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Thermodynamic Compatibility of Polymers

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It is shown on the basis of an examination of studies carried out in recent years that, by a correct thermodynamically well-founded choice of polymers between which hydrogen bonds can be formed or which can give rise to electron donor-electron acceptor complexes, it is possible to create thermodynamically compatible systems; compatibility can also be improved by mixing homopolymers with copolymers. Various thermodynamic situations observed on blending polymers and the temperature dependence of their thermodynamic compatibility are discussed.
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I. INTRODUCTION

The main trend in the modern technology of the processing of polymeric materials involves their preparation from mixtures (blends) of polymers. The thermodynamic compatibility of polymers with one another, to which numerous studies surveyed in monographs, reviews, and text books have been devoted, plays a major role in this.[1-16] However, new aspects have recently arisen concerning the methods of determination of the thermodynamic compatibility of polymers, its causes, procedures for its enhancement, and its temperature dependence.

The term "compatibility", borrowed from technological practice, is usually understood as the miscibility of polymers. The authors of a monograph[2] believe that, in relation to polymer blends, the term is inept and they have suggested that it be replaced by the term "miscibility". They suggest that one can speak of miscibility only in the case of an ideal solution whose formation is possible solely following the interaction of low-molecular-weight substances. However, in essence, this is incorrect because the formation of an ideal solution is an extremely rare phenomenon and true real solutions of low-molecular-weight substances are non-ideal in the vast majority of cases.[17] Nevertheless, the concepts of "solubility" and "miscibility", which are identical, are applied to them. Evidently in the case of polymer compositions there is also no point is distinguishing these two concepts and the terms "mutual solubility" and "miscibility" should be regarded as synonymous. By thermodynamic compatibility we shall understand (a) the ability of the components to mix with one another spontaneously with formation of a true solution, i.e. their thermodynamic affinity relative to one another, and (b) a transition from possibility to reality, i.e. the realisation of the above affinity which leads to the miscibility of the components.

The thermodynamic compatibility of polymers is estimated by thermodynamic and non-thermodynamic methods. The latter include methods for the investigation of the phase structures of blends—electron microscopy and X-ray diffraction and also all the methods for the determination of the glass point of blends which yield information about the independent behaviour of the components in incompatible compositions. However, it is more correct to estimate thermodynamic compatibility by thermodynamic methods, i.e. to determine the thermodynamic affinity and phase diagrams for polymer–polymer systems.

II. THERMODYNAMIC AFFINITY BETWEEN POLYMERS

The thermodynamic affinity between a polymer and a solvent is estimated quantitatively in terms of changes in the chemical potential of the components $\Delta\mu_i$ or its excess value μ_i^e, the Gibbs free energy of mixing ΔG or its excess value G^e, the Flory–Huggins interaction parameter χ_1, and the second virial coefficient A_2.

The same parameters also characterise the thermodynamic affinity between polymers. They can be determined experimentally by studying the static and dynamic sorption of the vapour of a liquid on individual polymers and their blends, the dissolution of different polymers in a common solvent, the mutual diffusion coefficient of the polymers, etc.

The methods of the static sorption of the vapour of a common solvent was first used to estimate the thermodynamic affinity of two polymers by Kwei et al.,[18] who calculated the interaction parameter χ'_{23} from the sorption isotherm by Scott's equation:[19]

$$\ln a_1 = \ln\varphi_1 + (1-\varphi_1) + (\chi_{12}\varphi_2 + \chi_{13}\varphi_3)(1-\varphi_1) - \chi'_{23}\varphi_2\varphi_3 \qquad (1)$$

where χ_{12} and χ_{13} are the parameters of the interaction of the polymer (2) and the polymer (3) with the common solvent (1) when the latter is sorbed on the polymer, a_1 is the activity coefficient of the solvent in the three-component polymer–polymer–solvent system, which is determined in the sorption of the vapour of the solvent on the polymer blends, and ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of the solvent and the polymers (2) and (3) in the three-component composition.

It has been shown[19] that the critical value of χ'_{23} for the polymer–polymer system tends to zero. This means that any positive value of χ'_{23} characterises the incompatibility of the polymers.

Eqn.(1) has been used to estimate the compatibility of a series of systems on the basis of the sorption isotherms of the vapours of various substances.[20-22] The calculation for cellulose nitrate (CN)–poly(vinyl acetate) (PVAC) systems leads to negative values of χ'_{23}, which are consistent with data obtained by other methods and indicate the compatibility of these polymers.[21] However, negative values have also been obtained for incompatible systems. The authors suggest that Scott's equation (1), derived on the basis of the Flory–Huggins theory proposed for the model of a true solution of polymers, describes only compatible single-phase polymer systems, the theory being inapplicable to two-phase colloidal systems.

In this respect, the method involving the determination of the Gibbs free energy of mixing of polymers, proposed by Tager and co-workers,[23,24] has an undoubted advantage. The method requires no models and is based solely on the assumption that the Gibbs free energy is a function of state of the system and is independent of the path followed by the process. For this reason, the Gibbs free energy can be calculated from the thermodynamic equation

$$-\Delta g_x = \Delta G_{III} - (\omega_1 \Delta G_I + \omega_2 \Delta G_{II}), \quad (2)$$

where Δg_x is the average Gibbs free energy of mixing of the polymers, ΔG_I, ΔG_{II}, ΔG_{III} are the Gibbs free energies of respectively 1 g of each polymer and their mixtures with the vapour of a common solvent (sorbate) having different compositions, and ω_1 and ω_2 are the weight fractions of the polymers in the polymer composition.

This method has been described in detail in original papers,[23,24] monographs, and textbooks.[2,3,16] It has been applied to polymer–oligomer[25] and polymer–polymer[26–29] systems, interpenetrating networks,[30,31] and graft[32] and block copolymers.[33–35] The physical significance of the quantities calculated by Eqn.(2) has been discussed.[35,36] For block copolymers, the quantity Δg_x reflects the work necessary to mix the blocks and is equal in magnitude but opposite in sign to the work of their separation, which has been calculated theoretically.[37,38] For polymer blends, Δg_x is an integral quantity, which depends on the chemical structure and the degree of dispersion of the system components. According to Gibbs,[39–42] any extensive thermodynamic property of a two-phase system can be regarded as the sum of three contributions: by the phase α, the phase β, and the interfacial region.

If the interface, which represents a conventional geometrical surface, is two-dimensional (has no volume), then the average Gibbs free energy of mixing, i.e. the energy per gram of the mixture, is defined by the expression

$$\Delta g_x = \Delta g_\alpha + \Delta g_\beta + \sigma S, \quad (3)$$

where Δg_α and Δg_β are the average Gibbs free energies of mixing in each phase, σ is the surface tension, and S the specific area of the interface.

Since it is known that the interfacial tensions in polymer blends are very low,[43] the last term of Eqn.(3) does not contribute significantly to Δg_x, as shown by Kuleznev.[44]

However, for real two-phase systems the interface is not two-dimensional and has a definite thickness and volume. It is especially important to take this into account in relation to polymer systems where the thickness of the transition layer may be considerable.[3,45,46] In this case it is more correct to use Guggenheim's method,[40–42] which leads to the differential equation[36]

$$dg_x = dg_0 + \underbrace{[\sigma + (\mu_1 dc_1 + \mu_2 dc_2)h]}_{dg_s} S, \quad (4)$$

where μ_1, μ_2, c_1, and c_2 are the chemical potentials and concentrations of the components in the transition layer, h is the thickness of the transition layer, and dg_0 the Gibbs free energy of mixing, which is independent of the degree of dispersion and is related solely to the chemical structure of the components and their affinity for one another. The second term of Eqn.(4) reflects the contribution of the structural factors, including the degree of dispersion and the volume of the transition layer. When there is a high affinity between the components and the latter are fully miscible, $S = 0$ and the second term is zero. Then $dg_x = dg_0$. In the complete absence of affinity (polymerophobic behaviour), $dg_0 = 0$ and dg_x is equal to the work of dispersion and depends on the degree of dispersion. In the intermediate cases, dg_x is given by the sum of both contributions: $dg_0 < 0$, $dg_s > 0$. The magnitude and sign of dg_x depend on the ratio of these quantities.

The method of dynamic sorption or reversed gas chromatography (RGC), which has been described in detail in books[47,48] and reviews,[49,50] is used widely to investigate the thermodynamic compatibility of polymers. In contrast to classical gas chromatography, the RGC method is used to solve the converse problem—the study of the behaviour of the stationary phase (SP) and its interaction with the mobile phase. The RGC method was applied to polymer systems for the first time by Smidsröd and Guillet.[51]

A theory of the method has been developed for ideal gas chromatography[52] on the assumption that, firstly, the Henry distribution isotherm for the sorbate between the carrier gas and the SP is linear, which is valid only for the infinitely dilute solution of the sorbate in the SP, and, secondly, that it is necessary to establish equilibrium in the sorption–desorption process, which is possible when certain conditions are maintained, but this is by no means always the case for polymeric SP. This applies particularly to polymers which exist in the vitreous state under the experimental conditions. For this reason, RGC experiments with polymeric SP are as a rule carried out at temperatures at least 50 °C above the glass point T_g of the polymer, where the latter exists in the highly elastic state.[53] However, in this case too the equilibration time may be very long as a consequence of the high viscosity of the polymer.

In the study of the compatibility of polymers, the stationary phases are polymer blends on which the vapour of a volatile liquid is sorbed. If the components of the mixed SP behave independently, then the specific retention volume is made up additively of its components;[54] if they interact with one another, then deviations are observed from the additivity of the chromatographic retention parameters.[54,55] In this case the excess Gibbs free energy G^e is calculated by the equation of Waksmundzki and Suprynowicz:

$$G^e = RT\left(\ln V_{\bar{M}} - \sum_i x_i \ln V_{M_i}\right), \quad (5)$$

where x_i is the mole fraction of the ith component in the mixture and V_{M_i} and V_M are the molar volumes of the sorbate retained respectively by the individual components and the entire mixed phase. Eqn.(5) has been used to determine G^e for mixed liquid[55–57] and polymeric[58] SP. For mixed polymeric SP, the interaction parameter χ'_{23} and the contact energy parameter X_{23}, introduced in the new Flory–Prigogine–Patterson theory,[60–62] are also calculated from the retention volume data.[59]

The thermodynamic compatibility of many oligomer–oligomer, polymer–oligomer, and polymer–polymer pairs have been investigated by the RGC method. The results have been surveyed in a number of communications.[2,48–50,63]

The method involving the determination of the second virial coefficients A_{23}, proposed by Kratochvil and co-workers for the investigation of the compatibility of polymers,[64–66] is based on the study of the light scattering by dilute solutions of polymer blends in a common solvent with subsequent calculation of A_{23} by the equation obtained on the basis of the Stockmeyer theory. The values of A_{23} have been calculated for the polystyrene–poly(methyl methacrylate) (PS–PMMA) system and for blends of different polymethacrylates and styrene–methyl methacrylate copolymers.[64–66]

The second virial coefficients have been determined[67] for binary polymer–polymer systems with the aid of the method based on neutron scattering by dilute solutions of one polymer

in another. For blends of deuteriated PMMA with statistical styrene—acrylonitrile copolymers containing 19.9 and 28.7% of acrylonitrile, $A_{23} > 0$ was obtained, which indicates the compatibility of the components. Later the same method was used to investigate blends of PS with poly(phenylene oxide) and its bromo-derivatives,[68,69] with poly(methyl vinyl ether),[70] and with polymethylstyrene[71] and also blends of PMMA with poly(vinyl chloride) (PVC) and blends of statistical copolymers of styrene and acrylonitrile.[72]

The advantage of the neutron scattering method compared with the scattering of visible light consists in the possibility of investigating components having similar refractive indices. However, the complexity of the experimental equipment and the need to use deuteriated polymers limit the wide-scale application of the method.

The mutual diffusion method[73] is based on the familiar relation between the mutual diffusion coefficient D_{mu} and the second derivative of the average Gibbs free energy or the first derivative of the chemical potential with respect to composition:

$$D_{mu} = D_i^* \frac{\varphi_i}{RT} \frac{d\mu_i}{d\varphi_i} = D_i^* \frac{\partial^2 g}{\partial \varphi_i^2} , \quad (6)$$

where D_i^* is the self-diffusion coefficient of the ith component characterising the thermal mobility of the molecules of the component and ϕ_2 is its volume fraction. The application of this method has been described in detail in a number of communications.[74–78]

III. CAUSES OF THE COMPATIBILITY OF POLYMERS AND METHODS FOR ITS IMPROVEMENT

The data on the compatibility of polymers quoted in the literature show that polymers with similar chemical structures are not compatible. On the other hand, polymers differing in their chemical nature are compatible. The question of the causes of the compatibility of polymers and of the role of their chemical structure naturally arises. This question can be considered from the thermodynamic and molecular points of view.

A thermodynamic condition for spontaneous mixing is a negative Gibbs free energy of mixing, which represents the algebraic sum of two contributions—the enthalpy (ΔH) and entropy ($T\Delta S$) contributions:

$$\Delta G = \Delta H - T\Delta S . \quad (7)$$

The view that the change in entropy on mixing polymers plays no role predominated in the literature for a long time. It was based on calculations by Gee,[79] who took into account only the combinatorial entropy of mixing determined by the number of transpositions of unlike molecules; for a polymer–polymer system, it is indeed very low. However, there exists a non-combinatorial contribution to the entropy of mixing originating from the interaction between the components. Flory and co-workers demonstrated theoretically that this contribution can be fairly large.[80] This was confirmed experimentally for the first time by Tager and co-workers.[24,26,27]

For many compatible polymer–polymer pairs, negative values of ΔH and ΔS are observed and the thermodynamic requirements which are needed for the satisfactory compatibility of the polymers have been formulated on this basis.[11]

1. The entropy of mixing of polymers $\Delta S < 0$. This means that the macromolecules in the mixture are distributed in a more ordered manner than among similar macromolecules, i.e. jointly ordered polymer structures are formed.

2. The enthalpy of mixing of polymers $\Delta H < 0$, which is possible if the interaction energy between unlike molecules is greater than between like molecules.

3. The algebraic sum of the absolute values of ΔH and $T\Delta S$ must be negative, i.e. $|\Delta H| > |T\Delta S|$.

Patterson and Robard,[13] who demonstrated theoretically that the compatibility of polymers with high molecular weight is possible provided that $\Delta H < 0$, arrived at an analogous conclusion. They state that negative enthalpies of mixing are frequently accompanied by negative entropies of mixing and that the competition between these quantities determines the sign of ΔG, i.e. the compatibility of polymers.

Thermodynamic predictions have played a major role in the understanding of the mechanism of the compatibility of polymers and have laid the scientific foundation for the creation of new compatible compositions. Together with the thermodynamic aspect, the compatibility of polymers has been considered also from the standpoint of the interaction of the macromolecules. This has been reflected in a monograph[2] whose authors indicate two ways of improving compatibility, i.e. of creating compatible polymer–polymer systems. The first consists in joining macromolecules together via chemical bonds, which is achieved as a result of the synthesis of block copolymers and interpenetrating networks and by carrying out reactions leading to the cross-linking of the mixture components. The presence of chemical bonds prevents macrolayer formation in the mixtures even if the components are thermodynamically incompatible.

The second way of improving compatibility consists in altering the chemical structure of the blended polymers in a manner which leads to a negative Gibbs free energy of mixing, which is achieved by two procedures: (1) by mixing polymers having functional groups capable of strong interaction; (2) by modifying one of the blended polymers by altering the chemical structure of the monomer units or by copolymerisation.

1. The Mixing of Polymers Having Functional Groups

This method of improving compatibility is based on the idea that large negative values of ΔH, favouring negative values of ΔG, are possible in the presence of specific interactions between the polymers. In their monograph, Olabisi et al.[2] put forward the concept of "complementary dissimilarity", according to which the unlimited mixing of polymers is possible when the macromolecules of each contain different functional groups capable of interacting. This concept is close to the idea[81] according to which the best mutual dissolution or blending is observed in substances whose molecules contain groups with opposite functionalities and not in substances with similar structures. For example, the molecules of one component may contain only proton-donating groups and those of the other only proton-accepting groups; in the blends, hydrogen bonds arise between the components which promotes dissolution. Blending is also favoured by the situation where the molecules of one component are electron donors and those of the other contain atoms having unoccupied orbitals. In this case electron donor–electron acceptor bonds (EDA bonds) are produced. The influence of the chemical structure of polymers on their miscibility has been considered in recent years from the standpoint of this concept.

There has been a cycle of studies on the compatibility of PVC with certain polymers. The hydrogen atom in PVC, activated by the electronegative Cl atom joined to a neighbouring carbon atom, can participate in the formation of a hydrogen bond.[2,83] Consequently PVC tends to enter into donor–acceptor interactions with polymers whose molecules

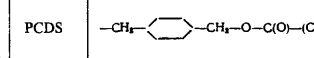
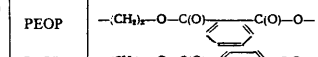
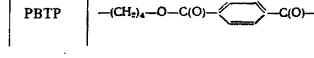
contain groups which function as electron donors with formation of hydrogen or EDA bonds. Poly(alkyl acrylates), poly(alkyl methacrylates), and polyesters belong to polymers of this kind. The compatibility of PVC with such polymers has been estimated from the T_g of the blends[84–90] and their transparency[84,86] and by IR spectroscopic[91–93] and DTA [differential thermal analysis] methods.[90]

It has been observed[84,94] that PVC is compatible with polyacrylates where the number of carbon atoms in the alkyl group is $n < 4$, and with polymethacrylates, where $n < 6$. The incompatibility of PVC with higher homologues has been explained by the decrease in the fraction of the $-C(O)-O$ groups in the macromolecules and by their shielding by long alkyl groups, which hinders the formation of hydrogen bonds between PVC and the ester groups of polyacrylates.

The studies considered above lead to the conclusion that PVC is compatible with PMMA, which disagrees with the data of other workers,[86,95,96] who demonstrated only their limited compatibility. The discrepancy between the results can be associated with the fact that Walsh and McKeown[84] estimated the compatibility from T_g and it is known that in the vicinity of T_g the components even in incompatible polymer systems have the same T_g.[4]

Table 1 presents data on the compatibility of PVC with polyesters. Despite the possibility of the formation of hydrogen bonds, not all the esters are compatible with PVC. The compatibility of PVC with aliphatic polyesters improves with increase in the number of CH_2 groups on passing from PBA to PCL and PHS (for the significance of the abbreviations, see Table 1), which is manifested by an increase of the negative values of the parameter χ'_{23}; when the content of CH_2 is even higher, the compatibility is impaired. It has been shown that the compatibility of aliphatic polyesters with PVC is observed in those cases where the ratio CH_x/COO ($x = 1, 2, 3$) is in the range 3 to 12.[90]

Table 1. The compatibility of PVC with polyesters.

Polyester	Designation	Structural formula	Compatibility	Refs.
Poly-β-propiolactone	PPL	$-CH_2-CH_2-C(O)-O-$	–	[92]
Poly(ethylene succinate)	PES	$-(CH_2)_2-O-C(O)-(CH_2)_2-C(O)-O-$	–	[90]
Poly(ethylene adipate)	PEA	$-(CH_2)_2-O-C(O)-(CH_2)_4-C(O)-O-$	–	[90]
Poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	$-CH_2-C(CH_3)_2-CH_2-O-C(O)-(CH_2)_2-C(O)-O-$	+	[90]
Poly(butylene adipate)	PBA	$-(CH_2)_4-O-C(O)-(CH_2)_4-C(O)-O-$	+	[90]
Polyvalerolactone	PVL	$-(CH_2)_4-C(O)-O-$	+	[90, 93]
Poly-ε-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	+	[83, 85, 91]
Poly(α-ethyl-α-methyl-β-propiolactone)	PEMPL	$-CH_2-C(CH_3)(C_2H_5)-C(O)-O-$	+	[88]
Poly(α-methyl-α-n-propyl-β-propiolactone	PMPPL	$-CH_2-C(CH_3)(C_3H_7)-C(O)-O-$	+	[88]
Poly(hexamethylene sebacate)	PHS	$-(CH_2)_6-O-C(O)-(CH_2)_8-C(O)-O-$	+	[90]
Poly(1,4-cyclohexylene-dimethyl succinate)	PCDS		+	[90]
Poly(ethylene o-phthalate)	PEOP		–	[90]
Poly(butylene terephthalate)	PBTP		+	[87]

Many studies have been devoted to the compatibility of fluorine-containing polymers with other polymers. Fluorine is the most electronegative halogen and its atom therefore forms strong chemical bonds with other atoms.[97] The strength of these bonds is the reason why many low-molecular-weight compounds containing fluorine are much less miscible with other substances and with one another than are compounds containing other halogens.[98] Thus solutions of low-molecular-weight fluorine-containing compounds are characterised by very large positive deviations from ideality and on cooling as a rule separate into layers. Fluorine-containing polymers are also inert. For example, polytetraflouroethylene does not dissolve in any known solvents.

Table 2. The compatibility of PVDF [poly(vinylidene fluoride)] with oxygen-containing polymers.

Polymer	Designation	Structural formula	Compatibility	Refs.
Poly(methyl methacrylate)	PMMA	$-CH_2-C(CH_3)-$ $C(O)-O-CH_3$	+	[101, 103, 105, 106]
Poly(ethyl methacrylate)	PEMA	$-CH_2-C(CH_3)-$ $C(O)-O-C_2H_5$	+	[101, 104]
Poly(isopropyl methacrylate)	PIPMA	$-CH_2-C(CH_3)-$ $C(O)-O-CH(CH_3)_2$	–	[101]
Poly(methyl acrylate)	PMA	$-CH_2-CH-$ $C(O)-O-CH_3$	+	[102]
Poly(ethyl acrylate)	PEA	$-CH_2-CH-$ $C(O)-O-C_2H_5$	+	[102]
Poly(isopropyl acrylate)	PIPA	$-CH_2-CH-$ $C(O)-O-CH(CH_3)_2$	–	[102]
Poly(vinyl acetate)	PVAC	$-CH_2-CH-$ $O-C(O)-CH_3$	+	[108]
Poly(vinyl propionate)	PVP	$-CH_2-CH-$ $O-C(O)-C_2H_5$	–	[108]
Poly(vinyl butyrate)	PVB	$-CH_2-CH-$ $O-C(O)-C_3H_7$	–	[108]
Poly(methyl vinyl ketone)	PMVK	$-CH_2-CH$ $C(O)-CH_3$	+	[109]
Poly(methyl vinyl ether)	PMVE	$-CH_2-CH-$ $O-CH_3$	–	[109]
Poly-ε-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	–	[109]

Poly(vinylidene fluoride) (PVDF) and fluororubber are less inert, because their molecules contain hydrogen atoms capable of forming hydrogen bonds.[97] PVDF therefore dissolves in liquids with a high electron donating capacity—dimethylformamide, dimethylsulphoxide, etc.[99] Fluororubber dissolves in acetone. These features of fluorine-containing polymers affect also their compatibility with other polymers. Thus it has been established by the RGC method that fluororubber is incompatible with ethylene–propylene rubber over a wide temperature range,[100] since hydrogen and EDA bonds cannot be formed between their macromolecules. In contrast to this, PVDF can form hydrogen bonds with oxygen-containing polymers. Numerous studies have been devoted to these blends[101–111] and their results have been surveyed[112] and are presented in Table 2. The common solvent method,[102, 108, 109] the method based on the determination of T_g[101,102,105,106, 108,109] and T_m (melting point) of PVDF,[103,104,112] the RGC[111] and NMR[107] methods, and also the study of phase diagrams of the mixtures[110] have been used to estimate the compatibilities.

It follows from Table 2 that PVDF is compatible with polymers containing the ester group and a small alkyl substituent (CH_3, C_2H_5) in the side chain. The increase in the size of the alkyl substituent on passing to PIPMA and PIPA leads to the incompatibility of these polymers with PVDF. When the methyl group is present in the side branches, structural isomerism does not play any role: PVDF is compatible with PVAC and PMA. It is believed[109] that the presence of the carbonyl group in the molecule of the oxygen-containing polymer is of decisive importance. This follows from the fact that PVDF is compatible with PVMK and incompatible with PVME. Analysis of the interaction parameters χ'_{23} showed that PVAC, in the macromolecules of which the carbonyl group is more remote from the main chain than in the other polymers investigated, shows the maximum affinity for PVDF. In terms of increasing impairment of compatibility with PVDF, oxygen-containing polymers can be arranged in the sequence PVAC > PMMA > PMA > PEMA > PVMK > PEA. The increase in the size of the alkyl substituent impairs the compatibility of the polymers with PVDF.

It is believed[112] that the compatibility of PVDF with oxygen-containing polymers is caused by the dipole–dipole interaction between unlike molecules. However, dipole–dipole interaction alone is insufficient. Hydrogen bonds in which the carbonyl group of the ester and the hydrogen atoms of PVDF participate may be formed in these systems. This hypothesis explains the role of the carbonyl group in ensuring the greater compatibility of poly(alkyl methacrylates) with PVDF compared with poly(alkyl acrylates): the electron-donating capacity of the carbonyl group in the former is higher than in the latter as a consequence of the inductive effect caused by the presence of the methyl substituent in the α-position.[113]

Studies of the compatibility of polycarbonates (PC) based on di(hydroxyphenyl)propane with polyesters are of considerable interest:[114–120] the compatibility has been estimated by the DTA and mechanical relaxation methods. It is seen from Table 3 that the majority of the linear aliphatic polyesters obtained are compatible with PC. With increase in the number of methylene groups per carbonyl group in the polyester molecule the compatibility with PC is impaired. Branched polyesters are incompatible with PC. The replacement of aliphatic dicarboxylic acid residues in the polyester molecules by aromatic residues (PETP, PEOP) leads to their incompatibility with PC.

It is believed[120] that the compatibility of PC with polyesters is caused by the strong energetic interactions between unlike molecules, which should entail negative enthalpies of mixing. To test this hypothesis, the authors used a model approach consisting in the determination of the heats of mixing of low-molecular-weight analogues of the polymers investigated. Diphenyl carbonate (DPC), propylene carbonate, and dimethyl carbonate were adopted as models. The models for the polyesters were different esters having analogous and similar structures. It was shown[120] that low-molecular-weight esters mix with aliphatic carbonates with absorption of heat and that the sign of the heat of mixing with DPC depends on the number n of carbon atoms in the ester molecules per carbonyl group: if $n < 6$, exothermic mixing is observed ($\Delta H < 0$) and, if $n > 7$, the mixing is endothermic ($\Delta H > 0$). The authors believe[120] that the magnitude and sign of ΔH for the mixing of esters with DPC are determined by the balance of two contributions, the exothermic contribution caused by the formation of donor–acceptor bonds between the C=O group of the ester and the aromatic ring of the carbonate molecule and the endothermic contribution arising as a result of the rupture of dispersion linkages. This explanation is similar to that proposed in a study[121] of the heats of solution and swelling of aromatic polymers in tetrachloroethane and DMF.

The authors[120] suggested that the positive ΔH for the model systems should correspond to the incompatibility of the polymers, while negative values should correspond to their compatibility. However, they did not observe this correlation for all systems and they reached the correct conclusion that the use of low-molecular-weight analogues to infer the compatibility of polymers is illegitimate.

Table 3. The compatibility of polycarbonate with polyesters.

Polyester	Designation	Structural formula	Compatibility	Refs.
Poly(ethylene succinate)	PES	$-(CH_2)_2-O-C(O)-(CH_2)_2-C(O)-O-$	+	[118]
Poly(ethylene adipate)	PEA	$-(CH_2)_2-O-C(O)-(CH_2)_4-C(O)-O-$	+	[118]
Poly(butylene adipate)	PBA	$-(CH_2)_4-O-C(O)-(CH_2)_4-C(O)-O-$	+	[118]
Poly-ε-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	+	[117]
Poly(hexamethylene sebacate)	PHS	$-(CH_2)_6-O-C(O)-(CH_2)_8-C(O)-O-$	−	[118]
Polypivalolactone	PPL	$CH_2-C(CH_3)_2-C(O)-O-$	−	[119]
Poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	$-CH_2-C(CH_3)_2-CH_2-O-C(O)-(CH_2)_2-C(O)-O-$	−	[119]
Poly(ethylene terephthalate)	PETP	$-(CH_2)_2-O-C(O)-C_6H_4-C(O)-O-$	−	[115]
Poly(ethylene *o*-phthalate)	PEOP	$-(CH_2)_2-O-C(O)-C_6H_4-C(O)-O-$	−	[120]
Poly(butylene terephthalate)	PBTP	$-(CH_2)_4-O-C(O)-C_6H_4-C(O)-O-$	−	[114]
Poly(1,4-cyclohexylenedimethyl terephthalate)	PCDTP	$-CH_2-C_6H_{10}-CH_2-O-C(O)-C_6H_4-C(O)-O-$	+	[116]
Copolyester based on terephthalic acid, isophthalic acid, and 1,4-cyclohexylenedimethanol	CPL	TP + IP + CD	+	[116]

In this connection, it is appropriate to consider in a general form the relation between the thermodynamics of mixing of polymers and their liquid low-molecular-weight analogues. There is no doubt that the affinity between macromolecules of different chemical structure is related to the affinity of their monomer units. For example, CN is effectively compatible with PVA as a consequence of the high affinity of CN for vinyl acetate ($\chi_1 = 0.2$).[122] In the absence of affinity between monomer units, the polymers are undoubtedly incompatible. However, the unlimited mixing of low-molecular-weight analogues of the given polymers by no means implies that the polymers themselves are miscible.

Detailed analysis of the thermodynamic relations permits the formulation of the following rule: the higher the positive deviations from ideality in the mixtures of two liquids, i.e. the higher the excess Gibbs free energy, the less compatible the polymers whose units are analogous in structure to the molecules of these liquids. Here and henceforth the average Gibbs free energies (Δg), the enthalpies (Δh), and the entropies (Δs) of mixing of their excess values (g^e, h^e, and s^e) corresponding to the maximum in the curves relating these parameters to the composition will be used to characterise the mixing of the solution components. Thus the mixing of aromatic hydrocarbons with alkanes is accompanied by large positive deviations from ideality and the values of g^e reach 500–600 J per mole of the solution.[98] This is caused by strong $\pi-\pi'$ interaction of the aromatic rings, leading to association.[123] With increase in the size of the molecules of aromatic hydrocarbons and other aromatic compounds, the degree of association rises. For this reason, the latter do not dissolve in alkanes and are not compatible with polymeric aliphatic hydrocarbons.

Analogous behaviour has been observed in the mixing of polar liquids with non-polar liquids or of substances capable of forming hydrogen bonds with those which are not. These compounds differ sharply in the density of cohesion energy (solubility parameters) and their mixing at 298 K is accompanied by a large positive value of g^e of the order of 1000 J mol of the solution.[124] For this reason, polar polymers are incompatible with non-polar polymers over a wide temperature range.[16]

More complex rules are observed in the mixing of two polar substances or substances capable of forming hydrogen bonds. The difference between the chemical structures and not their similarity plays frequently a decisive role for these systems. We shall consider several situations.

1. The components have dissimilar chemical structures and contain only proton-accepting groups; for example, two esters. Hydrogen bonds, cannot be formed between them and their mixing is accompanied by positive values of g^e and h^e. Polymers containing ester groups as substituents are frequently altogether incompatible. The classical example is provided by the PMMA–PBMA system.[11] An improvement in compatibility can be achieved in this instance only by reducing the number of butyl substituents in the molecule of the second component, i.e. by blending PMMA with copolymers (see below).

2. The components have similar chemical structures and both contain proton-donating and proton-accepting groups: alcohol–alcohol, acid–acid, and alcohol–acid systems. In these cases, the formation of hydrogen bonds between like and unlike molecules is equally probable. For this reason, when alcohols are mixed with one another or alcohols are mixed with acids, one observes small positive values of h^e, which increase with increase in the size of the alkyl group in the molecules of alcohols or acids.[124] However, a large number of OH and COOH groups in the molecules of the mixed components promotes their blending and polymeric alcohols (PVA) are readily compatible with polyacids (PAA) with formation of polycomplexes.[125–127]

3. One component contains proton-donating and proton-accepting groups, while the other contains only proton-accepting groups. Low-molecular-weight alcohols and acids mix with esters in all proportions, but their mixing is accompanied by positive deviations from ideality. Polyacrylic acid (PAA) is infinitely miscible with poly(ethylene glycol).[127]

4. Mixing characterised by a negative value of g^e is the most favourable. It is observed in systems whose components have the opposite features: for example, one of them contains only proton-donating groups ($CHCl_3$, TCE), while the other contains only proton-accepting groups (ketones); or one is an electron donor, while the other is an electron acceptor (aromatic hydrocarbons and chloro-derivatives). Very strong hydrogen bonds or EDA complexes are formed between unlike molecules; this is accompanied by very large negative values of h^e, of the order of several thousands of J mol^{-1}, and negative deviations from ideality ($g^e > 0$). Polymers containing such groups are thermodynamically compatible for the appropriate ratios of the number of the groups and the number of hydrocarbon residues (see above).

2. Chemical Modification of the Components of a Polymer Blend

The essential feature of this method of improving compatibility consists in the alteration of the chemical structure of one of the components of the polymer composition, which leads to negative values of Δg. This is attained by replacing the units in the macromolecule of one polymer by those of the other polymer, i.e. by blending polymers with copolymers. Three cases are then observed.

In the first case, the polymer A is incompatible with the polymer B but is compatible with the polymer C. The replacement of some of the units in the macromolecule of the polymer B by those of the polymer C leads to the compatibility of the resulting copolymer with the polymer A. For example, poly(phenylene oxide) (PPO) is incompatible with poly-*p*-chlorostyrene (PPCS) but is compatible with polystyrene (PS). The compatibility of PPO with styrene–*p*-chlorostyrene copolymers of different composition has been investigated by the scanning calorimetric and mechanical relaxation methods.[128] It has been shown that the copolymers containing less than 65.3 mole % CS are compatible with PPO, while those containing more than 68% CS are incompatible. Using an improved calorimetric method, it has been shown[129] that the transition from compatibility to incompatibility occurs when the contest of CS units in the copolymer changes by less than 1% (from 67.1 to 67.8 mol %). The analogous "critical", as the authors put it, character of the compatability–incompatibility transition has been observed for mixtures of PPO with statistical styrene–*p*-fluorostyrene (PFS) copolymers:[130] PPO is compatible with copolymers containing less than 56 mol % of FS but is incompatible with copolymers with a higher FS content.

In the second case, the polymer A is incompatible with either the polymer B or the polymer C but is compatible with the copolymer BC. For example, PVC is incompatible with either polybutadiene[6] or polyacrylonitrile[131] but is compatible with their copolymer containing 40 mol % of polyacrylonitrile.[132–134] The ethylene–vinyl acetate copolymers form homogeneous mixtures with PVC, provided that their vinyl acetate content is in the range from 65 to 70 mole %.[135] An analogous "compatibility window" has been observed in the blending of PVC with butyl acrylate–acrylonitrile copolymers.[136] It has been established[137] that PMMA is compatible with the styrene–acrylonitrile copolymer containing between 9 and 27 mole % of acrylonitrile. According to other data,[138] PPO is incompatible with either PPCS or poly-*o*-chlorostyrene, but is compatible with their copolymer in the range of PS contents from 25 to 64 mole %.

Finally, an improvement of the compatibility of the polymer A with the polymer B can be achieved by replacing some of the monomer units in the macromolecule of the polymer B by those of the monomer A, i.e. by blending homopolymers with their copolymers or by blending statistical copolymers consisting of the same monomers but differing in composition. As in the previous two cases, the transition from compatibility to incompatibility occurs very sharply at a strictly defined ratio of the monomers. This has been shown in relation to the blending of statistical copolymers of different composition: styrene–acrylonitrile[139] and styrene–butadiene,[140] methyl methacrylate–butyl acrylate,[141] and butadiene–acrylonitrile.[142] It has been shown[143] that PMMA becomes incompatible with the copolymers of methyl methacrylate (MMA) with ethyl methacrylate (EMA) or butyl methacrylate (BMA) when the content of MMA in their macromolecules is less than 60%.[143]

Thermodynamic studies of the processes involving the blending of homopolymers with their copolymers[144,145] greatly expanded the existing ideas about the thermodynamics of the blending of polymers and demonstrated the possibility of the existence of several different thermodynamic situations, which are illustrated in Fig.1.

1. For strong interactions between the macromolecules of the blended polymers and for favourable steric configurations and conformations, ensuring the formation of strong ordered joint structures, negative enthalpies and entropies of mixing are observed and we have $|\Delta h| > |T\Delta s|$ and $\Delta g < 0$, i.e. the polymers are compatible over the entire composition

range. This is observed also in the blending of the polar polymers (CN–PMMA, CN–PVAC),[11,26] aromatic polymers whose macromolecules are capable of forming π-complexes,[146] and also in rubber–rubber systems.[100] In the latter case, the compatibility of the polymer is promoted by the dense joint packing of the flexible macromolecules, ensuring a strong dispersion interaction on which the π–π′ interaction of the electrons of the double bonds is superimposed. The limiting case in this situation involves the formation of polycomplexes, for example the polycomplexes of polyacrylic acids with poly(vinyl alcohol) and PAA–PEO polycomplexes.[127]

Negative values of all the parameters of mixing are also observed for these systems and on the curves representing their concentration dependence there are singular points corresponding to a chemical compound with a stoichiometric component ratio (Fig.1*b*).

2. The blending of polymeric components is accompanied, as in the previous case, by a decrease of the enthalpy and entropy, but the values of $T\Delta s$ and Δh either cancel out, whereupon $\Delta g \cong 0$, or $|T\Delta s| > |\Delta h|$ and $\Delta g > 0$ (Figs.1*c* and 1*d*). This situation is characteristic of the blending of PVC with the copolymers of vinyl chloride (VC) and vinyl acetate (VAC),[145] containing 17.1 and 28.5 wt.% VAC, which is accompanied by the evolution of heat and a decrease of entropy as a consequence of the formation of hydrogen and EDA bonds between the macromolecules of PVC and the copolymers. However, the miscibility of PVC with these copolymers is limited and the positive Δg increase with increase of the content of VA units in the copolymer macromolecule.

3. All the thermodynamic parameters of mixing are positive (Fig.1*e*), i.e. the components are thermodynamically compatible over the entire composition range, since processes leading to the disruption of the structure, accompanied by an increase of entropy and enthalpy, predominate. A typical example of this situation is provided by the PMMA–PBMA system, for which $\partial^2 g/\partial \omega_2^2 < 0$ (ω_2 is the weight fraction of component 2), i.e. it is thermodynamically unstable.[26]

4. The compatibility of the components can be observed for positive values of Δh and Δs (Fig.1*f*). This has been noted in the blending of the oligomeric nitrile rubber SKN-40 with the ED-20 epoxy-resin.[77] The combinatorial entropy of mixing, which can be significant for oligomers, plays a role in this instance.

5. The polymeric components in one composition range are compatible ($\Delta g < 0$) while in another they are not ($\Delta g > 0$) (Fig.1*g*). Under these conditions, in the region of incompatibility ($\Delta g > 0$), the enthalpy and entropy of mixing are negative ($\Delta h < 0$ and $\Delta s < 0$), while in the region of compatibility ($\Delta g < 0$) these parameters are positive ($\Delta h > 0$ and $\Delta s > 0$). The antiparallel variation of the parameters, observed for example, for the system comprising PMMA and the copolymer of MMA and 26 wt.% BMA,[144] reflects the complexity of the processes occurring on blending the polymers, which is accompanied by the disruption of the structures of the components and the formation of new structures. The functional groups in PMMA and its copolymers are the same, but in BMA they are shielded by butyl groups. For this reason, PMMA molecules interact with one another more strongly than do the BMA units. If the copolymer macromolecules are inserted in the PMMA matrix, the energy expended on the disruption of the structure is greater than the energy gained in its interaction with PMMA. For this region, in the composition range enriched with PMMA, we have $\Delta h > 0$ and $\Delta s > 0$. Conversely, when PMMA molecules are inserted in the copolymer matrix, the energy gained is greater than the energy expended ($\Delta h < 0$ and $\Delta s < 0$). In the first case $T\Delta s > \Delta h$ and the components are compatible,

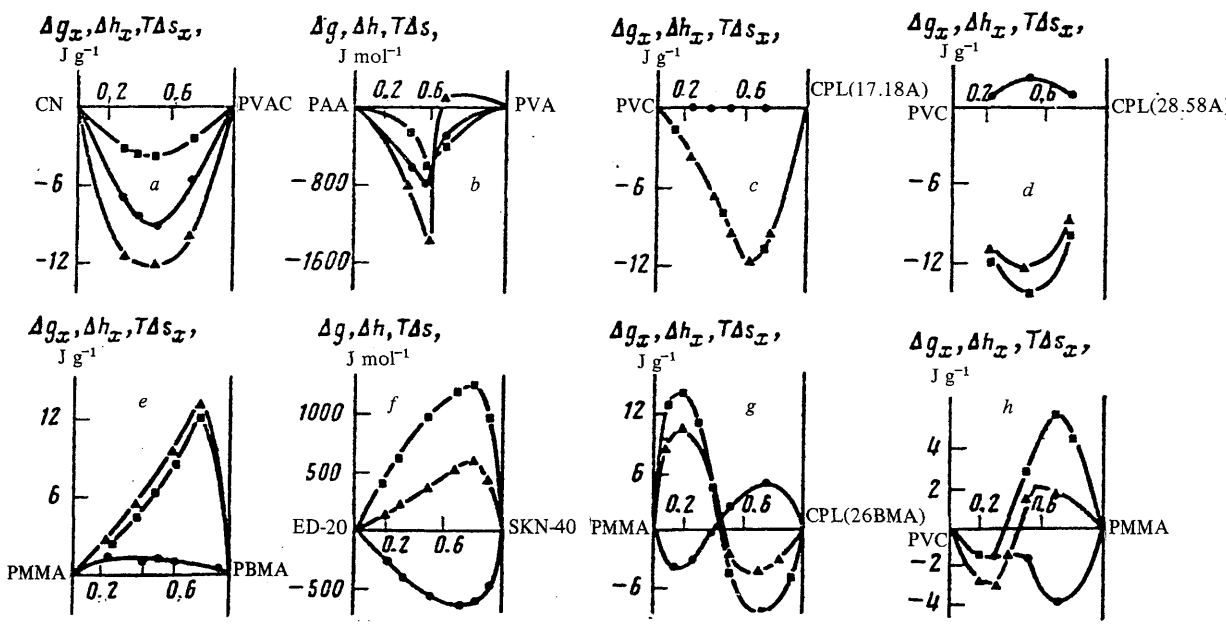


Figure 1. The possible cases of the dependence of the thermodynamic parameters of mixing on the composition of polymer blends (for the explanation, see text); the circles, triangles, and squares denote the values of Δg, Δh, and $T\Delta s$ respectively.

while in the second $|T\Delta s| > |\Delta h|$ and the blending of the components does not occur spontaneously.

It follows from Fig. 1*g* that the change in the sign of Δg (transition from compatibility to incompatibility) always occurs for a component ratio which is rigorously defined for each system, i.e. a "critical" value of this ratio, since this entails a change in the ratio of Δh and $T\Delta s$. This accounts for the repeatedly observed "critical" compatibility–incompatibility transitions in homopolymer–copolymer systems.[129,139–142]

6. The enthalpy and entropy of mixing have different signs for different component ratios, as in the previous system, but the Gibbs free energy of mixing is negative over the entire composition range. On the curve for the concentration dependence of Δg_x, there is then a convex section for which $\partial^2 g/\partial \omega_2^2 < 0$ (Fig. 1*h*). In this composition range, the system loses stability, but should separate into layers, which is usually observed for liquid–liquid systems.[17] However, as a consequence of the very high macroviscosity of polymer blends, layer formation does not occur and a colloidal two-phase system of this kind can exist indefinitely in a state of metastable equilibrium. This has been observed for the PVC–PMMA system[26,27] and for other similar systems.

IV. TEMPERATURE DEPENDENCE OF THE MISCIBILITY OF POLYMERS. PHASE DIAGRAMS

When the temperature is altered, single-phase binary liquid systems, including polymer solutions, undergo phase separation, which can be of the liquid–liquid type (amorphous separation) or liquid–crystal type (crystalline separation).[16,147] On the phase diagram, the boundary curve separating the homogeneous and heterogeneous regions is the binodal curve in the former case, while in the latter it is represented by the liquidus curve.

Depending on the nature of the components mixed, in amorphous phase separation binodal curves with upper and lower consolute temperatures (UCT and LCT), whose thermodynamic criteria are well known,[17] are observed. Thus for systems with UCT the excess enthalpies and entropies are positive ($h^e > 0$, $s^e > 0$) and the second derivatives of the average excess enthalpies and entropies with respect to composition are negative ($\partial^2 h/\partial \omega_2^2 < 0$, $\partial^2 s/\partial \omega_2^2 < 0$); $h^e < 0$ and $s^e < 0$ are characteristic of systems with LCT, whilst $\partial^2 h/\partial \omega_2^2 > 0$ and $\partial^2 s/\partial \omega_2^2 > 0$.

This applies fully to oligomer–oligomer and polymer–polymer systems. Consequently LCT are to be expected for systems characterised by the situations illustrated in Figs. 1*a* and 1*b*, i.e. polymer blends which are compatible at the usual temperatures should separate into layers on heating. Conversely, blends characterised by endothermic mixing and positive entropies of mixing, should have UCT, i.e. the miscibility of the polymers should increase on heating. All this should be reflected in the phase diagrams, which have been obtained for many polymer compositions by various methods.

The first phase diagram for a polymer–polymer system was obtained by Allen et al.[148] by the turbidity point method or Alekseev's method.[149] Subsequently this method was used also for other polymer compositions.

The phase diagrams for oligomer–oligomer and polymer–oligomer systems have been published in a number of communications[10,12,77,78,150–157] and some of these are presented in Fig. 2. They are characterised by binodal curves with UCT, limited mixing being observed even for oligomers with a very low molecular weight (MW). With increase in the MW of the components, the position of the UCT on the temperature scale changes in different ways. Thus the UCT increases steadily and the region of homogeneous mixing diminishes with increase in the MW of the components in the polydimethylsiloxane–polyisobutylene and polyethylene–polyisoprene systems (Figs. 2*a* and 2*b*). The miscibility of oligomers containing end groups capable of forming hydrogen bonds (OH and others) with non-polar polymers in the region of low MW improves with increase in MW and the UCT is reduced (Figs. 2*c* and 2*d*); this is associated with the decrease in the fraction of polar end groups, promoting the preferential interaction between like molecules. On further increase of MW, the end group no longer plays a decisive role and the UCT increases. In all cases at the usual temperatures, the components exhibit limited compatibility and their thermodynamic compatibility improves on heating. However, when polymers having very high molecular weights are blended, the region of homogeneous mixing is extremely small and the UCT lies in the unattainably high temperature range, i.e. does not occur in reality; this has been clearly demonstrated by Kuleznev.[3] The region of homogeneous mixing can be expanded and the UCT can be lowered by blending homopolymers with copolymers the macromolecules of which contain the residues of the same monomers. This is illustrated in Fig. 3, which presents the phase diagram for poly(vinyl chloride) with vinyl chloride–vinyl acetate copolymers.[145] The figure shows that the miscibility of PVC with the vinyl chloride–vinyl acetate copolymer containing 28.5 mole % of VAC is limited. The system exhibits a wide range of heterogeneous mixing, which narrows appreciably with decrease in the number of VAC units in the copolymer macromolecule.

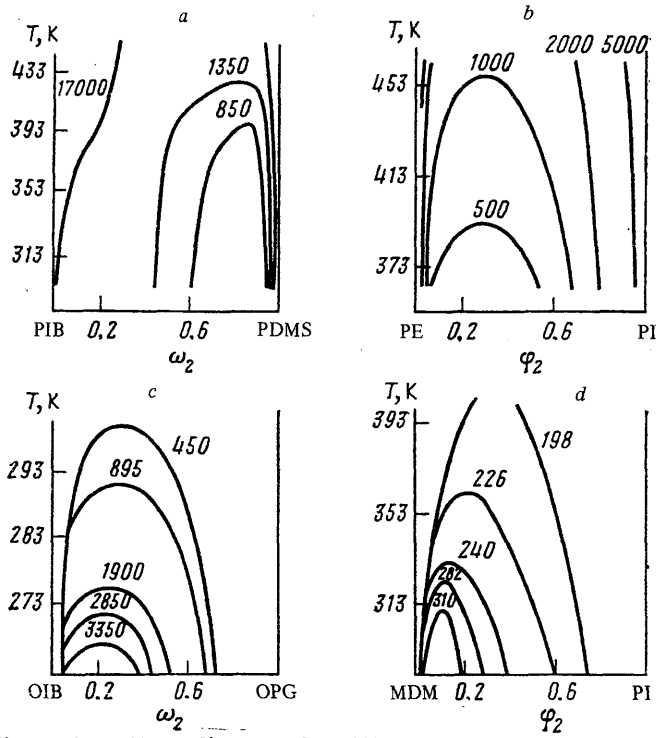


Figure 2. Phase diagrams for different systems: *a*) polyisobutylene (PIB, MW = 250)—polydimethylsiloxane (PDMS);[148] *b*) polyethylene (PE)—polyisoprene (PI, MW = 220 000);[154] *c*) oligoisobutylene (OIB, MW = 114)—oligo(propylene glycol) (OPG);[150] *d*) *p*-methylene dimethacrylate (MDM)—polyisoprene (MW = 220 000);[154] the numerals opposite the curves denote the molecular weight of the second component.

Polymers between the macromolecules where there is a possibility of specific interaction behave differently. At the usual temperatures they are miscible but their thermodynamic compatibility becomes impaired on heating and they are characterised by LCT. This was first predicted theoretically for polymer–polymer systems in two communications[8,13] and has been demonstrated experimentally for many polymer compositions (Table 4).

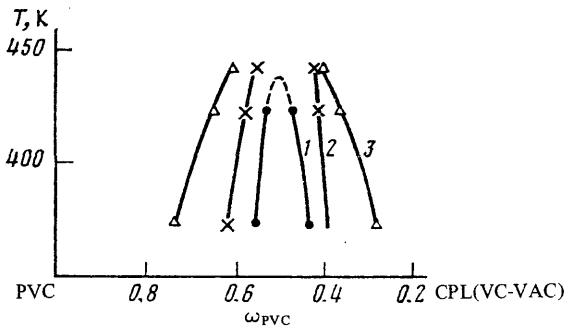


Figure 3. Phase diagram for blends of PVC with vinyl chloride–vinyl acetate copolymers containing different amounts of the latter (wt.%): *1*) 9.2; *2*) 17.1; *3*) 28.5.[145]

All that has been described above shows that the thermodynamic compatibility of polymers is promoted by the possibility of forming combined structures and by strong energetic interactions between their macromolecules. Amorphous oligomers and polymers whose macromolecules contain no functional group are incapable of specific interactions and for this reason their compatibility is as a rule limited over a wide temperature range. Their compatibility improves on heating. The compatibility of non-polar and weakly polar crystalline polymers with one another and with non-crystalline polymers is poor. Classical examples are provided by blends of polyethylene with polyisobutylene[4,134] and by blends of stereoregular rubbers—the polyisoprene and polybutadiene rubbers.[4] This can be explained by the impossibility of forming a common crystal lattice.

However, it is by no means permissible to draw from this the conclusion that the incompatibility of polymers is a rule, as has been assumed since the studies by Dobry and Boyer-Kamenoki.[172] By selecting polymers with functional groups having the opposite properties, between which there is a possibility of the formation of hydrogen bonds or electron-donor bonds, and also by reducing the size of the alkyl moieties shielding these groups, it is possible to create specifically thermodynamically stable polymer compositions, a procedure which should be followed by investigators and technologists in practice. Such compositions lose their thermodynamic stability on heating, i.e. they exhibit LCT and they must be obtained at temperatures below their LCT.

Table 4. Phase diagrams for polymer–polymer systems.

First component	M_1	Second component	M_2	Method*	Type and position of consolute temperature	Refs.
Poly(vinylidene fluoride)	88 000	poly(ethyl methacrylate)	762 000	M.T.P.	LCT; 480 K	[110]
Poly(vinylidene fluoride)	88 000	poly(methyl acrylate)	—	M.T.P.	LCT; 560 K	[110]
Poly(vinylidene fluoride)	88 000	poly(ethyl acrylate)	—	M.T.P.	LCT; 420 K	[110]
Poly-ε-caprolactone	10 000—40 000	polycarbonate	29 200	M.T.P.	LCT; 533–546 K	[110]
Poly(2,2-dimethyl-1,3-propylene succinate)	—	polyhydroxyester of bisphenol A	23 000	M.T.P.	LCT; 440 K	[158]
Poly(2,2-dimethyl-1,3-propylene adipate)	—	polyhydroxyester of bisphenol A	23 000	M.T.P.	LCT; 380 K	[158]
Poly(methyl vinyl ether)	51 500	polystyrene	10 000—200 000	M.T.P.	LCT; 370–480 K	[8,159]
Copolymer of styrene with 28% of acrylonitrile	88 600	poly(methyl methacrylate)	45 600	M.T.P.	LCT; 420 K	[160]
Copolymer of styrene with 28% of acrylonitrile	88 600	poly(ethyl methacrylate)	438 000	M.T.P.	LCT; 465 K	[161]
Copolymer of styrene with 28% of acrylonitrile	88 600	polycaprolactone	2 240	M.T.P.	LCT; 360 K	[8]
Copolymer of α-methylstyrene with 30% of acrylonitrile	57 000	poly(methyl methacrylate)	20 000—1 000 000	M.T.P.	LCT; 430–480 K	[162]
Copolymer of α-methylstyrene with 30% of acrylonitrile	57 000	poly(ethyl methacrylate)	438 000	M.T.P.	LCT; 440 K	[162]
Copolymer of *o*-chlorostyrene with 47% of *p*-chlorostyrene	220 000	poly(phenylene oxide)	17 000	D.N.P.	LCT; 550 K	[138]
Copolymer of styrene with 46% of *p*-fluorostyrene	52 000	poly(phenylene oxide)	16 900	D.N.P.	LCT; 578 K	[163]
Copolymer of acrylonitrile, butadiene, and styrene	—	poly(methyl methacrylate)	100 000	L.M.	LCT; 413 K	[164]
Polyethylene	29 000	polyisobutylene	1 800 000	L.M.	LCT; 363 K	[164]
Poly(vinyl nitrate)	—	poly(methyl methacrylate)	690 000	D.N.P.	LCT; 330 K	[165]
Chlorinated polyethylene (chlorine content 42%)	300 000	poly(vinyl chloride)	450 000	D.N.P., O.M.,E.M.	LCT; 400 K	[166]
Chlorinated polyethylene (chlorine content 27.4%)	15 200	poly(methyl methacrylate)	56 000	L.M.	UCT; 340 K; LCT; 353 K	[167]
Chlorinated polyethylene (chlorine contents 49.8 and 51.6%)	20 800—25 300	poly(methyl methacrylate)	12 200—72 800	L.M.	LCT; 370–410 K	[168]
Chlorinated polyethylene (chlorine contents 39.1 and 61.0%)	12 000	poly(methyl methacrylate)	64 000	E.-P. X.S.M.	**	[169]
Poly(vinyl chloride)	140 000	poly(methyl methacrylate)	64 000—726 000	E.-P.X.S.M.	***	[95, 156]
Poly(vinylidene fluoride)	65 000	poly(methyl methacrylate)	104 000	E.-P.X.S.M.	488 K	[170]
Copolymer of butadiene with 30% of styrene	—	*cis*-polybutadiene	—	D.N.P.	UCT; 423 K	[171]
Natural rubber	236 000	divinyl rubber	253 000	C.G.C.	LCT; 360 K	[100]
Ethylene-propylene rubber (SKEPT)	63 000	fluororubber	1 000 000	C.G.C.	UCT; 620 K	[100]

*Designations of the methods used to determine the phase diagrams: M.T.P.—method of turbidity points; D.N.P.—determination of the number of phases in the system from T_g; L.M.—light scattering method; O.M.—optical microscopy; E.M.—electron microscopy; E.-P.X.S.M.—electron-probe X-ray spectroscopic microanalysis; C.G.C.—calculation from gas-chromatographic data.

**The solubility improves on raising the temperature; UCT above 433 K.

***The solubility improves on raising the temperature; UCT above 470 K.

REFERENCES

1. J.A.Manson and L.H.Sperling, "Polymer Blends and Composites" (Translated into Russian), Izd.Khimiya, Moscow, 1979, p.60.
2. O.Olabisi, L.M.Robeson, and M.T.Shaw, in "Polymer–Polymer Miscibility", Acad.Press, New York–London–Toronto–Sydney–San Francisco, 1979, p.19.
3. V.N.Kuleznev, in "Smesi Polimerov" (Polymer Blends), Izd.Khimiya, Moscow, 1980, p.7.
4. D.R.Paul and S.Newman (Editors), "Polymer Blends" (Translated into Russian), Izd.Mir, Moscow, 1981.
5. A.E.Nesterov and Yu.S.Lipatov, in "Termodinamika Rastvorov i Smesei Polimerov" (Thermodynamics of Polymer Solutions and Polymer Blends), Izd.Naukova Dumka, Kiev, 1984, p.300.
6. S.Krause, J.Macromol.Sci.: Rev.Macromol.Chem., 1972, **C7**, 251.
7. V.N.Kuleznev and L.S.Krokhina, Uspekhi Khim., 1973, **42**(7), 1278 [Russ.Chem.Rev., 1973(7)].
8. L.P.McMaster, Macromolecules, 1973, **6**, 760.
9. V.N.Kuleznev, in "Mnogokomponentnye Polimernye Sistemy" (Multicomponent Polymer Systems) (Edited by R.F.Gold), Izd.Khimiya, Moscow, 1974, p.8.
10. R.Koningsveld, L.A.Kleintjens, and H.M.Schoffellers, Pure Appl.Chem., 1974, **39**, 1.
11. A.A.Tager, Vysokomol.Soed., 1977, **19A**, 1659.
12. R.Koningsveld and L.A.Kleintjens, J.Polym.Sci.: Polym.Symp., 1977(61), 221.
13. D.Patterson and A.Robard, Macromolecules, 1978, **11**, 690.
14. T.J.Nishi, Macromol.Sci.: Phys., 1980, **B17**, 517.
15. D.R.Paul and J.W.Barlow, J.Macromol.Sci.: Macromol. Chem., 1980, **C18**, 109.
16. A.A.Tager, in "Fizikokhimiya Polimerov" (The Physical Chemistry of Polymers), Izd.Khimiya, Moscow, 1978, p.471.
17. I.Prigogine and R.Defay, in "Chemical Thermodynamics" (Translated into Russian), Izd.Nauka, Novosibirsk, 1966, p.510.
18. T.K.Kwei, T.Nishi, and R.F.Roberts, Macromolecules, 1974, **7**, 667.
19. R.L.Scott, J.Chem.Phys., 1949, **17**, 279.
20. B.A.Golender, Z.G.Sagdieva, Sh.Fuzailov, and S.A.Tashmukhamedov, Vysokomol.Soed., 1976, **18B**, 688.
21. A.A.Tager and V.S.Blinov, Vysokomol.Soed., 1978, **20B**, 657.
22. D.D.Davis, G.N.Taylor, and T.K.Kwei, J.Appl. Polym.Sci., 1981, **26**, 2001.
23. A.A.Tager, Vysokomol.Soed., 1972, **14A**, 2690.
24. A.A.Tager, T.I.Scholohovich, and J.S.Bessonov, Europ.Polym.J., 1975, **11**, 231.
25. L.V.Adamova, A.A.Tager, N.D.Karpova, N.T.Nerush, S.N.Salazkin, Ya.S.Vygodskii, and I.A.Bulgakova, Vysokomol. Soed., 1979, **21A**, 388.
26. A.A.Tager, T.I.Sholokhovich, I.M.Sharova, L.V.Adamova, and Yu.S.Bessonov, Vysokomol.Soed., 1975, **17A**, 2766.
27. T.I.Sholokhovich, Abstract of Candidate's Thesis in Chemical Sciences, The Gorky Urals State University, Sverdlovsk, 1975.
28. I.N.Razinskaya, L.V.Adamova, L.S.Krokhina, V.A.Ageeva, and V.D.Mal'kov, Vysokomol.Soed., 1979, **21B**, 47.
29. L.V.Karabanova and N.A.Chesnokova, Dokl.Akad. Nauk Ukrain.SSR, 1980, **20B**(11), 47.
30. Yu.S.Lipatov, L.V.Karabanova, T.S.Khramova, and L.M.Sergeeva, Vysokomol.Soed., 1978, **20A**, 46.
31. Yu.S.Lipatov, L.V.Karabanova, L.M.Sergeeva, and E.A.Gorichko, Vysokomol.Soed., 1982, **24A**, 110.
32. S.A.Tashmukhamedov, V.I.Goloborod'ko, Kh.I.Akbarov, M.M.Gullyanov, Sh.A.Azizov, and R.S.Tillyaev, Vysokomol.Soed., 1981, **23A**, 670.
33. L.Z.Rogovina, A.E.Chalykh, L.V.Adamova, A.D.Aliev, E.A.Nekhaenko, P.M.Valetskii, G.L.Slonimskii, and A.A.Tager, Vysokomol.Soed., 1980, **22A**, 428.
34. A.A.Tager, L.V.Adamova, L.K.Kolmakova, N.N.Nokhrina, P.M.Valetskii, L.Z.Rogovina, and I.P.Storozhuk, Vysokomol.Soed., 1982, **24A**, 2040.
35. A.A.Tager and L.V.Adamova, in "Sintez i Svoistva Bloksopolimerov" (The Synthesis and Properties of Block Copolymers), Izd.Naukova Dumka, Kiev, 1983, p.54.
36. I.N.Razinskaya, A.A.Tager, V.A.Izvozchikova, L.V.Adamova, and A.P.Shtarkman, Vysokomol.Soed., 1985, **27A**, 1633.
37. D.I.Meier, J.Polym.Sci.: Polym.Symp., 1969(26), 81.
38. S.Krause, Macromolecules, 1970, **3**, 84.
39. E.A.Guggenheim, in "Modern Thermodynamics. An Account Based on Gibbs' Method" (Translated into Russian), Goskhimizdat, Leningrad–Moscow, 1941, p.145.
40. A.I.Rusanov, in "Termodinamika Poverkhnostnykh Yavlenii" (Thermodynamics of Surface Phenomena), Izd.Leningrad.Gos.Univ., Leningrad, 1960, p.9.
41. S.Ono and S.Kondo, "Molecular Theory of Surface Tension in Liquids" (Translated into Russian), Inostr. Lit., Moscow, 1963, p.13.
42. A.W.Adamson, in "Physical Chemistry of Surfaces" (Translated into Russian), Izd.Mir, Moscow, 1979, p.44.
43. S.Wu, J.Macromol.Sci.: Rev.Macromol.Chem., 1974, **C10**, 1.
44. V.N.Kuleznev, Kolloid.Zhur., 1977, **40**, 407.
45. Yu.S.Lipatov, Vysokomol.Soed., 1978, **20A**, 3.
46. Yu.S.Lipatov, in "Mezhfaznye Yavleniya v Polimerakh" (Interfacial Phenomena in Polymers), Izd.Naukova Dumka, Kiev, 1980, p.211.
47. V.G.Berezkin, V.R.Alishaev, and I.B.Nemirovskaya, in "Gazovaya Khromatografiya v Khimii Polimerov" (Gas Chromatography in Polymer Chemistry), Izd. Nauka, Moscow, 1972, p.287.
48. A.E.Nesterov and Yu.S.Lipatov, "Obrashchennaya Gazovaya Khromatografiya v Termodinamike Polimerov" (Reversed Gas Chromatography in the Thermodynamics of Polymers), Izd.Naukova Dumka, Kiev, 1976, p.127.
49. J.M.Braun and J.E.Guillet, Adv.Polym.Sci., 1976, **21**, 107.
50. D.E.Gray, Progr.Polym.Sci., 1977, **5**, 60.
51. O.Smidsröd and J.E.Guillet, Macromolecules, 1969, **2**, 272.
52. Ya.I.Gerasimov (Editor), in "Kurs Fizicheskoi Khimii" (Textbook of Physical Chemistry), Izd. Khimiya, Moscow, 1969, p.518.
53. J.M.Braun and J.E.Guillet, Macromolecules, 1975, **8**, 557.
54. M.S.Vigdergauz and R.I.Izmailov, "Primenenie Gazovoi Khromatografii dlya Opredeleniya Fiziko-khimicheskikh Svoistv Veshchestv" (Application of Gas Chromatography in the Determination of the Physicochemical Properties of Substances), Izd.Nauka, Moscow, 1970, p.69.
55. A.Waksmundzki and L.Suprynowicz, J.Chromatog., 1965, **18**, 232.
56. A.Waksmundzki and L.Suprynowicz, in "Gazovaya Khromatografiya. Trudy III Vsesoyuznoi Konferentsii po Gazovoi Khromatografii" (Gas Chromatography.

Proceedings of the IIIrd All-Union Conference on Gas Chromatography), Dzerzhinsk, 1966, p.260.
57. M.S.Vigdergauz and V.V.Pomazanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 2835.
58. R.N.Novitskaya and M.S.Vigdergauz, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2798.
59. D.D.Deshpande, D.Patterson, H.P.Schreiber, and C.S.Su, Macromolecules, 1974, 7, 530.
60. I.Prigogin, A.Bellemans, and R.Naar-Colin, J.Chem. Phys., 1957, **26**, 751.
61. G.Delmas, D.Patterson, and T.Samsynski, J.Polym. Sci., 1962, **57**(165), 79.
62. B.E.Eichinger and P.J.Flory, Trans.Faraday Soc., 1968, **64**, 2035.
63. T.I.Kirillova, Abstract of Candidate's Thesis in Chemical Sciences, Gorky Urals State University, Sverdlovsk, 1963.
64. P.Kratochvil, J.Polym.Sci.: Polym.Symp., 1975(50), 487.
65. P.Kratochvil, J.Vorlicek, D.Strakova, and Z.Tuzar, J.Polym.Sci.: Polym.Phys.Ed., 1975, **13**, 2321.
66. P.Kratochvil, D.Strakova, and Z.Tuzar, Brit.Polym. J., 1979, **9**(9), 217.
67. W.A.Kruse, R.G.Kirste, J.Haas, B.J.Schmitt, and D.J.Stein, Macromol.Chem., 1976, **177**, 1145.
68. G.D.Wingmal, H.R.Child, and F.Li-Aravena, Polymer, 1980, **21**, 131.
69. R.P.Kambour, R.C.Bapp, A.Maconnachie, and W.J.MacKnight, Polymer, 1980, **21**, 133.
70. G.Hadziioannou, R.Stein, and J.Higgins, Amer.Chem. Soc.Polym.Prepr., 1983, **24**(2), 213.
71. G.H.Ballard, M.G.Rayner, and J.Schelten, Polymer, 1976, 17, 641.
72. J.Jelenic, R.G.Kirste, B.J.Schmitt, and S.Schmitt-Strecker, Macromol.Chem., 1979, **180**, 2057.
73. A.E.Chalykh, Yu.M.Mikhailov, N.N.Avdeev, and Yu.M.Lotmentsev, Dokl.Akad.Nauk SSSR, 1979, **247**, 890.
74. G.F.Roginskaya, V.P.Volkov, A.E.Chalykh, N.N.Avdeev, and B.A.Rozenberg, Vysokomol.Soed., 1979, **21A**, 2111.
75. N.I.Druz', A.E.Kreitus, and A.E.Chalykh, Izv. Akad.Nauk Latv.SSR, 1981(2), 199.
76. V.P.Volkov, G.F.Roginskaya, A.E.Chalykh, and B.A.Rozenberg, Uspekhi Khim., 1982, **51**(10), 1733 [Russ.Chem.Rev., 1982(10)].
77. G.F.Roginskaya, V.P.Volkov, A.I.Kuzaev, A.E.Chalykh, and B.A.Rozenberg, Vysokomol.Soed., 1984, **26A**, 1020.
78. A.E.Chalykh and I.N.Sapozhnikova, Uspekhi Khim., 1984, **53**(11), 1827 [Russ.Chem.Rev., 1984(11)].
79. G.Gee, Quart.Rev.Chem.Soc., 1947, **1**(1), 265.
80. P.J.Flory, B.E.Eichinger, and R.A.Orwoll, Macromolecules, 1968, **1**, 287.
81. A.A.Tager, Vysokomol.Soed., 1984, **26A**, 659.
82. B.P.Shtarkman, "Plastifikatsiya Polivinilkhlorida" [The Plasticisation of Poly(vinyl chloride)], Izd. Khimiya, Moscow, 1975, p.248.
83. O.Olabisi, Macromolecules, 1975, **8**, 316.
84. D.J.Walsh and J.G.McKeown, Polymer, 1980, 21, 1330.
85. J.V.Koleske and R.D.Lundberg, J.Polym.Sci.: Polym. Phys.Ed., 1969, **A2**, 795.
86. J.W.Schurer, A.de Boer, and G.Challa, Polymer, 1975, **16**, 201.
87. L.M.Robeson, J.Polym.Sci.: Polym.Letters, Ed., 1978, **16**, 261.
88. M.Aubin and R.E.Prud'homme, Macromolecules, 1980, **13**, 365.
89. M.Aubin and R.E.Prud'homme, J.Polym.Sci.: Polym. Phys.Ed., 1981, **19**, 1245.
90. J.J.Ziska, J.W.Barlow, and D.R.Paul, Polymer, 1981, **22**, 918.
91. M.H.Coleman and J.Zarian, J.Polym.Sci.: Polym. Phys.Ed., 1979, **17**, 837.
92. M.H.Coleman and D.F.Varnell, J.Polym.Sci.: Polym. Phys.Ed., 1980, **18**, 1403.
93. D.F.Varnell and M.H.Coleman, Polymer, 1981, **22**, 1324.
94. D.J.Walsh and J.G.McKeown, Polymer, 1980, 21, 1335.
95. A.E.Chalykh and I.N.Sapozhnikova, Vysokomol. Soed., 1979, **21A**, 1664.
96. I.N.Razinskaya, B.P.Shtarkman, L.I.Batueva, B.S.Tyves, and M.N.Shlykova, Vysokomol.Soed., 1979, **21A**, 1860.
97. W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972, p.480.
98. J.S.Rowlinson, in "Liquids and Liquid Mixtures", Butterworths Sci.Publ., London, 1959, p.171.
99. Yu.A.Panshin, S.G.Malkevich, and U.S.Dunaevskaya, "Ftoroplasty" (Fluorinated Plastics), Izd.Khimiya, Leningrad, 1978.
100. T.I.Kirillova, A.A.Tager, and R.Sh.Frenkel', Vysokomol.Soed., 1984, **26A**, 1584.
101. J.S.Nolands, N.N.-C.Hsu, R.Saxon, and J.M.Schmitt, Advances in Chemistry Series, 1971(99), 15.
102. D.C.Wahrmund, R.E.Bernstein, J.W.Barlow, and D.R.Paul, Polym.Eng.Sci., 1978, **18**, 677.
103. T.Nishi and T.T.Wang, Macromolecules, 1975, **8**, 909.
104. T.K.Kwei, G.D.Patterson, and T.T.Wang, Macromolecules, 1976, **9**, 780.
105. D.J.Hourston and I.D.Hughes, Polymer, 1977, 18, 1175.
106. E.Roerdink and G.Challa, Polymer, 1978, **19**, 173.
107. D.C.Douglass and V.J.McBrierty, Macromolecules, 1978, **11**, 766.
108. R.E.Bernstein, D.R.Paul, and J.W.Barlow, Polym. Eng.Sci., 1978, **18**, 683.
109. R.E.Bernstein, D.C.Wahrmund, J.W.Barlow, and D.R.Paul, Polym.Eng.Sci., 1978, **18**, 1220.
110. R.E.Bernstein, C.A.Cruz, D.R.Paul, and J.W.Barlow, Macromolecules, 1977, **10**, 681.
111. G.Di Paola-Baranyi, S.J.Fletcher, and P.Degre, Macromolecules, 1982, **15**, 885.
112. D.R.Paul, J.W.Barlow, R.E.Bernstein, and D.C.Wahrmund, Polym.Eng.Sci., 1978, **18**, 1225.
113. J.D.Roberts and M.C.Caserio, in "Basic Principles of Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1968, Vol.1, p.460.
114. D.C.Wahrmund, D.R.Paul, and J.W.Barlow, J.Appl. Polym.Sci., 1978, **22**, 2155.
115. T.R.Nassar, D.R.Paul, and J.W.Barlow, J.Appl. Polym.Sci., 1979, **23**, 85.
116. R.N.Mohn, D.R.Paul, J.W.Barlow, and C.A.Cruz, J.Appl.Polym.Sci., 1979, **23**, 575.
117. C.A.Cruz, D.R.Paul, and J.W.Barlow, J.Appl. Polym.Sci., 1979, **23**, 589.
118. C.A.Cruz, D.R.Paul, and J.W.Barlow, J.Appl. Polym.Sci., 1979, **24**, 2102.
119. C.A.Cruz, J.W.Barlow, and D.R.Paul, J.Appl. Polym.Sci., 1979, **24**, 2399.
120. C.A.Cruz, J.W.Barlow, and D.R.Paul, Macromolecules, 1979, **12**, 726.
121. A.A.Tager, Yu.S.Bessonov, E.Ya.Sivkova, V.A.Anufriev, Ya.S.Vygodskii, and S.N.Salazhin, Vysokomol. Soed., 1979, **21A**, 2136.

122. W.R.Moore, Symposium, "Cellulose and Its Derivatives" (Edited by N.Bicles and L.Segal) (Translated into Russian), Izd.Mir, Moscow, 1974, p.412.
123. M.I.Shakhparonov, "Vvedenie v Sovremennuyu Teoriyu Rastvorov" (Introduction to the Modern Theory of Solutions), Izd.Vys.Shkola, Moscow, 1976, p.102.
124. V.P.Belousov and A.G.Morachevskii, in "Teploty Smesheniya Zhidkostei" (Heats of Mixing of Liquids), Izd.Khimiya, Leningrad, 1970, p.30.
125. E.A.Bekturov and L.A.Bimendina, in "Interpolimernye Kompleksy" (Interpolymer Complexes), Izd.Nauka, Alma-Ata, 1977, p.264.
126. B.A.Kabanov and I.M.Papisov, Vysokomol.Soed., 1979, **21A**, 243.
127. A.A.Tager, L.V.Adamova, and L.I.Morkvina, Vysokomol.Soed., 1983, **25A**, 1413.
128. A.R.Schulz and B.M.Beach, Macromolecules, 1974, **7**, 902.
129. J.R.Fried, F.E.Karasz, and W.J.MacKnight, Macromolecules, 1978, **11**, 150.
130. R.Vucovic, F.E.Karasz, and W.J.MacKnight, J.Appl. Polym.Sci., 1983, **28**, 219.
131. D.Feldman, A.Crusos, and C.J.Unggureanu, Macromol.Sci.: Phys., 1977, **B14**, 573.
132. R.A.Reznikova, A.F.Zaionchkovskii, and S.S.Voyutskii, Kolloid.Zhur., 1953, **15**, 108.
133. R.S.Kiseleva, Kh.G.Mindiarov, V.S.Ionkin, E.F.Gubanov, G.G.Ushakova, F.A.Golikova, Yu.V.Zelenev, and V.A.Voskresenskii, Vysokomol.Soed., 1972, **14A**, 2078.
134. Yu.K.Godovskii and N.P.Bessonov, Vysokomol.Soed., 1979, **21A**, 2293.
135. C.F.Hammer, Macromolecules, 1971, **4**, 69.
136. J.Piglowski and T.Skowronski, Angew.Makromol. Chem., 1980, **88**(1365), 165.
137. D.J.Stein, R.H.Jung, K.H.Illers, and H.Hendus, Angew.Makromol.Chem., 1974, **36**(520), 89.
138. P.Alexandrovich, F.E.Karasz, and W.J.MacKnight, Polymer, 1977, **18**, 1022.
139. G.E.Molau, J.Polym.Sci.: Polym.Letters.Ed., 1965, **B3**, 1007.
140. N.F.Bakeev, Z.F.Zharikova, Yu.N.Malinskii, and A.L.Izyumnikov, Vysokomol.Soed., 1977, **19B**, 832.
141. F.Kollinsky and G.Markert, Advances in Chemistry Series, 1971(99), 175.
142. V.R.Landi, Rubber Chem.and Technol., 1975, **45**, 222.
143. F.Amrani, Ju Ming Hung, and H.Morawetz, Macromolecules, 1980, **13**, 649.
144. A.A.Tager, V.S.Blinov, Yu.S.Bessonov, V.Yu.Khokhlev, D.I.Emel'yanov, and V.A.Myachev, Vysokomol. Soed., 1984, **26A**, 482.
145. V.S.Blinov, A.A.Tager, A.E.Chalykh, T.A.Rodionova, A.G.Kronman, and A.E.Rubtsov, Vysokomol.Soed., 1985, **27A**, 2286.
146. A.A.Tager, Yu.S.Bessonov, and I.V.Rudenko, Vysokomol.Soed., 1980, **22B**, 436.
147. S.P.Papkov, in "Ravnovesie Faz v Sisteme Polimer–Rastvoritel'" (Phase Equilibrium in the Polymer–Solvent System), Izd.Khimiya, Moscow, 1981, p.20.
148. G.Allen, G.Gee, and J.P.Nicholson, Polymer, 1961, **2**, 8.
149. V.F.Alekseev, Zhur.Russ.Fiz.-Khim.Obshch., 1877, **9**(1), 208.
150. B.A.Wolf and G.Blaum, J.Polym.Sci.: Polym.Symp., 1977(61), 251.
151. S.Nojima and T.Nose, Polymer J., 1982, **14**(4), 269.
152. A.Friday, D.R.Cooper, and C.Booth, Polymer, 1977, **18**, 171.
153. T.T.Wang and H.M.Zupko, J.Appl.Polym.Sci., 1981, **26**, 2391.
154. A.E.Chalykh, N.N.Avdeev, A.A.Berlin, and S.M.Mezhikovskii, Dokl.Akad.Nauk SSSR, 1978, **238**, 893.
155. A.E.Chalykh, N.N.Avdeev, and S.M.Mezhikovskii, Vysokomol.Soed., 1980, **22B**, 464.
156. A.E.Chalykh and I.N.Sapozhnikova, Vysokomol. Soed., 1981, **23B**, 169.
157. A.V.Kotova, A.E.Chalykh, N.N.Avdeev, and S.M.Mezhikovskii, Vysokomol.Soed., 1982, **24A**, 460.
158. J.E.Harris, S.H.Goh, D.R.Paul, and J.W.Barlow, J.Appl.Polym.Sci., 1982, **27**, 839.
159. T.Nishi and T.K.Kwei, Polymer, 1975, **16**, 285.
160. L.P.MacMaster, Advances in Chemistry Series, 1975(142), 43.
161. S.H.Goh, D.R.Paul, and J.W.Barlow, Polym.Eng. Sci., 1978, **22**, 34.
162. J.S.Chiou, D.R.Paul, and J.W.Barlow, Polymer, 1982, **23**, 1543.
163. R.Vukovic, V.Kuresevic, F.E.Karasz, and W.J.MacKnight, Thermochim.Acta, 1982, **54**, 349.
164. V.M.Andreeva, I.S.Tyukova, A.A.Tager, N.A.Glazovskaya, and L.V.Zaitseva, Vysokomol.Soed., 1985, **27B**, 526.
165. S.Akiyama, I.Katsumoto, M.Nakata, and R.Kaneko, Kobunshi ronbunshi, 1976, **33**(4), 238; Ref.Zhur. Khim., 19S157 (1976).
166. C.P.Doube and D.J.Walsh, Polymer, 1979, **20**, 1115.
167. D.J.Walsh, Shi Laighe, and Chai Zhikuan, Polymer, 1981, **22**, 1005.
168. D.J.Walsh, J.S.Higgins, Chai Zhikuan, Polymer, 1982, **23**, 336.
169. A.E.Chalykh and I.N.Sapozhnikova, Dokl.Akad. Nauk SSSR, 1983, **270**, 382.
170. A.E.Chalykh, A.D.Aliev, and A.E.Rubtsov, Vysokomol.Soed., 1983, **25A**, 2217.
171. S.S.Pestov, V.N.Kuleznev, and V.A.Shershnev, Kolloid.Zhur., 1978, **40**, 705.
172. A.Dobry and F.Boyer-Kamenoki, J.Polym.Sci., 1947, **2**, 90.

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