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Phase equilibria and phase structures of polymer blends

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Abstract. Experimental, methodical and theoretical studies dealing with phase equilibria and phase structures of polymer blends are generalised. The general and specific features of the change in solubility of polymers with changes in the molecular mass and copolymer composition and upon the formation of three-dimensional cross-linked networks are described. The results of the effect of the prehistory on the phase structure and the non-equilibrium state of polymer blends are considered in detail. The bibliography includes 125 references.

I. Introduction

The problem of phase equilibria and phase structures of polymer systems is one of the central problems in physical chemistry of polymers. This problem combines surprisingly interests of fundamental science and requirements of practice, polymer materials science and technology of polymer processing, the thermodynamics of polymer solutions and blends, the kinetics of phase decomposition and structure formation. This field of science has been extensively studied, and each investigation concerned different aspects of this problem to a lesser or greater extent.

Studies of phase equilibria of polymers can be divided into two periods. The first period can be tentatively called the 'period of compatibility'. In studies of this period, phase structures of particular polymer composites prepared under certain blending conditions were examined by various methods (mechanical, relaxation, thermochemical and sorption). Based on these results, conclusions were drawn about the polymer compatibility or incompatibility without regard for the temperature and concentration conditions for the preparation of composites.[1–9]

The second period of studies is being continued. It can be called the period of 'phase diagrams'. In investigations of this period, particular attention is given not to estimation of the polymer compatibility based on indirect data,† but to the directed construction of phase diagrams in broad ranges of temperature, compositions and molecular weights of the components. A comparative analysis of the monographs and reviews of the first and second periods shows that phase diagrams of binary, ternary or multicomponent systems were reported in virtually all modern large studies dealing with the properties of polymer and oligomer blends.[11–15]

However, the available extensive experimental data, which have partially been surveyed in the monographs,[15,16] demonstrate that, in spite of obvious progress, many results concerning phase structures and phase diagrams are contradictory with respect to both compositions of co-existing phases and positions of critical points. Besides, radically different phase diagrams were obtained for a number of systems by different researchers with the use of various methods of investigation and procedures for the preparation of blends. For example, diagrams with an upper critical solution temperature (UCST), a lower critical solution temperature (LCST) or two critical temperatures were reported for the same systems in different studies.

The paradox of the situation in this area of physical chemistry of polymers is that some researchers ignore results inconsistent with their point of view, other researchers believe that discrepancies in the experimental results are associated with the specificity of the methods used, whereas yet other researchers explain the contradictory results in the context of particular theories of polymer solutions.[16–24]

In our opinion, investigations of polymer blends have now come to a new stage. The main aim of such investigations is to obtain balanced non-contradictory information on phase equilibria and thermodynamic parameters of polymer blending. We consider the published data on phase compositions and characteristics of polymer blends from this standpoint. A detailed analysis of all experimental results is beyond the scope of our brief review. We focussed our attention on the most prominent examples, analysed the reasons for the above-mentioned contradictions and made attempts to find ways of resolving these contradictions.

II. Methods of construction of phase diagrams

The classification of methods which are used or will be used for constructing phase diagrams (rather than for estimating compatibility between components of polymer systems or the phase composition of materials) should be based not on methods of measurement, as suggested in the studies,[7,16,23,25] but on phenomena occurring in the system under study in the course of

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† It should be noted that such studies are still published.[10]

measurements. Within the framework of this approach, all available and newly developed methods for the construction of phase diagrams can be divided into three groups.

Methods of determining critical points in the temperature–concentration field of polymer systems from the appearance and/or dissolution of particles of a dispersed phase of a particular nature belong to the first group. The second group includes methods associated with the determination of the compositions of co-existing phases. Calculation (semiempirical) methods for the construction of boundary lines in phase diagrams comprise the third group.

Two ways of performing experiments are used in the first group of methods. In one case, the composition of a solution, melt or blend remains constant throughout the experiment, and the figurative point (*A* in Fig. 1) moves along the temperature scale in response to changes in external conditions. In the second approach, phase decomposition or homogenisation of a polymer system initiated by forced changes in the composition of the system is performed under isothermal conditions. In this case, the figurative point of the system (*B* in Fig. 1) moves over the isotherm along the axis of compositions. It should be noted that in the first approach, measurements for a given composition are carried out continuously and the periodicity appears only on going from one composition of the system to another, whereas periodic measurements are almost always carried out in the second approach. This is associated with the procedure for changing the composition: a particular component is either additionally introduced into or removed from the mixture. In polymer–solvent or polymer(1)–polymer(2)–solvent systems, this is achieved by either dilution of the mixture or evaporation of a low-molecular-weight component.[1,8,26–28] In the case of polymer blends, all operations associated with the preparation (blending, pressing, thermal annealing, quenching) are carried out, but each time for blends of different compositions.[3,5,12] Evidently, to obtain reproducible results, particularly in the latter case, conditions under which components are mixed and samples for analysis are prepared should be rigorously constant, which is often impossible to achieve.

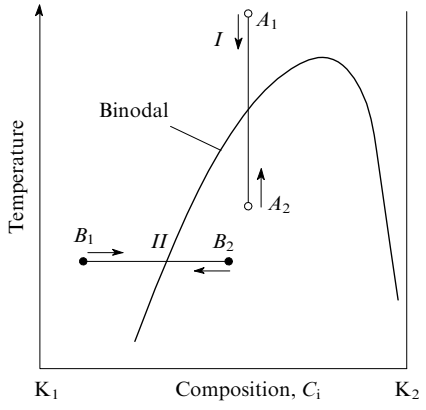


Figure 1. Scheme for performing experiments on the construction of phase diagrams (K_1 and K_2 are components of the system). Method *I*, the figurative point *A* moves along the temperature scale. Method *II*, the figurative point *B* moves along the composition axis.

In both approaches, the temperature $T_{ph.s}$ (at a given composition) or the composition $C_{ph.s}$ (at a given temperature), at which the phase state of the system changes, is determined from one of the chosen parameters (optical or electron density, intensity of light or neutron scattering, refractive index, thermal effect or changes in the local mobility of macromolecules and their fragments, labels, viscosity of the system as a whole, *etc.*). Particles of a dispersed phase either appear, if a true solution or melt is used as the starting system, or dissolve, if the starting state of the system corresponds to a heterogeneous region in the phase diagram.[29–37]

Methods belonging to the second group allow one to determine compositions of co-existing phases at different temperatures. These methods also employ different techniques for performing experiments. One of these techniques is based on interdiffusion. In this case, the phases of the starting components are brought into contact and then the character of the concentration distribution in the region of their spontaneous diffusion mixing is studied *in situ* by a particular local method.[38,39] Numerous experiments demonstrated[15,40–42] that there is a pronounced relationship between the character of the concentration distribution in the region of interdiffusion of semi-infinite phases and the phase diagram, which reflects the essence of processes of their spontaneous mixing. If phase conjugation is carried out at a temperature higher than UCST (or lower than LCST), $T > T_m$ or at a temperature higher than the isotropisation temperature, the formation of a concentration profile accompanied by a continuous change in the composition from one component to another is observed in the region of interdiffusion (Fig. 2 *a*).

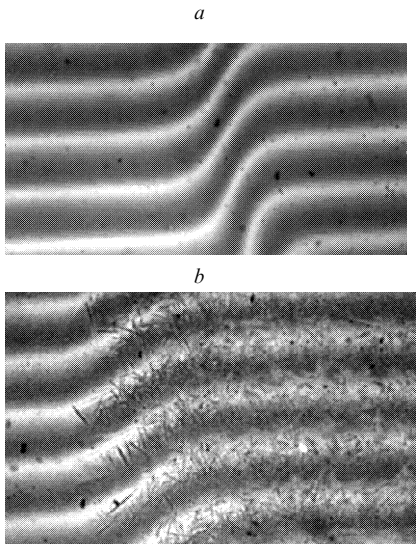


Figure 2. Concentration profiles of the CS ($M_w = 5.1 \times 10^4$)–PDMS ($M_w = 1.8 \times 10^3$) system above (*a*) and below (*b*) the isotropisation temperature of CS. The diffusion time is 4 min.[43]

If phase conjugation is performed at a temperature lower than UCST (or higher than LCST), $T < T_m$ or below the isotropisation temperature, the interface which separates the regions of diffusion mixing of components appears in the region of interdiffusion (Fig. 2 *b*). For systems with amorphous layering, these are regions of true solutions (to the right and left of the binodal curve) but with a variable composition. For crystalline or liquid-crystalline equilibrium systems,‡ these are the region of solutions to the left of the liquidus line in phase diagrams and the region of dissolution of an amorphous component in an amorphous phase of a crystalline or liquid-crystalline component (region below the liquidus line).

In all cases, the concentrations of solutions corresponding to compositions of co-existing phases are established on each side of the interface. Therefore, information required for the construction of phase diagrams can be obtained by performing interdiffusion at different temperatures and determining the compositions of co-existing phases in each experiment.

‡ In our review, we restrict ourselves to the consideration of thermotropic liquid-crystalline systems. Phase equilibria for lyotropic liquid-crystalline systems have been described in sufficient detail in the monograph.[44]

It should be borne in mind that in systems characterised by rather high diffusion mobility of components ($10^{-10} < D < 10^{-5}$ cm^2 s^{-1}), the above-described measurements are carried out *in situ*, which enables one to obtain phase diagrams on modern diffusiometers [45] within very short periods of time.

For systems characterised by low translational mobility of components ($D < 10^{-10}$ cm^2 s^{-1}), steps of formation of the diffusion zone and studies of the concentration distribution in this zone are, as a rule, separated in temperature and time. For example, interdiffusion in such systems [most often, these are polymer(1) – polymer(2) systems] is generally carried out at high temperatures ($T \geqslant T_g + 50°$; T_g is the glass transition temperature) over a long period of time. This process is followed by quenching of the gradient structure, the preparation of a sample and investigation of the concentration profile. If these conditions are met, the measured concentration profiles and the compositions of co-existing phases should be assigned to the annealing temperature of the system under study.

Another method of performing experiments involves an examination of swelling. In the practice of investigation of phase equilibria, this method is named the 'method of limited swelling' [25] and is recommended for determining the right branch of the binodal.[28] However, the traditional version (weight or volumetric determination of the equilibrium degree of swelling [1] followed by the calculation of the composition of the sample) of this method can be used only in the case of strictly limited swelling, *i.e.*, when the left branch of the diagram is actually absent. Apparently, this requires not only special preliminary measurements of the kinetics of polymer swelling but also the simultaneous determination of the composition of the liquid in which swelling occurs. These measurements can be used for the construction of a fragment of the binodal curve only if the composition of the liquid remains unchanged in the course of swelling. One must verify experimentally that the degree of swelling determined for the same sample is reproduced when moving along the temperature axis. In all other cases, this method can be recommended only as a preliminary step.

The third group of methods involves semiempirical calculation methods. These methods are based not on direct experimental data on phase decomposition of systems but on concentration dependences of the thermodynamic characteristics of solutions, whose extrapolation provides estimates of the positions of binodal or spinodal curves. Methods of measuring excess light scattering,[23] calculations of the thermodynamic correction $(\partial \ln a_i / \partial \ln \varphi_i$, where a_i are the activities of components, φ_i are their bulk concentrations) in experiments on self-diffusion and interdiffusion [31, 46, 47] or evaluation of the effective parameter of interaction from the results of inverse gas chromatography [1, 48] are used most extensively.

Most of the above-mentioned methods in combination with differential scanning calorimetry,[24, 49] static sorption,[50] relaxation spectroscopy,[51, 52] X-ray microanalysis,[39] electronic and atomic force microscopy [53] or photoelectron spectroscopy [54] are used for studying phase structures and compositions of polymer blends. The specificity of these studies is associated not with the organisation of experiments or interpretation of the results but with the determination of the position of the figurative point for the sample under investigation in the temperature – concentration field of the phase diagram.

As an example, we refer to the results of structural – morphological studies of blends of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) prepared according to different methods: using a common solvent, polymerisation of methyl methacrylate in PVC, extrusion and pressing.[55, 56] It should be noted that investigations of the phase structures of these materials were carried out either at room temperature (static sorption of tetrahydrofuran and X-ray microanalysis) or using continuous heating to determine the glass transition temperatures and rheological parameters at temperatures higher than their flow temperatures. The results of measurements for this system are summarised in Fig. 3 (ω is the weight concentration) as isoconcentration lines in the temperature – concentration field of the phase diagram, because the assignment to temperatures is ambiguous. All these lines are located in a heterogeneous metastable or labile region of the diagrams,[58] and the compositions of co-existing phases measured for these blends (in the study,[57] these lines are called the compatibility boundaries) differ substantially from equilibrium values. Evidently, these structures are unstable in spite of the fact that the free energies of mixing (to be more precise, the free energies of formation of the phase structure) for some of these structures have negative values, and heating to temperatures higher than the glass transition temperature leads to secondary phase decomposition accompanied by changes in the composition of co-existing phases and their dispersion characteristics.

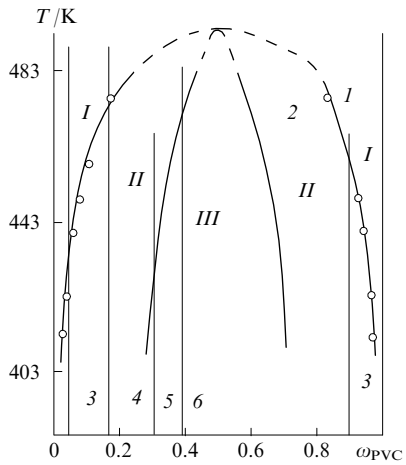


Figure 3. Phase diagram of the PVC – PMMA system.
(*1*) Binodal, (*2*) spinodal; vertical lines correspond to the compatibility limits for blends prepared by different methods: extrusion (*3*), pressing (*4*), using a common solvent (*5*), polymerisation of methyl methacrylate in PVC (*6*);[50, 57 – 59]
(*I*, single-phase solution; *II*, metastable region; *III*, region of labile solutions.)

We are sure that structural methods can also be used for the construction of phase diagrams, if special studies confirming the reversibility and equilibrium of the compositions of co-existing phases determined by a particular method are carried out and the phase transition temperature is identified.

III. State-of-the-art studies of phase equilibria

As mentioned above, the characteristic feature of the state-of-the-art studies of polymer blends is that researchers seek to obtain balanced non-contradictory data on phase equilibria and phase structures. When solving this problem, it is necessary to take into account the following facts:

— different research teams obtain experimentally reliable and adequate information on phase structures and properties of polymer blends using various methods;

— interpretation of the results is the subjective opinion of researchers, and different conclusions can be drawn based on the same experimental data;

— analysis of phase equilibria should be uniform [§] for all regions of phase diagrams and for all possible types of phase equilibria rather than being restricted to particular fragments of boundary curves (sometimes, of an unidentified phase nature);

§ Taking into account the temperature and concentration dependences, for example, for pair interaction parameters, the effect of the molecular mass, the composition of a copolymer, *etc*.

— experimental information on the phase state of particular polymer blends carries, among other things, information on the thermal prehistory of blends, conditions of preparation, thermal stability and reactivities of the components.

Polymer systems with amorphous layering are, as a rule, characterised by the following features.

1. An increase in the molecular mass (MM) of one of the components in systems with UCST generally leads to an increase in the critical temperature, extension of the two-phase region and a shift of the critical point in accordance with the Flory – Huggins theory (Fig. 4 – 6). Recall that the dependence of the solubility of polymers and oligomers on their MM (Fig. 7) served as the starting information for the development of the concept of segmental solubility of polymers in interface layers.[5] In the studies,[14, 42, 60] the dependence of the solubility on the molecular weight at a constant temperature was demonstrated to be described by linear equations on the $\varphi - (1/M)$ coordinates in a broad MM range (Figs 8, 9). These equations, in turn, can be used for the determination of critical molecular masses and compositions.

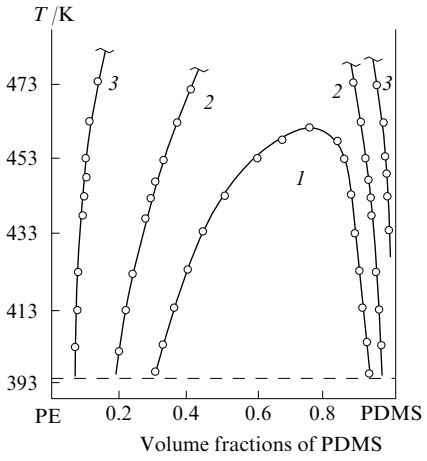


Figure 4. Phase diagrams[60] of the PE (5×10^3) – PDMS system. (Hereinafter, M_n are given in parentheses)
Molecular masses of PDMS: (*1*) 310; (*2*) 400; (*3*) 1200.

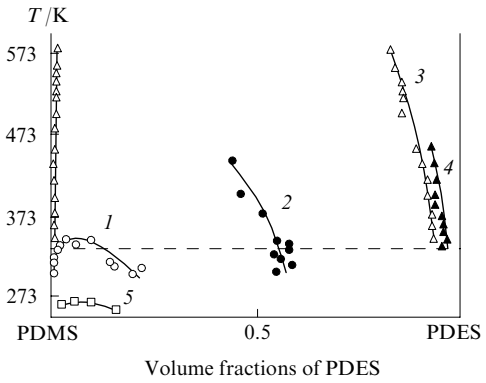


Figure 5. Phase diagrams of the polydiethylsiloxane (PDES) (3×10^5) – PDMS systems.
Molecular masses of PDMS: (*1*) 1×10^3, (*2*) 2.5×10^3, (*3*) 5.5×10^3, (*4*) 8.1×10^3 (see Ref. 42), (*5*) 1×10^3 (see Ref. 61).

Systems with LCST (Fig. 10) are characterised by somewhat different features. For these systems, an increase in the molecular mass leads to a decrease in the critical temperature, extension of the two-phase region and a shift of the critical point toward a higher-molecular-mass component.

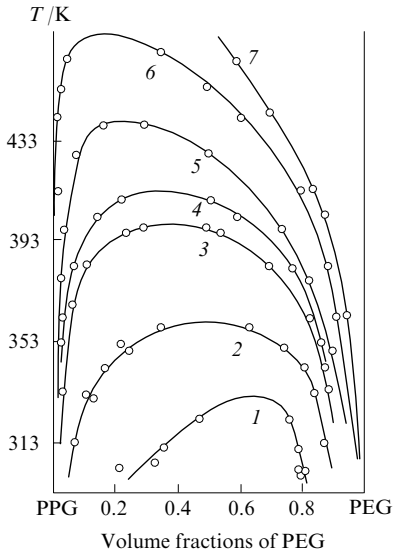


Figure 6. Phase diagram of the PPG (1×10^3) – PEG systems with different molecular masses.[15]
Molecular masses of PEG: (*1*) 600, (*2*) 1000, (*3*) 3000, (*4*) 4000, (*5*) 6000, (*6*) 15000.

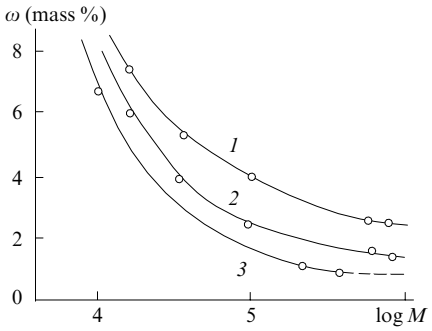


Figure 7. Solubilities of PS in PMMA (*1*, *3*)[5, 62] and PMMA in PS (*2*)[62] as functions of the molecular mass of PMMA.

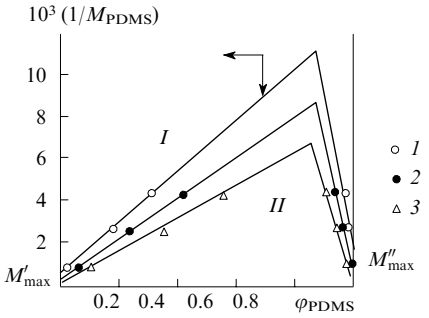


Figure 8. Isothermal sections of binodals on the $\varphi - (1/M)$ coordinates for the PE – PDMS systems at 398 (*1*), 428 (*2*) and 453 K (*3*) (*I*, one-phase region; *II*, two-phase region).[60]

2. For blends of statistical copolymers with homopolymers, the influence of the change in the molecular mass is consistent with the above-described effects. A change in the composition of a copolymer (in the case of constant molecular masses of the components) fulfils the following unified rule: the closer is the composition of the copolymer to that of the homopolymer (which is identical to a decrease in the difference in the solubility parameters of the copolymer and homopolymer), the lower is the

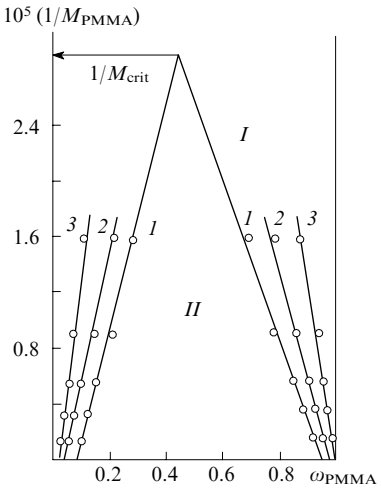


Figure 9. Isothermal sections of binodals on the $\omega-(1/M)$ coordinates for the PVC–PMMA systems at 473 (*1*), 453 (*2*) and 433 K (*3*) (*I*, one-phase region; *II*, two-phase region).[58]

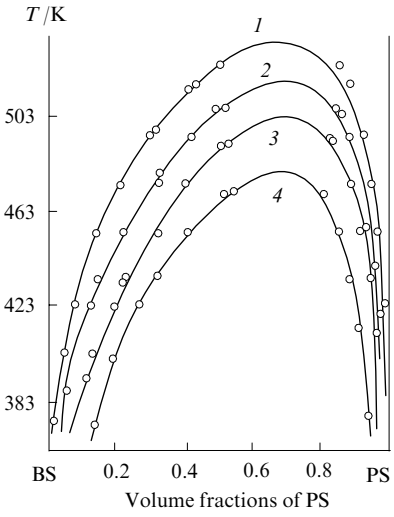


Figure 11. Phase diagrams of the PS (7.7×10^3) – BS (1.8×10^5) systems.[15] The composition of the copolymer [number of styrene units (%)]: (*1*) BS-25, (*2*) BS-65, (*3*) BS-75, (*4*) BS-85.

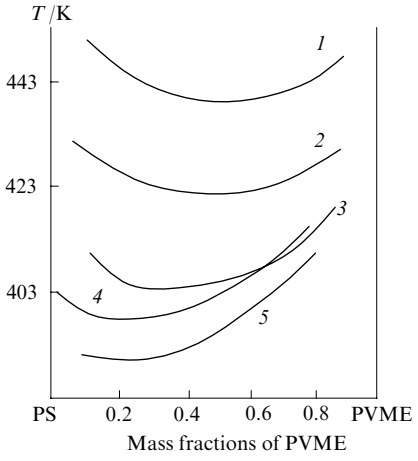


Figure 10. Phase diagrams of the PS – PVME (5.4×10^4) systems.[63] Molecular masses of PS: (*1*) 2×10^4, (*2*) 3.57×10^4, (*3*) 6.7×10^4, (*4*) 10.6×10^4; (*5*) 23.3×10^4.

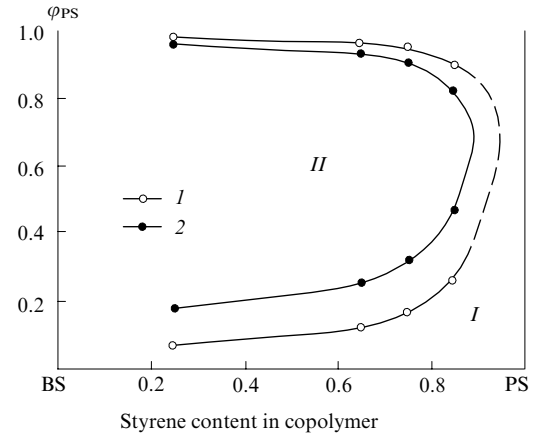


Figure 12. Isothermal sections of binodals of the PS – BS system at 423 (*1*) and 463 K (*2*) depending on the composition of the copolymer (*I*, one-phase region; *II*, two-phase region).

critical temperature of mixing (for systems with UCST) and the smaller is the region of the heterogeneous state, *i.e.*, the binodal curve as a whole is shifted downward along the temperature axis with retention of the position of the critical point. An example is a system of polystyrene (PS) and butadiene–styrene random copolymers (BS) (Fig. 11). It should be noted that the construction of isothermal sections of binodal curves allows one (as can be seen from Fig. 12) to determine the critical compositions of copolymers and the critical concentration of a blend containing components with particular molecular masses at a particular temperature. For example, in the PS–BS system with MM $\approx10^5$, the critical composition of the copolymer above which the system is compatible corresponds to 90 mass % and 95 mass % of polystyrene units in the copolymer chain at 463 and 423 K, respectively.

3. The formation of a three-dimensional cross-linked network in one of the components leads to extension of the two-phase region, a shift of the branch of the binodal curve corresponding to solubility of the sol fraction toward the axis of the linear homopolymer (and its degeneration at high degrees of conversion) and location of UCST in the region of thermal destruction of the material.[64,65]

It should be noted that a series of systems described in the literature are not characterised by the above features. For example, the solubility in the PMMA–poly(ethylene glycol) (PEG) system (Fig. 13), unlike that in poly(propylene glycol) (PPG) (Fig. 14), increases with increasing molecular mass of PEG in spite of the fact that the former system has UCST. At MM (PEG) $>3\times10^3$, UCST is lower than the melting point of PEG, and the dome of the binodal is located under the liquidus line of high-molecular-mass PEG. In this case, the position of the critical point, as expected, is shifted to the middle of the composition region. It should be noted that a phase diagram reported in the studies[22,67] for the same system but with another ratio between the molecular weights of the components has both a binodal and a liquidus line (Fig. 15). This behaviour is not specific to the above systems. Analogous results were obtained in the studies[14,68,69] for the following systems: butadiene–acrylonitrile random copolymers (BAN) and acrylated oligoesters (AOE), PVC–AOE and polyethylene (PE)–saturated alcohols, respectively. For these systems, unusual dependences of isothermal sections of phase diagrams on the molecular masses of the components were obtained. As can be seen from Fig. 16, the polyisoprene (PI)–acrylated oligoester system is completely compatible if the number of methylene groups (*n*) in the hydrocarbon frag-

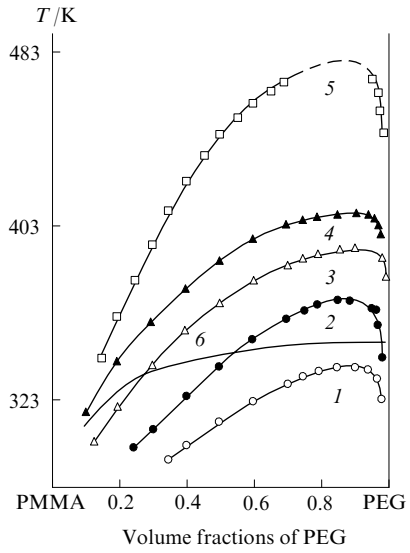


Figure 13. Phase diagrams [66] of the PMMA (2×10^5) – PEG systems: (*1*) PEG-600, (*2*) PEG-400, (*3*) tetraethylene glycol, (*4*) triethylene glycol, (*5*) ethylene glycol, (*6*) liquidus line for PEG (2×10^4).

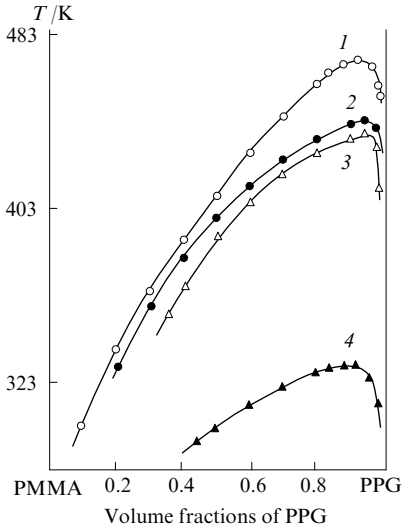


Figure 14. Phase diagrams [66] of the PMMA (2×10^5) – PPG system with different molecular masses.
Molecular masses of PPG: (*1*) 2025, (*2*) 1200, (*3*) 1025, (*4*) 425.

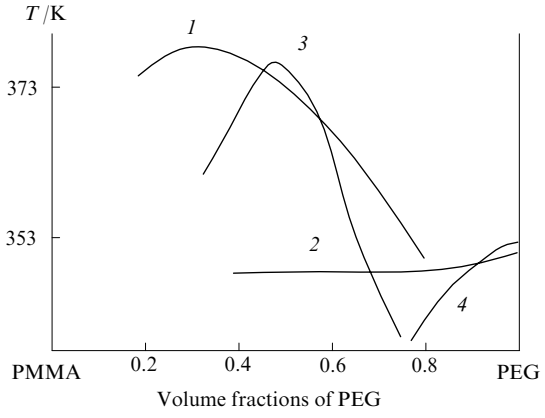


Figure 15. Phase diagrams of the PMMA – PEG system.
(*1*, *3*) Binodal curves, (*2*, *4*) liquidus lines. Curves (*1*, *2*),[22] curves (*3*, *4*).[67]

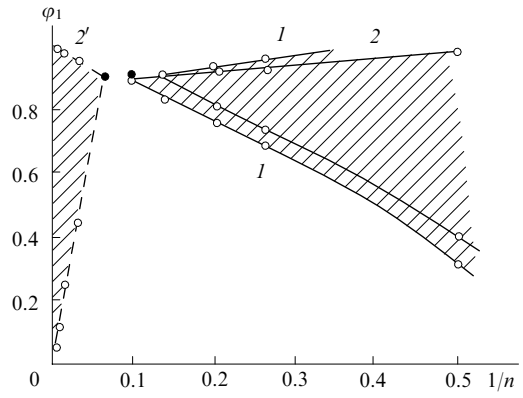


Figure 16. Isothermal sections of binodals [70] for the *cis*-PI – *p*-methylene dimethacrylate (*1*, *2*) and *cis*-PI – low-molecular-mass PE (*2′*) systems at 313 (*1*) and 323 K (*2*, *2′*) (φ_1 is the solubility of the low-molecular-mass component). Black points indicate UCST calculated according to Eqn (1).

ment is 10, whereas this system is only partially compatible at $n > 15$. This effect should be related to the influence of the terminal groups on the solubility parameter of oligomers.

Other examples of the anomalous behaviour of polymer – polymer systems are substantial differences in UCST (Fig. 17) with retention of the critical concentration, the presence of two critical temperatures in the same temperature – concentration region [PVC – PMMA, Fig. 18; poly(vinyl methyl ether) (PVME) – PS, Figs 10 and 19; PE – polyisobutylene melt],[60, 73] substantial differences in the shape of the binodal curve in the vicinity of the critical temperature (PS – PI) [74, 75] and independence of the critical concentration of the molecular mass of the components with retention of the usual dependence of the critical temperature in the polycarbonate (PC) – epoxide oligomer (EO) systems (Fig. 20).[76]

The results of studies of polymer systems containing crystallisable components are also often contradictory. Generally, liquidus curves for polymer – solvent systems obtained by different researchers by various experimental methods are identical or close to each other,[77, 78] the melting point depressions being in satisfactory quantitative agreement in a broad composition range for a homologous series of solvents (Fig. 21),[79] whereas there is no

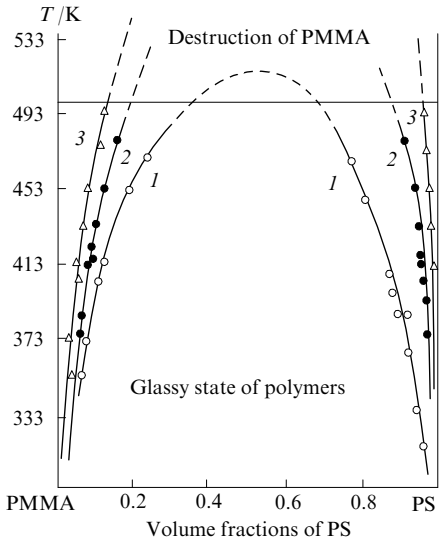


Figure 17. Phase diagrams of the PMMA – PS (800) system.[15]
Molecular masses of PMMA: (*1*) 1.5×10^3, (*2*) 3.3×10^4, (*3*) 8.9×10^4.

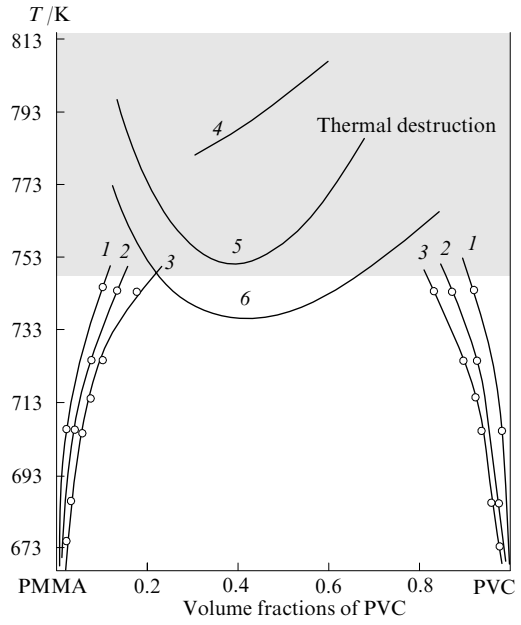


Figure 18. Phase diagrams of the PVC – PMMA system with the following molecular masses: $1.4 \times 10^5 - 7.3 \times 10^5$ (*1*), $1.4 \times 10^5 - 3 \times 10^5$ (*2*), $1.4 \times 10^5 - 1.9 \times 10^5$ (*3*), $1.6 \times 10^4 - 8 \times 10^4$ (*4*), $5.5 \times 10^4 - 8 \times 10^4$ (*5*), $5.5 \times 10^4 - 6 \times 10^4$ (*6*). Curves (*1–3*),[55] (*4–6*).[71]

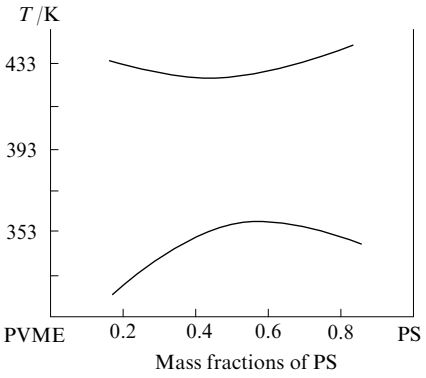


Figure 19. Phase diagrams of the PS (3.7×10^4) – PVME (4.6×10^4) system.[72]

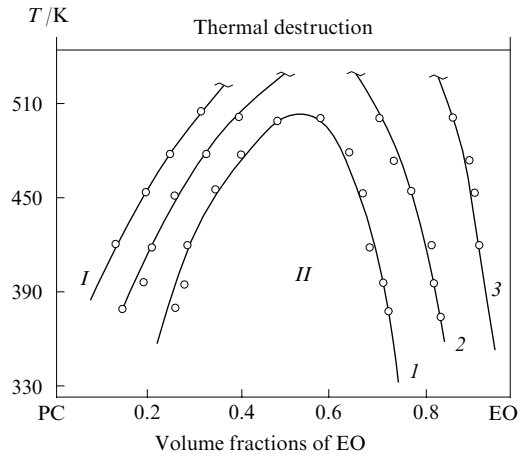


Figure 20. Phase diagrams of the PC – EO system.[76]
Molecular masses of EO: (*1*) 380, (*2*) 600, (*3*) 2750 (*I*, one-phase region; *II*, two-phase region).

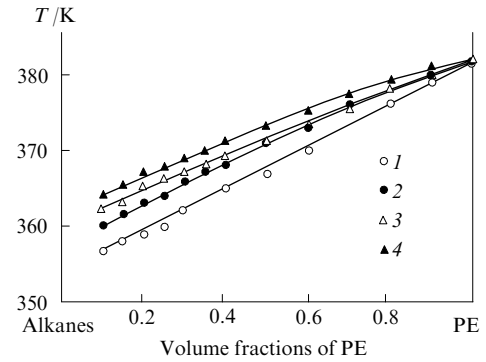


Figure 21. Melting point depressions of PE (3×10^4) in the presence of alkanes: heptane (*1*), decane (*2*), tridecane (*3*), hexadecane (*4*).[79]

quantitative agreement between the melting point depressions for polymer – polymer systems even if extrapolations to the equilibrium melting temperatures are used.[24, 80–82] Unfortunately, the preliminary experimental data on liquidus curves rather than equilibrium melting temperatures were reported in most studies.[24] Besides, the results of these measurements were often considered as the most suitable data for calculations of pair interaction parameters (χ) of the components.[83, 84]

Fragments of the diagrams for crystalline equilibrium in the PMMA – PEG system are shown in Fig. 22. It can be seen that the melting point decreases in all cases, which is consistent with the general thermodynamic relations.[85, 86] However, different researchers reported substantially different melting point depressions. For example, it was found [67] that a change in the composition by 20% led to depression of 10 – 15 K, whereas this value was estimated at 1 – 5 K in the studies.[22, 87, 88] The estimates of χ obtained from these data in the context of the approach proposed by Nishi and Wang [84] demonstrate a scatter from -5.0 to -0.5, which cannot evidently be ignored.

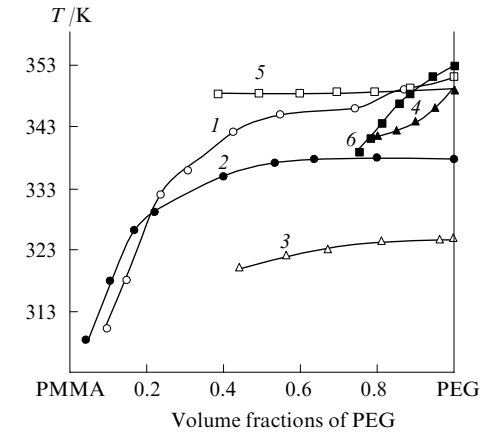


Figure 22. Curves of melting point depressions for PEG in a mixture with PMMA according to the results obtained by different researchers: (*1*, *2*),[88] (*3*),[87] (*4*),[89] (*5*),[22] (*6*).[67]

The same problems arise in the analysis of data on liquid-crystalline equilibrium in blends of thermotropic polymers. Data on blends of polydimethylsiloxane (PDMS) and cyclolinear siloxanes (CS) [40] are exemplified in Fig. 23. Interestingly, the isotropisation temperature depression (ΔT_{iso}) is substantially larger than the melting point depression (ΔT_m). In the system presented in Fig. 23, $\Delta T_m \approx 5^\circ$, whereas $\Delta T_{iso} \approx 30^\circ$ at the same concentration of amorphous PDMS.

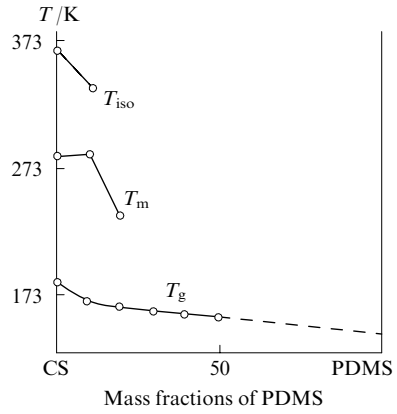


Figure 23. Phase diagram of the CS (4.4×10^4) – PDMS (600) system.[40]

The equilibrium in the poly(butylene terephthalate) (PBTF) – liquid cristalline polyether (PET) system belongs to complex equilibria (Fig. 24)[41] involving liquid-crystalline components, which undergo the mesomorphic transition. The problem of the equilibrium mesomorphic transition was virtually not discussed, *i.e.*, it was implicitly assumed that the mesomorphic component passes completely into a liquid-crystalline phase. However, this assumption requires structural validation.

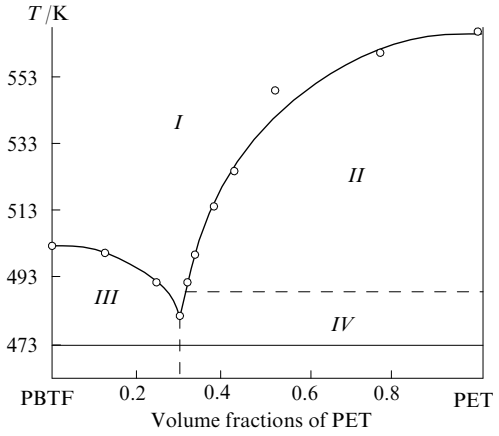


Figure 24. Phase diagram of the PBTF – PET system.[41]
(*I*) Region of isotropic solutions, (*II*) region of the liquid-crystalline state of PET, (*III* and *IV*) regions of the crystalline state of PBTF and PET, respectively.

Since all the above-described diversity in the phase behaviour of polymer blends seems to be a rule rather than the exception, the questions arise of whether it is possible to obtain a balanced general picture of phase equilibria in the context of the physico-chemical concepts and which parameters and/or conditions should be additionally used to obtain information on equilibrium and non-equilibrium states of the compositions of co-existing phases.

IV. Theoretical analysis

Although there are several theories of polymer solutions, we believe that it is possible to use the simplest and most widely accepted one, *viz.*, the classical version of the Flory – Huggins theory,[90] for several reasons. First, it was demonstrated[6,12] that the predictive ability of this theory is no worse than that of the new Flory theory, the Prigogine – Patterson theory, the Sanchez – Lacombe theory and the new Huggins theory. Second, the basic concepts of this theory are simple and evident. Third, we are sure that this theory has a high undisclosed potential.

Recall that the Flory – Huggins theory, as applied to polymer – polymer systems, gives the following expressions[91–93] for the free energy of mixing ¶

$$\Delta G_m = RT\left[\frac{\varphi_1 \ln(\varphi_1)}{r_1} + \frac{\varphi_2 \ln(\varphi_2)}{r_2} + \chi\varphi_1\varphi_2\right],$$

the chemical potentials of components

$$\Delta\mu_1 = RT\left[\frac{\ln(\varphi_1)}{r_1} + \left(\frac{1}{r_1} - \frac{1}{r_2}\right)\varphi_2 + \chi\varphi_2^2\right],$$

$$\Delta\mu_2 = RT\left[\frac{\ln(\varphi_2)}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1}\right)\varphi_1 + \chi\varphi_1^2\right],$$

the parameters of critical points

$$\chi_{crit} = \frac{1}{2}\left(\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right)^2,$$

$$\varphi_{2,crit} = \frac{\sqrt{r_1}}{\sqrt{r_1} + \sqrt{r_2}}, \qquad (1)$$

the spinodal concentration

$$\frac{1}{r_1\varphi_{1,s}} + \frac{1}{r_2\varphi_{2,s}} - 2\chi = 0,$$

the melting point depression[77,84]

$$\Delta T_m = \frac{\Delta\mu_{2,cr} T_m^\circ}{\Delta H_m}$$

and the isotropisation temperature depression[94]

$$\Delta T_{iso} = \frac{\Delta\mu_{2,meso} T_{meso}^\circ}{\Delta H_{meso}},$$

where ΔG_m is the molar free energy of mixing, φ_1 and φ_2 are the volume concentrations of the components, r_1 and r_2 are the ratios of the molar volumes to the reference volume, which are approximately equal to the degrees of polymerisation of the components, χ is the pair interaction parameter, $\Delta\mu_1$ and $\Delta\mu_2$ are the chemical potentials of the components in the amorphous state, χ_{crit} and $\varphi_{2,crit}$ are the parameters of the critical point, $\varphi_{1,s}$ and $\varphi_{2,s}$ are the spinodal concentrations, ΔT_m is the melting point depression, T_m° is the melting point of a pure component, ΔH_m is the enthalpy of melting, $\Delta\mu_{2,cr}$ is the chemical potential of the crystallisable component in the crystalline state, ΔT_{iso} is the isotropisation temperature depression, T_{iso}° is the isotropisation temperature of a pure component, ΔH_{meso} is the enthalpy of the mesomorphic transition and $\Delta\mu_{2,meso}$ is the chemical potential of a component in the liquid-crystalline state.

The following conclusions can be drawn from these equations:

— the isotropisation temperature depression is larger than the melting point depression $\Delta T_{iso} = \Delta T_m \Delta H_m / \Delta H_{meso}$ in the case of equal chemical potentials and phase transition temperatures of a pure component;

— the position of the critical point is always determined by the molecular mass ratio; hence, if the molecular mass of one component is known, the mass of another component can be calculated from the experimentally determined positions of critical points;

¶ All thermodynamic potentials are excessive with respect to the standard state (pure components).

— this theory allows one to analyse the region of true solutions from the viewpoint of the existence of concentration fluctuations, which are considered as clusters by Zimm and Lundberg:[95–97]

$$\frac{G_{11}}{v_1} = -(1-\varphi_1)\left[\frac{\partial(a_1/\varphi_1)}{\partial a_1}\right] - 1\,,$$

$$\frac{G_{11}}{v_1} = \frac{1}{\varphi_1}\left[\frac{1}{\varphi_1(1/r_1\varphi_1 + 1/r_2\varphi_2 - 2\chi)} - 1\right],$$

$$N_c = \frac{\varphi_1 G_{11}}{v_1} + 1 = \frac{1}{\varphi_1(1/r_1\varphi_1 + 1/r_2\varphi_2 - 2\chi)},$$

where G_{11}/v_1 is the integral of clusterisation and N_c is the number of molecules in the cluster.

It can be seen that the integral of clusterisation is determined by the distance to the spinodal curve. Hence, traditional phase diagrams can be supplemented with regions in the vicinity of binodal curves, where the appearance of heterophase fluctuations and cluster structures would be expected.[98] The results of NMR spectroscopy using pulsed gradient magnetic field (Fig. 25)[32] provide direct evidence for the existence of such heterophase fluctuations and cluster structures.

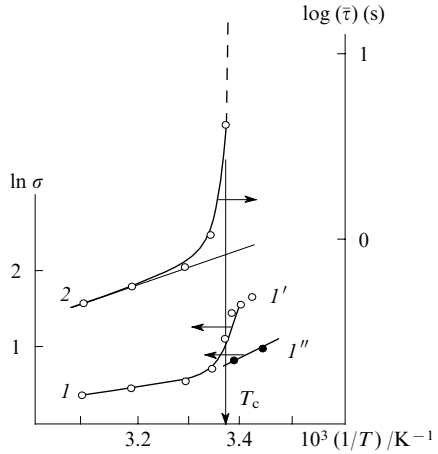


Figure 25. Temperature dependences of the spectral width (σ), the self-diffusion coefficients (*1*, *1′*, *1″*) and the average lifetime ($\bar{\tau}$) of macromolecular associates (*2*) in the PS – cyclohexane system.[32] $\varphi_{PS} = 0.15$; (*1′*) microlayering, (*1″*) macrolayering of the system.

Phase diagrams not only contain information on temperature – concentration regions of co-existence of phases, miscibility of components and the ratio between the dispersed phase and dispersion medium but also enable one to obtain information on the thermodynamic parameters of interaction, in particular, on the pair interaction parameter.

Figure 26 exemplifies the temperature dependence of the parameter χ for the PMMA – PEG system. It can be seen that χ for systems characterised by one critical temperature (UCST or LCST) depends linearly on $1/T$. Consequently, χ can be divided into the enthalpy (χ_H) and entropy (χ_S) components,[99] and the critical temperature can be estimated by extrapolating to χ_{crit}. For systems possessing two critical temperatures, the dependence takes the form shown in Fig. 27. For these systems, both critical temperatures (Fig. 28) can be estimated by extrapolating χ to χ_{crit}.

The thermodynamic parameters of mixing determined from analysis of complex equilibria should be characterised by similar dependences on the concentration, temperature and molecular mass. If the boundary curves of different types intersect at a single point (see, for example, Figs 15 and 22), the thermodynamic parameters should be equal in magnitude. In many cases, this condition is not fulfilled. For example, according to the results of

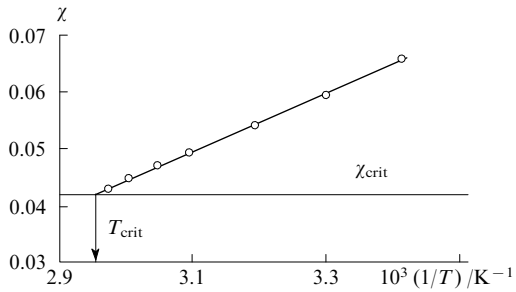


Figure 26. Plot of the pair interaction parameter *vs.* the inverse temperature for the PMMA (2×10^5) – PEG-600 system. (The phase diagram of this system is shown in Fig. 13.)

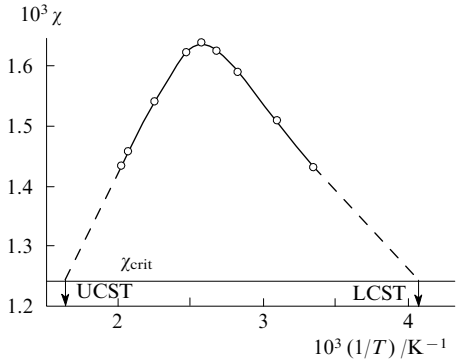


Figure 27. Plot of the pair interaction parameter[100] *vs.* the inverse temperature for the PCP (1.2×10^5) – BAN-26 (2.3×10^5) system.

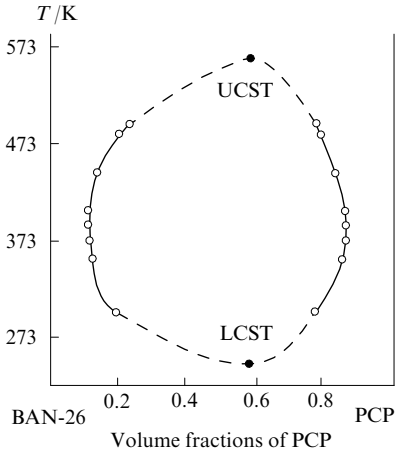


Figure 28. Phase diagram[100] of the BAN-26 (2.3×10^5) – PCP (1.2×10^5) system; UCST and LCST are extrapolated.

the study,[22] the parameter χ for the PMMA – PEG system, which was calculated from the crystalline equilibrium state at the point of tangency of the binodal and liquidus curves, is -0.584, whereas, according to the results of another study,[67] this parameter for the same system at the same tangency point is -4.97. At the same point, the parameters χ calculated from the data on amorphous equilibrium are 2.7×10^{-4} and 2.5×10^{-4}, respectively. Evidently, these facts require a more thorough thermodynamic and structural analysis.

In the study,[60] it was demonstrated that the phase behaviour of a polymer system can be predicted based not only on the pair interaction parameter but also on the solubility parameters of components (δ_1 and δ_2), which are related to χ by the following equation

$$\chi = \frac{z\Delta\omega_{12}}{kT} = \frac{z(\delta_1 - \delta_2)^2}{kT}, \qquad (2)$$

where z is the coordination number of the system and $\Delta\omega_{12}$ is the exchange energy.

The positions of the boundary curves of the miscibility region of a particular polymeric component and any other component can be calculated according to Eqn (2). For PMMA and a PE melt, these regions are presented in Figs 29 and 30, respectively. As can be seen from these figures, the higher is the molecular mass of the component, the smaller is the hypothetical region of mutual compatibility of this component and other components, which agrees with the Flory – Huggins theory.

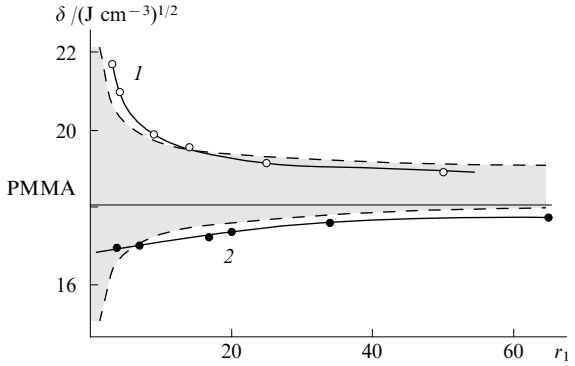


Figure 29. Plots of the solubility parameters of PEG (*1*) and PPG (*2*) *vs.* the degree of polymerisation (r_1) of oligoglycol.[88] The region of compatibility with PMMA is shaded.

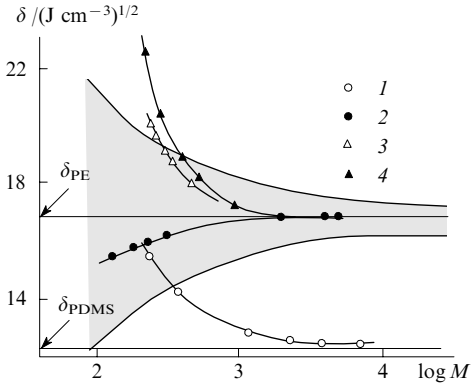


Figure 30. Plots of the solubility parameters of PDMS (*1*), saturated hydrocarbons (*2*), *p*-methylene dimethacrylates (*3*) and phthalic esters (*4*) *vs.* their molecular masses. The region of complete compatibility of oligomers with polyethylene is shaded.[60]

The position of the figurative point of the second component, which is determined by the degree of its polymerisation, the solubility parameter and the nature of the terminal groups and monomer units, shows how the compatibility between components changes with the molecular mass. This representation of the data on miscibility enables one to reveal the influence of the terminal groups, which generally differ in nature from monomer units, and, correspondingly, differ in the local solubility parameter, on the compatibility between components. As the molecular mass increases, this influence decreases and the trajectory of motion of the figurative point of the second component on the $\delta - \log M$ coordinates becomes flatter.

Let us consider the trajectories of motion of the figurative points for PEG and PPG (Fig. 29) in more detail. As the molecular mass of PEG increases, its figurative point goes from the two-phase region into the one-phase region and then again passes into the two-phase region at very high MM ($\sim 100\,000$). For PPG, the situation is simpler and more traditional: the figurative point is initially located in the one-phase region and then leaves this region and moves farther and farther away as the molecular mass of PPG increases. Based on Fig. 29, one can predict how the compatibility between the components will change depending on the nature of the terminal group of polyglycol or on going from a homopolymer to copolymers of ethylene glycol and propylene glycol. Analogous changes in the compatibility are observed in blends of PE with low- and high-molecular mass compounds.[101] Therefore, information on the influence of the terminal groups on the compatibility between components is also indirectly present in the Flory – Huggins theory of polymer solutions.

In conclusion of this section, it should be noted that knowing the temperature dependence of χ (experimentally determined or calculated)[12] and the starting phase state of the components, the possible phase states can be estimated in a broad temperature range and the full concentration range. The generalised phase diagram of the PDMS – CS system[94] is exemplified in Fig. 31.

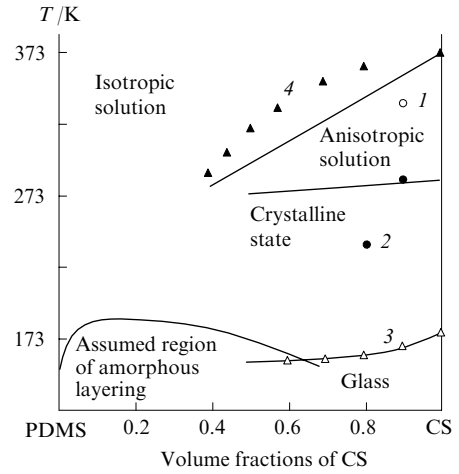


Figure 31. Generalised diagram of phase and physical states[94] of the PDMS (600) – CS (5.1×10^4) system.
Calculated curves are indicated by solid lines. Circles and triangles represent the experimental temperatures of the mesomorphic transition (*1*)[40] and (*4*),[94] crystallisation temperature (*2*)[40] and glass transition temperatures (*3*).[40]

The above-considered facts lead to the following important conclusions.

1. If data obtained for a polymer system by different researchers using various methods are consistent with each other, the results would be expected to be equilibrium or close to equilibrium. The thermodynamic parameters calculated from these data should demonstrate self-consistent behaviour depending on external parameters and do not contradict the major theoretical conclusions.

2. If there is a discrepancy between data obtained by different researchers with the use of various methods, one cannot say with certainty which experimental data are close to equilibrium or how much they differ from equilibrium without resorting to additional structural and, sometimes, kinetic studies. In this case, one can speak only about trends in changes in the boundary curves. The thermodynamic parameters of the compounds with the same phase structure may, for good reason, differ from each other, but their changes depending on external parameters should be of the same character. In our opinion, it is this requirement that is the distinguishing feature of the present stage of investigation of phase equilibria in polymer systems.

The results [71] (see Fig. 18) for the PVC – PMMA system, which has been studied many times and in sufficient detail, provide a prominent example of a fundamental contradiction in the experimental data on phase structures and phase equilibria. It can be seen that the binodals with LCST are located in the region of active thermal destruction of PVC, and the observed turbidity is, most likely, attributable to a change in the chemical structure of the macromolecular chain (formation of polyene sequences [102]) and the appearance of gaseous destruction products. This problem was discussed in detail in the study.[103] A change in the phase state of the system under changes in the chemical nature of the components is of its own interest. At present, theoretical aspects of this problem are in their developmental stage and the required experimental data are being accumulated.[14, 20, 64, 104]

V. Non-equilibrium and metastable states

In a general way, the non-equilibrium state of any system, including polymer systems, can be determined as a deviation from equilibrium. This deviation can be estimated from one of the following parameters: the density, compositions of co-existing phases, the presence of the concentration gradients, dispersion and interface characteristics, *etc*. The metastable state of a system is a special case of a non-equilibrium state in which phase decomposition of the system is hindered or does not occur at all. It should be noted that the location of the figurative point of a system in metastable or labile regions of the phase diagram is necessary but insufficient evidence for the assignment of a material with a particular composition to a metastable state or to materials with a spinodal structure. It is more probable that this is the initial state of a blend, which is responsible for the trajectory of further structural transformations as the system approaches equilibrium.[105 – 107]

Right there the simplicity and obviousness of characterisation of a non-equilibrium state end, because it is necessary to determine experimentally and characterise the equilibrium state and its parameters for each particular system under study; otherwise, one cannot speak about the equilibrium or non-equilibrium state of a particular sample or material prepared under certain conditions.

Non-equilibrium states of polymer blends occur much more frequently than the equilibrium state.[108] However, the thermodynamic description of materials, which is presently used in physical chemistry of polymers and polymer materials science, is based on theories of polymer systems belonging to equilibrium states of blends, solutions and melts.[109] The reasons for this fact are known and have been discussed in many monographs.[14, 15, 110]

In one of his publications, Prigogine [110] determined the place of equilibrium thermodynamics within the framework of non-equilibrium thermodynamics as a limiting case of non-equilibrium thermodynamics with energy fluxes tending to zero. Based on this opinion, we believe that the non-equilibrium state of polymer blends can be described, but only on condition that the time of experiment is much shorter than the time it takes for the structure to be noticeably changed, *i.e*., shorter than the time it takes for the non-equilibrium state of the mixture to be essentially changed.[31]

In studies of particular polymer systems by various methods, the temperature dependences of the compositions of co-existing phases are found, the structure and morphology of blends are determined and the thermodynamic potentials of mixing are calculated. Evidently, to compare experimental data and reveal possible contradictions, it is necessary that the thermodynamic parameters under consideration should have the same physical sense. For this purpose, we interpreted [100] results using the following sequences.

1. Phase diagrams → calculation of the temperature dependence of the pair interaction parameters → construction of the generalised diagram → calculation of the concentration dependence of the free energy of mixing.

2. Sorption isotherms of a common solvent → determination of the chemical potential of the polymeric component → calculations of partial free energies of pure polymers and their mixtures → calculation of the free energy of mixing of a polymer blend with a particular composition possessing a certain processing prehistory.

3. Phase structure → determination of the compositions of co-existing phases (from results of X-ray spectral analysis) → determination of the medium size of the dispersed phase and its size distribution → calculation of the interface surface energy → calculation of the total free energy of a particular sample.

Therefore, all experimental evidence reduces to the only comparable characteristic, *viz*., the free energy of mixing of a particular object possessing a certain processing prehistory.

The phase diagram of the polychloroprene (PCP) – BAN-18 system [100, 111] is shown in Fig. 32. Processing of this diagram gave the temperature dependence of the pair interaction parameter and the concentration dependence of the free energy of mixing for the isotherm corresponding to the temperature at which sorption measurements were carried out (Fig. 33). The dashed line links the free energies of co-existing phases, *i.e*., the free energies of mixing of a completely equilibrated two-phase system. The solid line located between the binodal concentrations corresponds to a non-equilibrium one-phase solution. The difference between these lines

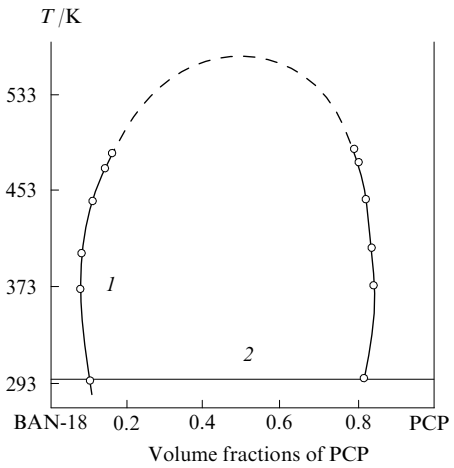


Figure 32. Phase diagrams [15] of the PCP (1.2×10^5) – BAN-18 (2.2×10^5) system.
(*1*) Binodal, (*2*) isotherm corresponding to the temperature at which sorption measurements were carried out.

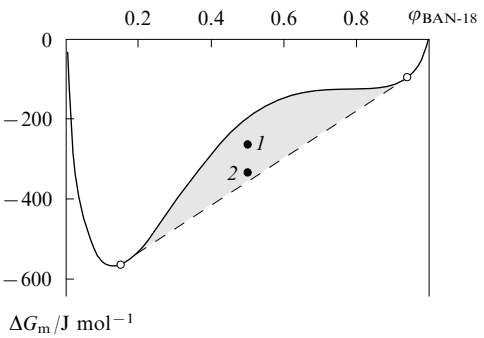


Figure 33. Dependence of the free energy of mixing [112] for the PCP (1.2×10^5) – BAN-18 (2.2×10^5) system.
The common tangent is shown by a dashed line. The compositions of co-existing phases are represented by empty circles. Solid circles indicate $\Delta G_{m,sorp}$ for samples prepared by milling (*1*) and using a common solvent (*2*).

is equal to a gain in energy achieved on going from the one-phase non-equilibrium state to the two-phase equilibrium state.

A traditional thermodynamic analysis of sorption isotherms [113] of tetrahydrofuran on the same polymer blends using the Gibbs–Duhem equation [114] and the Hess cycle [1] allows one to determine free energies of mixing of polymer blends (points *1* and *2* in Fig. 33). As can be seen from Fig. 33, calculated $\Delta G_{m,sorp}$ have negative values in spite of the fact that the systems under study are heterogeneous, and the experimental values for samples of materials prepared under particular conditions of mixing of polymers differ from each other as well as from the theoretical values for equilibrium and non-equilibrium states of the system. The free energies of polymer materials, which were determined from sorption measurements, are located in the shaded region some distance from the equilibrium state.

We believe that with a knowledge of these thermodynamic data, it is possible to characterise quantitatively the non-equilibrium state of a particular material by determining the degree of non-equilibrium (α) as follows

$$\alpha = \frac{\Delta G_{object} - \Delta G_{sep}}{\Delta G - \Delta G_{sep}}. \qquad (3)$$

The notations are explained in Fig. 34.

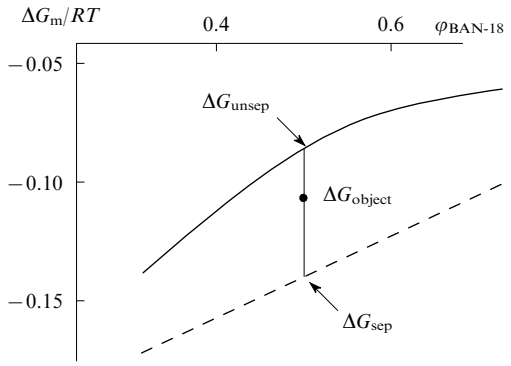


Figure 34. Fragment of the dependence (Fig. 33) of ΔG_m on the composition of the blend; ΔG_{sep} and ΔG_{unsep} correspond to the layered and non-layered systems, respectively.

It should be noted once again that the degree of non-equilibrium calculated according to this equation characterises all non-equilibria (with respect to compositions, particle size, the state of interfaces, *etc*.) resulting in a deviation of the position of the figurative point of the sample from its projection onto the common tangent line.

Analysis of the structural and morphological organisation of blends and estimations of interface surface energies revealed the reasons for the appearance of non-equilibrium in this system in more detail.[115, 116] It was demonstrated [100] that the compositions of co-existing phases in materials subjected to sorption studies (Fig. 35) correspond to binodal concentrations, and the samples differ from each other in the particle size distribution. Therefore, the non-equilibrium state of these materials is associated with an excess interface surface and, correspondingly, with the excess Gibbs free energy

$$\Delta G_m = \varphi \Delta G' + (1 - \varphi)\Delta G'' + \sigma S,$$

where $\Delta G'$, $\Delta G''$ are the free energies of mixing of each phase, φ is the fraction of a dispersed phase and σS is the interface energy.

Taking into account the latter expression for ΔG_m, the numerator of Eqn (3) is σS. The average sizes of phases estimated from structural and morphological data are in satisfactory agreement with the estimates based on thermodynamic data.[100]

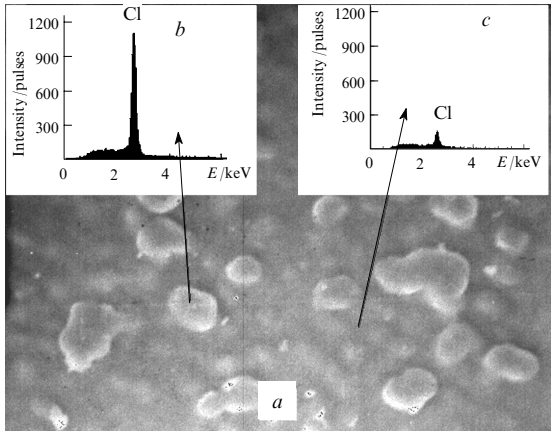


Figure 35. Surface morphology of a low-temperature chip of the PCP (1.2×10^5) – BAN-26 (2.3×10^5) blend obtained by scanning electron microscopy (*a*). The spectra of characteristic X-ray radiation of the dispersed phase (*b*) and the dispersion medium (*c*) are shown in insets.

Other systems also show analogous non-equilibrium behaviour upon the formation of polymer blends in solution in a common solvent.

In the study,[112] the above-described approach and the results of structural–morphological investigation were used for calculating free energies of mixing for equilibrium, non-equilibrium and real systems. As can be seen from Fig. 36, the character of changes in the free energy of mixing upon the formation of a binary polymer blend from a three-component solution is analogous to that described above. Using Eqn (3), it is also possible to estimate quantitatively the degree of non-equilibrium for various composites, which is associated with the excess Gibbs free energy located in interface layers of co-existing phases. It should be noted that the figurative points of particular samples are remote from non-equilibrium curves. It was demonstrated [112] that this effect may be attributed to the energy spent for nucleation of a dispersed phase.[117]

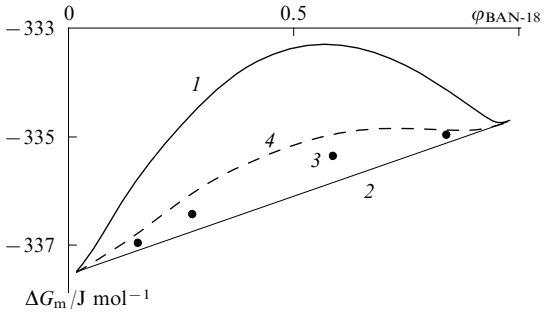


Figure 36. Plot of the free energy of mixing *vs*. the concentration of one of the polymers for the PVC – BAN-18 – dichloroethane system.
(*1*) Non-equilibrium one-phase system, (*2*) equilibrium two-phase system, (*3*) (circles) free energies of materials taking into account the total interface energy, (*4*) free energies of materials taking into account the total interface energy of critical nuclei.

A more complex situation is observed for the PVC–PMMA system. Analysis of the experimental data on the prehistory of the preparation of polymer blends shows that the largest discrepancy in the results is observed when THF or ethyl methyl ketone is used as a common solvent. As can be seen from Fig. 37, a change in the composition of solutions on going from a ternary system to a binary one gives rise to a region of stable phase structures in the

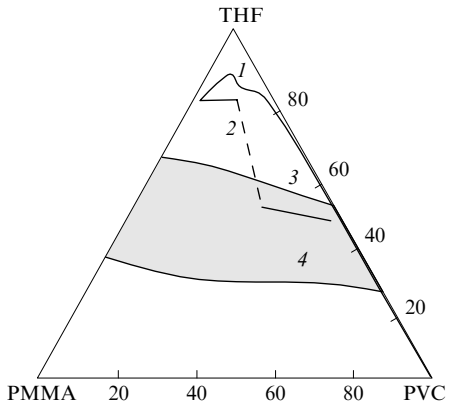


Figure 37. Diagram of phase and physical states[118] for the PVC – PMMA – THF system at 293 K.
(*1*) Binodal, (*2*) line of stabilisation of the phase structure, (*3*) line of critical viscosity, (*4*) glass transition.

middle region of the phase diagram.[118] The structure formed in this region remains unchanged upon removal of the solvent and going to a binary system.

Such materials are characterised by several types of non-equilibrium: first, the deviation of the compositions of co-existing phases of particular composites from equilibrium values (see Fig. 3); second, high dispersity and, as a consequence, a high excess surface energy; third, a large excess free volume because evaporation of the solvent is accompanied by the glass transition of the system and the latter is rather far removed from the glass transition temperature.

All the above-mentioned types of non-equilibrium are most pronounced when a binary polymer blend is prepared with the use of a common solvent and are much less pronounced in the case of mixing in a melt or polymerisation of the MMA monomer in the PVC matrix.

Direct structural – morphological studies[39, 119, 120] demonstrated that annealing of non-equilibrium structures led to secondary phase decomposition resulting in degeneration of the first and third types of non-equilibrium. In the phase diagram, the character of the binodal curve in the vicinity of the critical point is noteworthy. It should be noted that the double-hump shape of the curve is reversible and highly reproducible, depends only slightly on the molecular mass of PMMA and is observed only in experiments with the use of a limited range of common solvents.

Detailed IR spectroscopic studies of the conformational states of macromolecular chains of PVC in solutions, melts and starting powders prepared under various conditions of suspension polymerisation revealed[121, 122] three stable conformational states of PVC characterised by different glass transition temperatures, melting points and supramolecular organisation. The first state has regular helical TGTGTGT conformations of the chain with an isotactic sequence as well as long planar TGTG conformations in a syndiotactic configuration and appears in the synthesis of PVC. This state corresponds to a supramolecular structure of the fringed-micelle type. The second state is formed from solution and is characterised by short TT sequences and the micellar folded morphology. The third (intermediate) type is characterised by a set of conformers of the first and second types.

Following the principle of independence of phase equilibria proposed by Papkov,[28] it can be assumed that the double-hump shape of the binodal curve results from the presence of two conformational states of PVC in the system; the ratio between these states varies depending on the nature of the solvating agent.

Based on the aforementioned facts, a new type of non-equilibrium, which is associated with the possible existence of the temperature – concentration region of stable conformers of macromolecular chains, should be taken into account. In this case, the appearance of LCST (see Fig. 18) is, presumably, caused by a change in the set of conformations.

An analogous effect of the change in the character of the phase equilibrium under the influence of the solvent and the appearance of UCST (see Fig. 19) were observed in the PS – PVME system characterised by LCST.[62]

This complex phase behaviour is typical of many systems containing PVC as a component. Examples are provided by the PVC – dioctyl phthalate[105] and PVC – BAN-40 – solvent systems.[123]

Pseudobinodal curves, which are not reproduced in heating – cooling cycles, were also observed. In a number of studies, two glass transition temperatures and melting points were detected.[124] The influence of the nature of the solvent on the phase state of a system was also reported.[125] Interestingly, all these anomalous phenomena are correlated to the position of the region of conformational rearrangements.

VI. Conclusion

The main characteristic features of the influence of the molecular-mass characteristics on phase equilibria in polymer – polymer systems were revealed and confirmed in studies of many binary and ternary systems. The deviations from these features described in original studies reflect the specificity of the behaviour of particular polymers rather than argue against these general features. The development of polymer materials science is associated with both further accumulation of experimental data, primarily, on phase diagrams, and elucidation and classification of specific features of the behaviour of polymer systems.

We believe that the notions 'system' and 'material' should be distinguished for a more clear understanding of experimental and theoretical data. Systems are characterised by a phase equilibrium and a phase diagram, equilibrium and reproducible thermodynamic parameters, parameters determining the translational characteristics, the identity of the intermediate region of conjugated phases and the interface, the minimum interface surface.

Materials are characterised by a specific phase structure, which depends on the thermal and processing prehistory, and a set of non-equilibria of various types. The interface is only a part of the intermediate region of conjugated phases. Both the translational and thermodynamic characteristics depend on the prehistory of the material and can vary with time.

This classification seems to be necessary and fruitful for the development of the concept of the determination of equilibrium characteristics and the degree of non-equilibrium of particular materials.

In our opinion, the following conditions should be met to solve the problem of non-equilibrium states of binary and ternary polymer systems.

— Researchers must overcome the psychological barrier associated with the identification of the thermodynamic parameters for particular materials (thermal capacity and its temperature dependence, free energy of mixing, interaction parameters) with the thermodynamic parameters of equilibrium systems. For example, the results of determination of ΔG_m for polymer blends from sorption measurements[1] or by inverse gas chromatography[48] characterise not ΔG_m for the equilibrium state but the free energy of mixing of a particular sample with a particular phase structure prepared under particular conditions.

— Further investigation of the mechanism of formation of the non-equilibrium structural – morphological organisation of materials is required. It is customary to assume that materials in which mutual dissolution or structure formation and establishment of the thermodynamic equilibrium are complicated by the glass transition of solutions, melts and blends, should be assigned to non-equilibrium materials. However, in a number of studies,[5, 62, 118] it was demonstrated that the structural – morphological organisation of a sample is stabilised also in highly elastic and plastic states, if partial coefficients of translational diffusion of

components, which are responsible for nucleation of a new phase and nucleus growth, amount to as much as 10^{-12} cm^2 s^{-1}.

Within the framework of the proposed approach, a number of important problems remain to be solved and call for special systematic studies.

1. For amorphous equilibrium systems, the most important aims are to study experimentally and elucidate the behaviour of the composites of co-existing phases in the vicinity of a dome of double-hump binodals, find the number and positions of critical points and determine the spinodal curve.

2. Based on the available experimental data, polymers can be considered as sets of stable conformers. Evidently, in this case, the phase diagram should be constructed in another concentration – temperature field.

3. Partially crystalline polymers are, generally, non-equilibrium primarily with respect to their supramolecular and phase structures. This initial non-equilibrium state of a material has a determining effect on the thermodynamic characteristics of polymer solutions and blends and complicates seriously calculations of the thermodynamic parameters of mixing for crystalline equilibrium systems.

4. The observed changes in the positions of boundary curves in the temperature – concentration field of phase diagrams under mechanical effects of various types call for interpretation from the structural, conformational and thermodynamic standpoints.

In the future, fundamental investigations of phase equilibria and phase structures of polymers can be applied to prediction problems in materials science, *i.e.*, predictions of processing conditions, efficiency and service life of polymer materials. However, theoretical predictions are years in the future. At present, semiempirical methods are used. For these methods, information on phase diagrams is of most importance. One of the major aims is still to improve methods for the empirical and semiempirical prediction of equilibrium states of polymer systems.

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