate a series of boundary curves. It was shown that in the general case, both an increase and a decrease in the solubility of components can be expected in a mechanical field. The overall pattern is determined by the relative behaviour of the concentration dependences of ΔG_γ, ΔG, and G_s (Fig. 5). For solutions of polymers with low molecular weight, a concentration higher than the critical concentration φ_2^{cr} corresponds to the maximum G_s, and in this case the contribution of G_s to ΔG of the system can result in the system homogenisation in the flow and hence in a change in the shape of the $\Delta G - \varphi_2$ curve. For solutions of polymers with high molecular weights, the concentration at the maximum G_s and φ_2^{cr} are comparable. In this case, a homogeneous system whose $\Delta G - \varphi_2$ curve is concave (which corresponds to the thermodynamically stable state) separates into two phases in mechanical

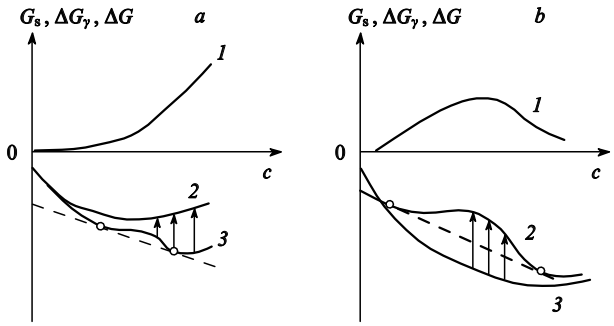


Figure 5. Concentration dependences of the stored free energy (G_s) and the free energy of solution formation under dynamic (ΔG_γ) and static (ΔG) conditions.[152]
(*a*) shear-dissolution; (*b*) shear-demixing; (*1*) G_s, γ = const; (*2*) ΔG_γ; (*3*) ΔG; c is the polymer concentration.

field, and extremums appear on the $\Delta G_\gamma - \varphi_2$ curve. According to the calculations,[149, 154] polymer solutions can separate into three coexisting phases at certain τ values. An eulytic point was introduced, where two binodals, which appear upon deformation from one original binodal corresponding to the undisturbed system, intersect.

The change in the free energy of mixing due to flow is related[127, 177] to a decrease in chain flexibility on deformation. The Flory equation[178] for f, *i.e.* the fraction of flexible chains in a macromolecule, was supplemented by parameter A, which describes the work of an external mechanical field required for stretching a macromolecule,

$$f = \frac{(z-2)\exp(-\varepsilon/kT - A)}{1 + (z-2)\exp(-\varepsilon/kT - A)}\,, \tag{1}$$

where z is the coordination number in the quasi-lattice model, ε is the difference between the free energies of the flexible and rigid macromolecule conformations, and $A = Fl/kT$ (F is the stretching force applied to a segment of length l). It was shown[177] that an isotropic solution can become anisotropic on imposing a mechanical field. This approach does not take into account the enhancement of the miscibility of components in the flow observed experimentally.

The authors of Ref. 127 analysed the latter two approximations. They used Eqn (1) under the condition that Fl is an increase in the free energy due to the translation of macromolecular segments with characteristic length l. In this case, the free energy of a system of semi-flexible chains in a flowing solution containing n_2 polymeric molecules and n_1 solvent molecules was written as:

$$\Delta G = kTn_2\left\{(x-1) - \ln\left(\frac{xz}{2}\right) + (x-2)[f\ln f + \right. \tag{2}$$
$$\left. + (1-f)\ln(1-f) - f\ln(z-2)]\right\} + n_2\{f(x-2)(\varepsilon + Fl)\} +$$
$$+ kT(n_1\ln\varphi_1 + n_2\ln\varphi_2 + \chi x n_2\varphi_1)\,,$$

where x is the number of segments of length l in the macromolecule. From Eqns (1) and (2), an equation was obtained for the free energy of mixing, ΔG. Using this equation, the chemical potentials of the components and the change in the free energy per mol of the polymer under flowing conditions were calculated

$$\Delta G_f = RT(x-2)\ln[(1-f)(z-1)]\,. \tag{3}$$

It was shown[127] that Eqn (3) for the calculation of a binodal can be solved only if, after phase separation, the chains in the concentrated phase are straightened to a larger extent than in the dilute phase. The approximation for accumulated energy was

analysed and the following expression for the energy of mixing of a flowing solution was obtained:

$$\Delta G_\gamma = RT\left\{N_1\ln\varphi_1 + N_2\ln\varphi_2 + \chi x N_2\varphi_1 - \right.$$

$$\left. -N_2\left[\ln\frac{x}{2} + \ln\frac{z}{z-1} + (x-1)\ln\left(\frac{z-1}{\mathrm{e}}\right)\right]\right\} + N_2 G_3\,,$$

where N_1 and N_2 are the mole numbers of the solvent and the polymer, respectively, G_s describes the free energy change due to stretching of one mole of macromolecules, and 'e' is the base of natural logarithms. It should be noted that the expressions for G_s presented in Ref. 127 were derived with account of the properties of the solution rather than of separate macromolecules. At $G_s' = G_s$ (the prime mark corresponds to the more concentrated phase), no displacement of the binodal should occur. It follows from the equation obtained in the same work

$$G_s' - G_s = RT(x-2)\ln\left(\frac{1-f'}{1-f}\right),$$

that the approximation of chain flexibility decrease is identical with the approximation of accumulated energy if G_s is interpreted as the free energy of the coil–stretched chain transition. In this case, the two-phase region broadens as the rigidity of macromolecules in the concentrated phase increases, and the binodal is shifted to higher temperatures with an increase in $(1-f)/(1-f')$; the critical concentration decreases in the flow, which is in accord with the experimental data.

The liquid phase separation of polymer solutions in a mechanical field has also been analysed theoretically in other papers.[143, 179–181]

2. Crystalline phase separation

One of the first studies dealing with crystallisation of polymers under deformation was carried out by Flory,[89] who derived the dependence between the melting point and the degree of stretching of a loosely cross-linked polymer

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \frac{R}{\Delta H_m}\left[\left(\frac{6}{\pi m}\right)^{1/2}\lambda - \frac{\lambda^2}{2m} - \frac{1}{\lambda m}\right], \qquad (4)$$

where T_m^0 is the equilibrium melting point of non-deformed polymer, ΔH_m is the heat of melting of one mole of statistical segments, m is the number of statistical segments between cross-linking points, and λ is the stretching ratio. At small λ, Eqn (4) gives overestimated melting point values, since it was derived with the assumption that crystals grow only along the direction of stretching.

Krigbaum and Roe[90] suggested the following relationship between the deformation and the melting point:

$$\frac{1}{T_m^0} - \frac{1}{T_m} = \left(\frac{R}{2\Delta H_m}\right)m\left[\lambda^2 + \frac{2}{\lambda} - 3\right].$$

This equation makes it possible to obtain equilibrium melting points for non-deformed specimens as well. However, as the authors themselves admit,[90] Eqn (4) gives a better fit of the experimental data over a broad range of λ values.

Flory[89] explains the increase in the melting point on stretching by a decrease in the polymer entropy by a value of the orientation entropy S_{or}. According to Yeh *et al.*,[85, 86] the increase in the rate and temperature of crystallisation in the flow occurs for the same reason. They compared the following equations:

(1) for the melting point

$$T_m = \frac{\Delta H_m}{\Delta S_m}\ \text{(under statical conditions)};\quad T_m = \frac{\Delta H_m}{\Delta S_m - |\Delta S_{or}|}$$

(under shearing conditions), where ΔH_m and ΔS_m are the specific enthalpy and entropy of melting and ΔS_{or} is the change in entropy caused by molecular orientation.

(2) for the nucleation rate N

$$\frac{N_{\gamma>0}}{N_{\gamma=0}} = \exp\left[-\frac{B}{RT}\left(\frac{1}{\Delta g} - \frac{1}{\Delta g + T|\Delta S_{or}|}\right)\right],$$

where Δg the free energy of nucleation and B is a constant.

It follows from the equations that an increase in the shearing rate, and hence $|\Delta S_{or}|$, increases the nucleation rate and the melting point. The decrease in polymer entropy due to the orientation of macromolecules in the flow has been calculated[126] for the polyethylene–xylene system according to the equation

$$|\Delta S_{or}| = \frac{\Delta S_m}{1 + T_m/\Delta T}.$$

The values of ΔS_{or} obtained are of the same order of magnitude as those reported for the polycaproamide–caprolactam system.[124] The dependence of S_{or} on the concentration has a maximum, which indicates that the dependence of the coefficient of molecular extension on the concentration, which depends on S_{or} according to the equation[84]

$$\alpha = 1 + A|\Delta S_{or}|\,,$$

where A is a constant for a particular system, also has an extremum. In fact, polymeric chains in dilute solutions are isolated and can change their conformations in the flow almost without interacting with each other, hence one should not expect a considerable effect of mechanical field on the phase behaviour of the system. As the polymer concentration increases, a fluctuation entanglement network, which does not yet hinder the orientation processes, is formed in solution. In this case, the interaction between the macromolecules is strong, which results in an increase in viscosity, and hydrodynamic field affects considerably the phase transition temperature. As the concentration is increased further, the network density increases, thus hindering the orientation processes. This diminishes the effect of mechanical field on phase transitions. The decrease in the molecular orientation due to the formation of a spatial network has been reported[96] for a polyethylene melt. The higher the shear rate, the lower concentration is required for the formation of a fluctuation entanglement network. Therefore, the maximum ΔS_{or} is reached at lower polymer concentrations.

V. Conclusion

Mechanical deformations (shearing, stretching) of polymer solutions lead to changes of the macromolecule conformations, their aggregation, and eventually to the phase separation of the systems. In some cases, on the contrary, the hydrodynamic field enhances the mutual solubility of the components. This is observed as a shift of boundary curves and depends largely on the difference in the surface energies of the components, σ_{12}. At $\sigma_{12} > 10^{-2}$ J m^{-2}, the miscibility of the components decreased in the flow and increased at $\sigma_{12} < 10^{-4}$ J m^{-2} (Table 3), because the energy of the mechanical field is sufficient for the destruction of the new phase nuclei at low σ_{12}.

For systems with crystalline phase separation, no enhancement of the solubility of the components under flowing conditions was observed. Mechanical stress leads only to an increase in the polymer melting point in melts and solutions. The increase in the melting point is caused by a decrease in the entropy of the system due to the uncoiling and orientation of the macromolecules. Systems with crystalline phase separation are more sensitive to mechanical stress than systems with liquid phase separation. Mechanical field even affects the crystallisation of low-molecular-weight compounds with molecular weights of *ca.* 10^2, and this effect becomes stronger as the molecular weight of the solute

Table 3. Values of σ_{12} and effect of shearing deformation on the mutual solubility of components.

System	$10^3\,\sigma_{12}$ /J m^{-2} (293 K)	Solubility in mechanical field
PS – dioctyl phthalate	12.6	decreases
PS – decalin	15.3	"
PS – cyclohexane	20.2	"
PMMA – butanol	30.5	"
PEO – water	32.0 (363 K)	"
DAC [a] – acetone – water	0.3	increases
PS – ethylcellulose – benzene	10^{-2}	"
PDMS [b] – ethyl methyl ketone	0.2	"

[a] DAC is cellulose diacetate; [b] PDMS is polydimethylsiloxane.

increases. In systems with liquid phase separation, the shearing field manifests itself as a change in the T_{ph} of solutions of polymers with molecular weights above 10^5.

The dependences of ΔT on shear rate (stress) contain maxima. This does not depend on the type of phase separation and is caused by the existence of two oppositely directed processes in the system: uncoiling of macromolecules and their orientation in the flow (which favours phase separation) and destruction of new phase nuclei by the mechanical field at high shear rates (which hinders phase separation). Fig. 6 gives examples of dependences of ΔT on γ for different systems.

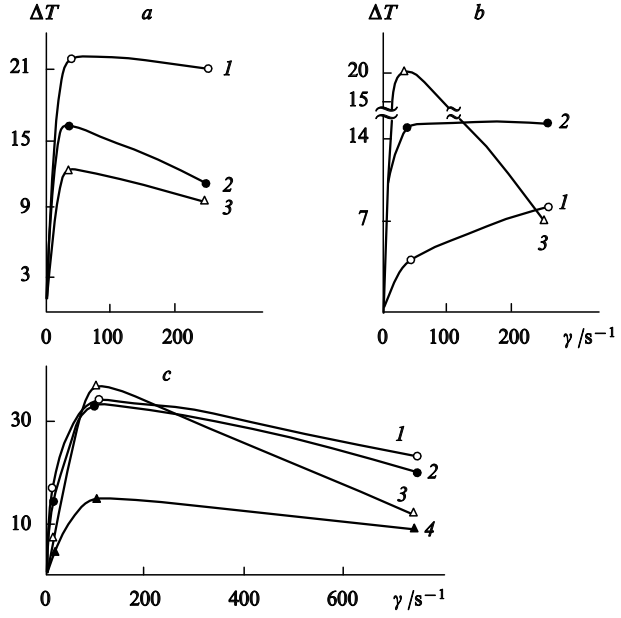


Figure 6. Dependence of ΔT on γ for various systems. (*a*) PEG ($\bar{M}_\eta$ = 800) – PPG ($\bar{M}_\eta$ = 3100): c_{PEG} /mass %: 1.1 (*1*), 3.51 (*2*), 5.42 (*3*); (*b*) PE ($\bar{M}_\eta = 2.3 \times 10^5$) – xylene: c_{PE} /mass %: 10.0 (*1*), 30.0 (*2*), 40.0 (*3*); (*c*) PS ($\bar{M}_\eta = 3.3 \times 10^6$) – di(2-ethylhexyl) phthalate: c_{PS} /g dl^{-1}: 7.01 (*1*), 4.60 (*2*), 2.83 (*3*), 1.00 (*4*).

The concentration dependence of the effect of hydrodynamic field on ΔT has an extremum (Fig. 7). The maximum effect is observed in moderately concentrated solutions. This is valid for liquid and crystalline phase separation as well as for gel formation and is a result of the extremal concentration dependence of normal stresses that appear in the flow.

An inversion of the effect of the mechanical field on the mutual solubility of the components as a function of the polymer concentration and molecular weight and the shearing rate has been observed for a number of systems with liquid phase separation.

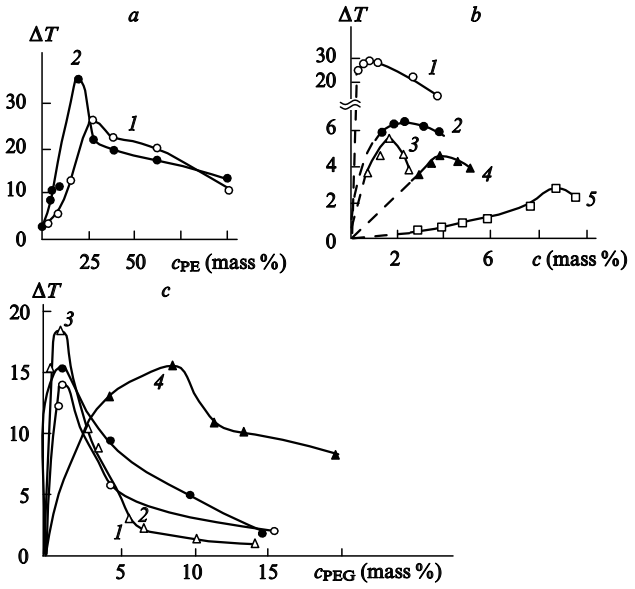


Figure 7. Concentration dependences of ΔT for different systems. (*a*) PE ($\bar{M}_\eta = 2.3 \times 10^5$) – xylene, γ = 47 (*1*) and 246 s^{-1} (*2*); (*b*) (*1*) PEO ($\bar{M}_\eta = 4.0 \times 10^4$) – water, $\gamma = 9.5 \times 10^3$ s^{-1}; (*2*) PS ($\bar{M}_\eta = 3.3 \times 10^6$) – di(2-ethylhexyl) phthalate, γ = 246 s^{-1}; (*3*) PMMA ($\bar{M}_\eta = 9.9 \times 10^4$) – butanol, $\gamma = 3 \times 10^4$ s^{-1}; (*4*) PS ($\bar{M}_\eta = 3.3 \times 10^6$) – cyclohexane, $\gamma = 2.1 \times 10^4$ s^{-1}; (*5*) cellulose acetate ($\bar{M}_\eta = 6.9 \times 10^4$) – acetone/water (1.6/1.0), γ = 170 s^{-1}; (*c*) PEG ($\bar{M}_\eta$ = 800) – PPG ($\bar{M}_\eta$ = 3100), γ = 248 (*1*) and 47 s^{-1} (*2*); PEG ($\bar{M}_\eta = 3.3 \times 10^4$) – glycerol/water (80/20), γ = 248 s^{-1} (*3*); PEG ($\bar{M}_\eta = 1.8 \times 10^3$) – glycerol/water (90/10), γ = 248 s^{-1} (*4*).

These data make it possible to suggest the following mechanism for the effect of shearing field on the phase separation of polymer solutions. In dilute solutions, polymeric chains are isolated and can change their conformations in the flow almost without interactions. When the thermodynamic quality of the solvent gets worse (due to temperature changes), macromolecules can form associates. However, these structures are unstable and are easily destroyed by a mechanical field, which leads to enhancement of the mutual solubility of the components in the flow, *i.e.* to the displacement of the binodal ($\Delta T < 0$ for systems with upper critical solution temperatures). As the polymer concentration is increased, a fluctuation entanglement network, which does not yet hinder orientation processes, is formed in solution. In this case, the interaction between the macromolecules is strong, the hydrodynamic field affects the temperature of phase separation, and $\Delta T > 0$. As the concentration is increased further, the network density increases, thus hindering the orientation processes. This diminishes the effect of mechanical field on phase transitions, hence ΔT decreases. An increase in the polymer molecular weight favours the formation of a fluctuation network, therefore the concentration at the inversion point c_i and the concentration at the maximum ΔT decrease as these parameters increase.

This review does not deal with the destruction of macromolecules that occurs in polymer solutions at very high deformation rate and stress, as this phenomenon has been analysed in sufficient detail elsewhere.[182–186]

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