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Intermolecular Interaction in Solutions of Graft Copolymers

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Experimental data for the intermolecular interaction in block and graft copolymers and also the relation between their molecular structure and the properties of their solutions are examined systematically and critically. Problems concerning micelle formation, the microstructure, the conformation, and especially the thermodynamic properties of solutions of graft copolymers are described and the characteristic features of the influence of individual factors on the properties of solutions of graft copolymers are discussed.
The bibliography includes 100 references.

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I. INTRODUCTION

The macromolecules of graft copolymers consisting of two or more polymeric sections of different nature, linked chemically to one another, are branched, in contrast to the statistical and block copolymers which have a linear structure. The combination of the properties of several macromolecular compounds in graft copolymers is determined by the specific features of their molecular structure. The properties of graft copolymers are determined by the number and molecular weight of the grafted branches, the molecular weight of the main chain, their molecular weight distribution, and the inhomogeneity of the composition of the macromolecules, and also the nature of the main chain and the grafted branches, the degree of their compatibility, and the conformations of the macromolecules in the solvents employed. By altering the parameters enumerated above, it is possible to regulate the molecular and supermolecular structures and to impart to them the necessary properties. Graft copolymers have found industrial applications as impact resistant thermoelastic plastics, polymeric emulsifying agents, stabilisers for multicomponent polymer systems, membranes for reverse osmosis, etc. The two-phase structure of the polymers, caused by the separation of the microphases of the incompatible components into distinct domains (in the solid state), plays a significant role in the development of such products. The degree and nature of such separation depend on many factors, which were enumerated above. Numerous studies of the characteristic features of the formation of the two-phase structure of block copolymers, the ease of formation of which is determined by the linear structure of the macromolecules, have been described in the literature.

Studies of the macromolecular interaction in ternary systems have been analysed[1-5] and a number of communications have been devoted to different aspects of the intermolecular interaction in polymer blends.[6-20] The literature data on the microphase separation in block copolymers and the influence of various factors on their properties in solution and in the solid state have been analysed;[1,21] in addition reviews and monographs have been published.[22-34] The available literature data on the macromolecular interaction in graft copolymers require a systematic treatment and need to be surveyed. On the other hand, new studies on block copolymers, which also need to be surveyed, have been published in recent years.

II. MICROPHASE SEPARATION IN MULTICOMPONENT SYSTEMS

Numerous publications on studies of the structure of block copolymers[1,21,22,25,29] permit the conclusion that the incompatibility of the blocks in block copolymers promotes phase separation. This leads in its turn to the formation of microdomains, which are arranged regularly in space and form mesophases in the presence of a solvent. It has been noted[22,26] that the best methods for the investigation of such systems are low-angle X-ray scattering and electron microscopy, which have shown that the microdomains have the form of either lamellae, or cylinders, or spheres. The same conclusions concerning the phase separation of block copolymers have been reached by investigators who studied microphase separation by thermomechanical,[35-40] scanning calorimetric,[41,42] and sorption[43-45] methods. Investigation of the influence of the molecular structure of the block copolymer on the microphase separation have shown that, for the same molecular weight of the block copolymer, an increase in the number of blocks hinders separation into layers[35] and that the critical parameter of the interaction between blocks in "star-shaped" block copolymers is lower than for linear block copolymers.[46]

Since the microphase separation process begins to be manifested at the molecular level, the question of the dependence of the conformation of the macromolecule on the segregation factor χ_{AB}, which determines both the formation and the stability of the supercrystals, becomes significant.[8] In dilute solutions of block and graft copolymers the use of selective solvents or the addition of a precipitant to a copolymer solution causes the formation of micelles at the molecular level as a consequence of the intramolecular "precipitation" of the insoluble components. Different forms of the macromolecular micelles of block and graft copolymers in dilute and concentrated solutions have been described.[1,21,22] The characteristics of the formation of

monomolecular and polymolecular micelles from block and graft copolymers have been discussed and the influence of various factors on the micelle formation process has been examined in a number of investigations.[25,26,32-34,47-54]

The literature data on the micelle formation in block and graft copolymers do not provide an answer to the question how the molecular weight of the blocks or grafted branches influences the formation of monomolecular or polymolecular micelles. However, it has been noted that, as the number of block or grafted branches increases, only monomolecular micelles can be formed in solutions of copolymers, because a large number of block or grafted branches protects the nucleus of the micelle, which hinders the formation of polymolecular micelles. The nature of the solvent also influences the formation of micelles: in solvents which are "good" for both components of the copolymer, the microphase separation is impaired, while in selective solvents the heterocontacts between unlike segments are reduced to a minimum and the possibility of the formation of monomolecular or polymolecular micelles is sharply increased. These data confirm the finding that, with increase in the difference between the parameters of the thermodynamic interaction of the components of the copolymer with the solvent $\chi_{12} - \chi_{13} = \Delta\chi$ (the "$\Delta\chi$ effect"), the compability of the components is impaired, which leads to microphase separation in the copolymers and the formation of micelles.

Micelle formation by the macromolecules of block and graft copolymers is a very important factor, since, by using different solvent–precipitant systems, it is possible to regulate the type of micelle, which enables one to obtain "hard" or "soft" forms of the polymer.[21,22] Concentrated solutions of block copolymers form ordered mesomorphic phases resembling lyotropic liquid crystals. In reality these microheterogeneous highly ordered segregated domains, made up of blocks of one type, are typical of supercrystals.[1,8,21]

III. CHARACTERISTICS OF THE BEHAVIOUR OF GRAFT COPOLYMERS IN SOLUTION

In contrast to block copolymers, graft copolymers do not tend to form supercrystals owing to the branched structure of their macromolecules and steric hindrance. However, despite the branched macromolecular structure of copolymers, the possibility of the formation of highly organised structures of the type of dendrites as a consequence of strong specific interactions of the solvent with the grafted component via hydrogen bonding, leading to the unwinding of the grafted branches and the establishment of a definite order in the latter, has been demonstrated.[55]

It has been shown for graft poly(vinyl alcohol)–poly-2-vinylpyridine (PVA–P-2-VP), cellulose diacetate–polyacrylamide (CDA–PAA), and cellulose diacetate–poly-2-vinylpyridine (CDA–P-2-VP) graft copolymers[55-57] that an increase in the strength of donor–acceptor interactions of acetic acid molecules with PAA and P-2-VP chains causes the formation of structures of the "fern leaf" type with a distinct centre of growth, which become more ideal with increase in the content of the grafted polymer. This phenomenon is encountered fairly rarely for amorphous graft copolymers, because, under the usual conditions, the crystallisation of CDA is hindered by the breakdown of the regularity of the chain structure when some of the acetate groups are replaced by hydroxy-groups.

When solutions of the given copolymers in acetic acid are diluted, the intrinsic viscosity $[\eta]$ increases sharply, exceeding the value for the initial polymer severalfold. An even greater effect of this kind has been observed for the PVA–P-2-VP solution in formic acid, which indicates the occurrence of strong interactions of solvent molecules with the grafted chains, these being responsible for the uncoiling of the grafted chain and the sharp increase in the size of the coils. The weak temperature dependence of the viscosities of the solutions may be an indication of the stability of this conformation. In solvents without an affinity for the grafted branches (for example, in acetone), the values of $[\eta]$ for CDA–P-2-VP solutions initially decrease sharply with increasing content of the grafted P-2-VP and then remain almost unchanged. The different character of the variation of the intrinisic viscosities of solutions of graft copolymers in solvents of different nature can be readily accounted for by the characteristics of the supermolecular structure and the thermodynamic properties of the solutions. For example, the main structural element of the CDA–P-2-VP copolymers obtained from acetone solutions are globules with an indistinct aggregation, in contrast to the CDA network structures. The formation of globules is associated with the coiling up of the grafted branches of the copolymer, because P-2-VP does not dissolve in acetone. The postulated strong binding of solvent molecules by the grafted chains of the copolymer molecule is reflected in the sharp increase in the heats of solution of the CDA–P-2-VP graft copolymers in acetic acid and in the character of the variation of the Flory–Huggins interaction parameters,[55-57] calculated from sorption isotherms.

The poly(vinyl alcohol)–polyvinylpyrrolidinone (PVA–PVP) graft copolymers represent a combination of water-soluble polymers; they are known to be capable of entering into a complex formation reaction as a result of the formation of intermolecular hydrogen bonds between the hydroxy-groups of PVA and the carbonyl group of PVP (this has been confirmed by the large negative free energies of mixing of PVA and PVP [58]). A decrease of $[\eta]$ compared with the initial polymer, the absence of extrema on plots of the temperature dependence of viscosity, and also an increase of $[\eta]$ after the introduction of dimethylformamide (DMF) into the aqueous solution have been demonstrated for aqueous PVA–PVP solutions.[59] The possibility of the occurrence of specific intramolecular interactions in such systems is determined by the ability of the solvent to favour or hinder such interactions.

The differences between the behaviour of two types of macromolecules of graft copolymers based on chlorinated poly(vinyl chloride) (CPVC–PS, CPVC–PVAC†) can be traced from the variation of $[\eta]$ of their solutions in mixed solvents, one of which is selective or is a general precipitant.[56] The extremum in the variation of the viscosity with the composition of the mixed solvent, associated with the microphase separation of the branches of the graft copolymers, which is caused by the incompatibility of the main chain and the grafted chain, is observed only for CPVC–PS.[56] The observed extremum in the variation of $[\eta]$ with the composition of the mixed solvent for the CDA–PVAC, cellulose triacetate–poly(vinyl acetate) (CTA–PVAC), CDA–PVP, and CDA–PAA graft copolymers can be explained by the change in the conformational state of the macromolecules as a result of the rupture of the intramolecular hydrogen bonds.

The different types of behaviour in mixed acetone–methanol solvents of the CDA–PVAC and CDA–PVP graft copolymers are striking.[56] Whereas the variation of the viscosity for the CTA–PVAC system is determined mainly by the characteristics of the interaction of the molecules of the second

† Poly(vinyl acetate).

component of the mixture of solvents with the main copolymer chain, in the CDA–PVP system the influence of the interaction of the grafted branches with the methanol molecules is more pronounced. Furthermore, specific interactions of the type of hydrogen bonding are possible for both components of the CDA–PVP graft copolymers in the binary solvents investigated. The CDA–PAA graft copolymers, whose macromolecules contain hydroxy- and amide groups, also belong to such systems. In the acetic acid–water mixed solvent, the conformational state of the CDA and PAA macromolecule is determined by the different character of their interaction with acetic acid molecules. The behaviour of the graft copolymers in the acetic acid–water system combines a series of effects characteristic of the homopolymers and a distinct dependence of the effects on composition has been observed. Conformational changes in the macromolecules of graft copolymers in mixed solvents have also been observed by Trakhtenberg et al.[60] and Dondos.[61]

The changes in the conformation of graft copolymers can also be traced by means of the anomalous changes in the plot of the viscosities of their solutions against temperature. The extrema in the temperature variation of $[\eta]$ correspond to the conformational transition in which a "segregated" conformation is replaced by a statistical conformation. Such behaviour is common for graft copolymers regardless of the degree of compatibility and the positions of the extrema are almost independent of the composition of the corresponding graft copolymers.[56] Furthermore, such effects are manifested even under the conditions of a strong interaction (of the type of hydrogen bonding). The CDA–PAA–formic acid system, for which the temperature variation of $[\eta]$ is very complex, is therefore of interest.[57] The changes in the conformation of the macromolecule under the influence of temperature in systems of this type can apparently proceed via a series of stages.

IV. DEPENDENCE OF THE THERMODYNAMIC AND CONFORMATIONAL PROPERTIES OF THE SOLUTIONS ON THE MOLECULAR STRUCTURE OF GRAFT COPOLYMERS

1. The Molecular Structure and Conformations of Graft Copolymers in Solution

Major advances have been achieved at the present time in the controllable synthesis of block and graft copolymers. However, few studies of the molecular characteristics and also of the thermodynamic, hydrodynamic, and other physicochemical properties of solutions of graft copolymers have been described in the literature. It is still not clear how the molecular weight, the number of grafted chains, and the degree of compatibility of the components of the graft copolymer, as well as the nature of the solvent influence the conformational parameters and physicochemical properties of such copolymers. By varying the above parameters, it is possible to alter particular properties of the graft copolymers, which enables one to obtain materials with previously specified properties. The influence of the length of the grafted branches on the properties of copolymers in solutions has been investigated.[62–65] It has been established for CDA–PS graft copolymers[62,63] that, firstly, the grafting of PS initially diminishes the $[\eta]$ of the graft copolymer compared with the initial CDA, when the molecular weight of the PS changes only slightly, and, secondly, it leads to an increase of $[\eta]$ of the solutions under conditions of a high content of PS chains, when their molecular weight increases sharply (to 1.08×10^6), i.e. in this region the influence of the branching and segregation is small and the overall change in $[\eta]$ is determined solely by the length of the grafted branches. Direct determinations of mean square radii of inertia $(\overline{R}_z^2)^{1/2}$ of the CDA–PS solutions in a solvent having the same refractive index as CDA, namely pyridine, have shown that the main contribution to the overall volume of the macromolecule of the graft copolymer comes from the side chain.

Measurements of light scattering by CDA–PS solutions in different solvents have shown[63] that tetrahydrofuran (THF) interacts more effectively with the components of the copolymer. For this reason, the values of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and virial coefficients (A_2) for solutions of the given copolymers in THF are greater than for DMF. A very sharp increase of $(\overline{R}_z^2)^{1/2}$ is observed in dioxan, where the values of A_2 are much smaller than in THF and DMF, which is a consequence of the association of the copolymer macromolecules, indicated by the very high molecular weight $\overline{M}_w$. It is noteworthy that CDA and PS are thermodynamically incompatible[62] and, according to the average free energy of the blending of these polymers, the degree of their incompatibility in THF is much greater than in DMF. Consequently the incompatibility of components of these copolymers promotes a more effective interaction with the solvent.

Another picture is observed for CDA–PVP graft polymers, where the effects of branching and segregation determine the characteristic features of the hydrodynamic properties of their solutions.[64]

The thermodynamic and conformational properties of CTA–PMMA graft copolymers, synthesised by non-terminable radical polymerisation,[66] which makes it possible to regulate the molecular weight and the number of grafted branches, have been investigated. It has been established that, with increase in the number of grafted branches, the values of $(\overline{R}_z^2)^{1/2}$ for comparable molecular weights of the grafted branches and the values of A_2 increase. A sharp increase of the molecular weight of the grafted branches entails an increase of the values of $(\overline{R}_z^2)^{1/2}$, while $[\eta]$ changes only slightly. The $[\eta]$ for graft copolymers are very sensitive to changes in the number of grafted branches and increase sharply with increase of the latter. The isotypical character of the variation of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and A_2 for solutions of copolymers with increase of the molecular weight of the grafted branches is noteworthy.

Graft copolymerisation in the presence of cobalt(III) salts, which permits the regulation of the process parameters, has been carried out.[67] The molecular parameters of the graft copolymers of CTA with poly-2-methyl-5-vinylpyridine (PMVP) vary with the polymerisation conditions: M_{cop} from 1.1×10^5 to 4.45×10^5, M_{CTA} from 7.5×10^4 to 3.2×10^5, and M_{PMVP} from 6.0×10^3 to 8.0×10^4. Despite the fact that the average number of units in the main chain between neighbouring branches varies within wide limits, from 45.0 to 712.0, the number of grafted branches increases only to 5.8, which is associated with the fact that oxidative properties, leading to a decrease of M_{CTA}, take place simultaneously with graft polymerisation.

The molecular characteristics and the hydrodynamic, thermodynamic, and conformational properties of CTA–PMVP copolymers have been investigated.[67,68] The intrinsic viscosities of the graft copolymers depend significantly on the molecular structure, because the latter determines the degree of branching. It is of interest to compare the dependence of $[\eta]$ on M_{cop} with the analogous data for CTA. The increase of $[\eta]$ for CTA on passing from methylene chloride to formic acid is caused by the change in the conformation of the molecules owing to the specific interaction with the solvent. The intrinsic viscosity $[\eta]$ varies

analogously also for the CTA–PMVP copolymers; [η] for the copolymer is higher in this instance than for CTA with the same molecular weight. Presumably the incompatibility of CTA and PMVP in the solvents indicated leads to an unusual conformation of the copolymer macromolecules, the character of which depends on the quality of the solvent. The difference between the behaviour of the mixture of homopolymers and their graft copolymers can serve as a demonstration, on the one hand, of the grating step which is in many cases responsible for the impairment of the solubility of the graft copolymers with increase of the molecular weight of the grafted branches, and, on the other, can indicate the influence of the nature of the solvent on the thermodynamic properties. The influence of the nature of the solvent is in this case so great that even the signs of the average free energy of blending of polymers are different for the graft copolymers and their blends.[68]

The constants K and a of the Kuhn–Mark–Houwink equation for graft copolymers have been determined.[63,65,69,70] The low value of the power exponent a is striking, indicating a weak thermodynamic interaction of the copolymer and the solvent in the absence of permeability of the copolymer macromolecules to solvent molecules. While the graft copolymers investigated by Klenin and co-workers[69,70] had a comb structure, that of the macromolecules of graft copolymers investigated by Akbarov and co-workers[63,65] must have been of the star type, because the molecular weights of the side branches were very high—much higher than the molecular weight of the main chain. For this reason, the low values of the exponent a for the given copolymers with incompatible components may be a consequence not so much of the branching as of the globular form of the macromolecules, predominantly owing to the long side branches: for long grafted branches, the probability of their selective interaction with one another to form microregions of identical chemical nature increases.

A possible confirmation of the foregoing concerning the dominant influence of long grafted branches on the conformation is the decrease of the values of A_2 with increase of the temperature of the solution of the CDA–PS copolymer in DMF, which is confirmed in its turn by data for the phase diagrams and sorption properties quoted by Tashmukhamedov et al.[62] In other words, the CDA–PS solution in DMF has upper and lower consolute temperatures and the region of solubility is extremely limited, while the initial CDA and PS do not separate into different layers either on cooling or on heating. Consequently, even in effective solvents there is a preferential interaction of the chemically homogeneous segments, promoting the formation of microgels and hence the precipitation of the graft copolymer.

2. Characteristic Features of the Phase Equilibrium in Solutions of Graft Copolymers

The characteristic features of the structure of graft copolymers consisting of units of chemically heterogeneous components suggest that the critical phenomena in their solutions occur somewhat differently than in homopolymers. Here the main role may be played by segregation or intramolecular phase separation processes caused by the incompatibility of the polymeric components of the graft copolymer. For this reason, the structure and conformational state of the macromolecules of the graft copolymer in solution may have a specific influence on the phase equilibrium, as a consequence of which a difference from the properties of the corresponding initial polymers is ultimately observed.

It follows from the phase diagram obtained[62,71] for CDA–PS solutions in THF, epichlorohydrin, dioxan, and DMF that a characteristic feature of such solutions is the presence in all solvents of a lower consolute temperature of the first type (in Tager's classification) caused by the strong intermolecular bonds between the components in solution, which are broken on heating. It is also evident that, with rare exceptions, an improvement in the solubility of the CDA–PS copolymers is to be expected at room and lower temperatures owing to the influence of the branching of the copolymers.

When the lower consolute temperatures for a solution of CDA in THF and for CDA–PS are compared,[62,71] the observed differences are manifested not only in the consolute temperature and its type but also in the character of the very phase transition in the system. The phase separation in CDA–PS solutions is manifested by the formation of particles of the polymer phase in the form of unusual block formations, leading to, as it were, the "displacement" of the solvent from the solution and to a phase transition in the system. The temperature of the appearance of the first signs of particles of the polymer phase is adopted in this instance as the temperature at which separation into layers occurs. In the case of homopolymers, this is usually preceded by the appearance of a turbidity of the solution (critical opalescence), which has not been observed for graft copolymers. Analysis of the phase diagrams for the system investigated showed that the solubility of CDA–PS is a function not only of temperature but also of the composition of the copolymer,[72] which is common to all the solvents investigated. However, with increased content of PS in the copolymer, a continuous impairment of the solubility is not observed. This interesting feature is demonstrated by the fairly sharp improvement in the solubility of the CDA–PS specimen containing 77.4% PS in all the solvents investigated compared with the copolymers having a lower PS content.[72] Yet another example of such behaviour of graft copolymers in solution is provided by the CTA–PMMA copolymers investigated by Akbarov,[65] thermodynamic properties of which we shall consider in detail below.

It is known that the effect of high pressure on solutions of homopolymers tends to shift the lower consolute temperatures towards higher values and the upper consolute temperatures towards lower values, i.e. it impairs the miscibility in the polymer–solvent system. The literature data for the influence of pressure on the phase equilibrium and the thermodynamic parameters of homopolymer solutions have been analysed.[73] For the phase equilibrium as a function of pressure in block and graft copolymers, there are only a few data in the literature. As an example, one may quote studies on the solutions of CDA–PS graft copolymers in THF.[74] According to the results, the application of a pressure of the order of 20–200 bar tends to improve the solubility of CDA–PS. However, a graft copolymer with a high PS content, characterised by a poorer solubility, requires a higher pressure in order to dissolve, which is a consequence of structural characteristics of the graft copolymers investigated.

3. Thermodynamics of the Phase Equilibrium in Solutions of the Graft Copolymers in the Light of the Prigogine–Patterson Theory

The Prigogine–Patterson theory[75,76] is a development of the thermodynamic Prigogine–Flory theory.[77,78] The applicability of the Prigogine–Flory theory, which describes liquid–liquid systems, to polymer solutions has been demonstrated in a number of investigations[79–82] in which reduced thermodynamic functions were calculated for certain polymer

systems. The expression arising from the Prigogine–Flory theory for the interaction parameter χ_1 is

$$\chi_1 = \left(-\frac{U}{RT}\right)\nu^2 + \left(\frac{C_p}{2R}\right)\tau^2 , \quad (1)$$

where U is the configurational energy or the evaporation energy of the solvent, ν the parameter referring to the cohesion energy and the segmental size of the components, C_p the configurational heat capacity of the solvent, which increases with temperature and tends to infinity as the critical temperature for the transition from the liquid to the vapour is approached, R the gas constant, and τ a structural parameter characterising the difference between the free volumes of the polymer and the solvent, which can be calculated from the formula $\tau = 1 - T_1^*/T_2^*$, where T_1^* and T_2^* are the characteristic reduced temperature parameters of the solvent and the polymer respectively.

It is exceedingly difficult to use the interaction parameters χ_1 in this expression in order to characterise the mixing of the polymer with the solvent including the region of the [given] phase state. A modified theory put forward by Patterson[75,76] therefore merits attention. He obtained a different expression for the critical interaction parameter having applied the van der Waals principle of the volume dependence of the configurational energy of liquid (this was pointed out previously in an early investigation by Flory[78]) and having expressed all the quantities in Eqn.(1) in terms of the reduced volume of the solvent:

$$\chi_{1,cr} = \frac{c_1\nu^2}{1-\tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2\left[(4/3)\tilde{V}_1^{-1}-1\right]} = \frac{1}{2}\left[1+r^{-1/2}\right]^2 , \quad (2)$$

where $\tilde{V}_1$ is the reduced volume of the solvent, c_1 the number of degrees of freedom of the solvent molecule, ν^2 and τ^2 are temperature independent parameters or, in terms of Patterson's theory,[76] $c_1\nu^2$ is a factor which depends on the chemical nature of the solvent and the polymer and $c_1\tau^2$ is the structural factor, and r is the number of polymer segments in the micromolecule. As in Eqn.(1), the first term of Eqn.(2) contributes to the variation of χ_1 with decrease of temperature and predicts the upper consolute temperature, whilst the second contributes to the variation of χ_1 with increase of temperature and predicts the lower consolute temperature. According to the theory, $\nu^2 = 0$ for systems having identical or very nearly identical chemical structures and in this case the parameter χ_1 is determined solely by the structural term. Eqn.(2) then has only one root:[76]

$$\tilde{V}_1^{-1/3} = 3/4\,(1 + c_1\tau^2 Q) , \quad (3)$$

where $Q = [1 + r^{-1/2}]^{-2}$. For systems where the polymer and the solvent have different chemical structures, the theory predicts the upper and lower consolute temperatures. Thus, by calculating the molecular parameters in Eqn.(2), it is possible to characterise quantitatively the mixing of the polymer with the solvent as the temperature is varied.

In the Flory equation,[80] the quantity r is determined by the ratio of the molar volumes of the polymer and the solvent, i.e. by V_2^*/V_1^*, and T_1 is calculated from the equation

$$\tilde{T}_1 = \tilde{V}_1^{-1}\left(1-\tilde{V}_1^{-1/3}\right) = T/T_1^* \quad (4)$$

where V_1 is the reduced volume of the solvent, which can be calculated from the formula

$$\tilde{V}_1 = \left[\frac{\alpha_1 T}{3\,(1+\alpha_1 T)} + 1\right] ,$$

where T is the experimental critical [consolute] temperature, and α_1 the coefficient of thermal expansion of the solvent.

The principle of the theoretical analysis of reduced temperatures involves the plotting of two graphs: the first represents the dependence of $\tilde{T}_1$ on $\tilde{V}_1^{-1/3}$ in accordance with Eqn.(4), where $\tilde{T}_1^* = T/T_1^*$ and $T_1^* = T\tilde{V}_1/(1 - \tilde{V}_1^{-1/3})$, while the second represents the dependence of $\chi_{1,cr}$, $c_1\nu^2$, and $c_1\tau^2$ on the same values of $\tilde{V}_1^{-1/3}$, the ranges of variation of the parameters $c_1\nu^2$ and $c_1\tau^2$ being taken from the literature data.[76] The main difficulty consists in the selection of critical values of the parameters $c_1\nu^2$ and $c_1\tau^2$, which must satisfy the theoretical data of Eqn.(2). The points corresponding to the intersection of the horizontal lines for the given values of $\chi_{1,cr}$ and the corresponding suitable values of $\tilde{V}_1^{-1/3}$ yield the temperature variation of χ_1 which is described by Eqn.(2). $\tilde{T}_{1,theor}$ is calculated from the theoretical values of $\tilde{V}_1^{-1/3}$ already obtained in this way. In order to compare the experimental and theoretical $\tilde{T}_1$, the temperature axes are displaced in such a way that these data coincide.

The applicability of the Prigogine–Patterson theory to the description of the phase equilibrium in solutions of polar-rigid-chain polymers of the copolymer type has been demonstrated:[83] CDA in THF and CTA in methylene chloride (MC). Lower and upper consolute temperatures have been observed for the first system and an upper consolute temperature for the second. In the CDA–THF system the shift of the theoretical axis at the upper and consolute temperatures is 12° and 55 °C, while for the CTA–MC system the shift [at the upper consolute temperature] is 1.5 °C. Such a significant difference between the experimental and theoretical data in the region of the lower consolute temperature is a consequence of the fact that the new phase initiation processes, in which the polymer macromolecules are structured and aggregated and there is a transition from homophase to heterophase fluctuations, whose dimensions vary with temperature, are already prepared for in the region remote from the consolute temperature. For systems having both types of consolute temperatures, the temperature dependence of χ_1 has an extremum, which can be below or above the ideal value $\chi_1 = 0.5$. The coordinates of this point are determined from the known limiting value of the parameters $c_1\nu^2$ for the case where an increase in the molecular weight of the polymer entails the mutual approach and possibly even the identity of the upper and lower consolute temperatures, giving rise to the so-called "hour glass" form.[76] This means that, when the molecular weight is greater than a certain critical value, the middle sections of the upper and lower branches of the phase diagrams merge, i.e. there appears a range of compositions where the system cannot exist as a single-phase system at any temperature. In this case the minimum in χ_1 is calculated from the equation

$$\tilde{V}_1^{-1/3} = \frac{7}{8} + \frac{3}{8}\left(c_1\tau^2 - c_1\nu^2\right)Q , \quad (5)$$

where Q assumes a value close to unity at $M \to \infty$. The limiting values of $c_1\nu^2$ calculated in this way are 0.0255 for CDA–THF and 0.01845 for CDA–MC and are correlated with the plot of χ_1 against $\tilde{V}_1^{-1/3}$ and with its temperature variation.[83]

It is noteworthy that the separation of the interaction parameter χ_1 in accordance with the Patterson theory into molecular parameters is important for the understanding of the temperature variation of the miscibility of the polymer solution. The temperature variation of these parameters obtained by Goloborod'ko et al.[83] from Eqn.(2) is characterised by their different role in χ_1, where the term $c_1\tau^2$, leading to the separation of the system into different layers at high temperatures, makes the dominant contribution. This is apparently a distinctive feature of solutions of cellulose acetates, which are involved in complex intermolecular interaction with the solvent by virtue of the specific features of their structure.

As for homopolymers, when the molecular weight of the graft copolymer increases, the consolute temperatures approach one another, i.e. the usual picture involving an impairment of miscibility with increase of the molecular weight is observed.[74] On the assumption that the CDA–PS specimen with 77.4% PS and a very long grafted chain ($\tilde{M}_\eta$ = 1.086×10^6) can be regarded by convention and with some approximation as homo-PS, an attempt has been made[74] to apply the Prigogine–Patterson theory to this copolymer.[75,76]

The study of the phase diagrams for solutions of CDA–PS fractions in THF and DMF has shown[74] that this approach to the quantitative description of the phase equilibrium in solutions of graft copolymers is entirely acceptable. The higher theoretical reduced consolute temperatures compared with the experimental temperatures may be regarded as a consequence of the presence of lower consolute temperatures of the first type in solutions of the graft copolymers, whilst the theory provides for the presence of a lower consolute temperature of the second type in polymer systems. Nevertheless the calculated temperature dependence of the parameters of the Patterson equation represents, in the case of CDA–PS solutions, a typical picture of the variation of the phase state of polymer solutions with temperature (Fig.1). The system investigated is characterised by definite values of the structural ($c_1\tau^2$) and chemical ($c_1\nu^2$) parameters, which satisfy the theoretical data of the Patterson equation $\chi_{1,cr} = \frac{1}{2}(1 + r^{-1/2})^2$. For certain values of $\chi_{1,cr}$ and suitable $\tilde{V}_1^{-1/3}$, points representing the temperature variation of χ_1 described by Eqn.(2) are obtained. The value of χ_1 at any point within the temperature range describes the behaviour of the system as a function of the degree of interaction of the polymer with the solvent. According to the results of the calculation of the temperature variation of these parameters, the graft copolymer interacts with the solvents employed to different extents.[74] This conclusion is based not only on data for the consolute temperatures but also on the analysis of the character of the influence of the nature of the solvent on the miscibility with the polymer.

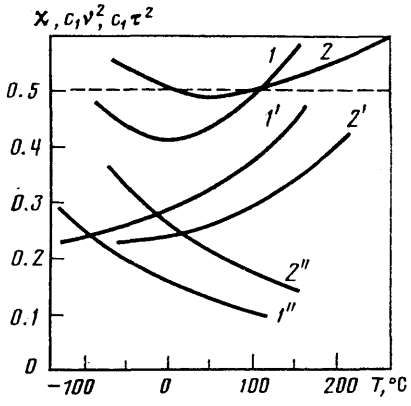


Figure 1. Temperature variation of the interaction parameters χ_1 (curves *1* and *2*) and the molecular parameters $c_1\tau^2$ (curves *1'* and *2'*) and $c_1\nu^2$ (curves *1''* and *2''*) of Eqn.(2) for different systems:[74] *1*), *1'*), and *1''*) CDA–PS–THF; *2*), *2'*), and *2''*) CDA–PS–DMF.

4. Relation between the Type of Consolute Temperature and the Signs of the Thermodynamic Parameters of Mixing in Solutions of the Graft Copolymers

According to thermodynamic predictions, systems with a lower consolute temperature should be characterised by negative enthalpies and entropies of mixing. On the other hand, for systems which have both an upper and a lower consolute temperature, the enthalpies and entropies of mixing should decrease (i.e. their absolute negative values should increase). The study of the temperature variation of the sorption of dichloroethane vapour by the EPVC–PS graft copolymer[84] has shown that the system becomes unstable with increase of temperature, which is manifested by a decrease in its absolute negative free energy Δg^m and indicates the impairment of the quality of the solvent. The data obtained[84] for the temperature variation of the free energy were used to calculate the enthalpies and entropies of mixing. They are negative over the entire temperature and concentration ranges and diminish in absolute magnitude with increase of temperature.

Comparison of the results obtained for the initial polymer and the graft copolymers show that the grafting step impairs the affinity of the solvent for the graft copolymer and limits the region of existence of the homogeneous solution, which is expressed by a decrease in the heat of solution and the free energy and by the appearance of a lower consolute temperature on the mixing diagrams. For CDA graft copolymers, whose grafted branches have different chemical nature, the change in the enthalpy component of the chemical potential makes a significant contribution to the change in the affinity of the solvent for the graft copolymer. Thus CDA–PVAC graft copolymers dissolve in acetone, which is a common solvent for the copolymer components, with a smaller heat change than the initial polymer[85] and the heat of solution falls sharply with increased content of the grafted PVAC in the copolymer.

On the basis of the finding that the interaction of grafted PVAC chains with acetone is almost athermal, one can assume that the observed decrease in the heat changes indicates not only a weakening of the interaction energy of the polar groups of the main chain of the copolymer with the solvent molecules but also a change in the structure of the graft copolymer with increased amount of the grafted polymer. This is also indicated by sorption data,[86] from which it follows that, with increase of the fraction of PVAC chains in the graft copolymer, the sorption capacity diminishes not only for acetone but also for methanol, although in the latter case an increase in the degree of sorption should have been seemingly expected, since methanol is a selective solvent for PVAC. Measurements of the specific volumes have shown[86] that the dissolution of CDA and CDA–PVAC in acetone is accompanied by a decrease in volume, i.e. the criterion of a lower consolute temperature, which obtains for the given system in the high temperature range, holds. The smaller contraction for solutions of the graft copolymer than for CDA is a consequence of the closer packing of the graft copolymer.

It is known that the contraction observed in solutions is frequently the cause of the negative contribution to the heat and entropy of mixing. According to the data obtained,[86] the Δg^m for the CDA–acetone system become less negative with increase of temperature, as predicted by thermodynamics for systems having a lower consolute temperature. The thermodynamic functions for PVAC are positive and increase with temperature. It has been found that the behaviour of the graft copolymers is determined by the presence of the grafted component, whereupon the

positive enthalpy and entropy of mixing decrease with increasing temperature. The discrepancy between the type of consolute temperature and the signs of ΔH^m and ΔS^m for CDA–PVAC solutions is caused by the sharp difference between the thermodynamic properties of the main and grafted copolymer branches, which is the reason for their incompatibility.

In the study of CDA–PVP and CDA–PAA graft copolymers, it has also been observed[64,87] that the variation of the solubility is determined mainly by the variation of the energy component of the chemical potential. Analysis of experimental data has shown that this situation is common to CDA graft copolymers in the solution of which the energy factor plays a dominant role.

5. The Flory–Huggins Theory and Tager's Method in the Study of the Thermodynamic Properties of Multicomponent Systems

The extent of intermolecular interactions in solutions of graft copolymers can be estimated with the aid of the Flory–Huggins theory based on the calculation of the Flory–Huggins parameter χ'_{12} from Scott's equation.[87] The published determinations of the parameter χ'_{12} for graft copolymers have been analysed.[7] However, the influence of the length and number of the grafted branches on χ'_{12} was not investigated in the above studies. Investigations[65,89,90] in which a difference between the behaviour of mixtures of CTA and PMMA polymers and their graft copolymers with different molecular structures was demonstrated are of great interest in this connection (Fig. 2).

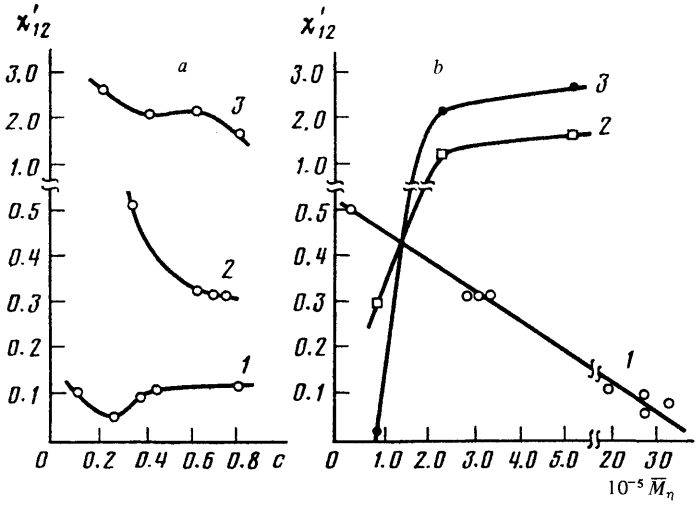


Figure 2. Dependence of the polymer–polymer–solvent interaction parameter χ'_{12} on the content c (a) and the molecular weight of PMMA (b) in methylene chloride:[65] a) CTA–PMMA graft copolymers having grafted branches with high $\bar{M}_\eta$ (1.95×10^6–3.30×10^6) (curve *1*), CTA–PMA graft copolymers with relatively short grafted branches (3.30×10^4 to 3.30×10^5) (curve *2*), and CTA–PMMA mixtures (curve *3*); (b) CTA–PMMA graft copolymers (curve *1*) and mixtures of CTA and PMMA in which the proportions of PMMA are 0.4 (curve *2*) and 0.6 (curve *3*).

The polymer–polymer–solvent interaction parameters χ'_{12} [or $\psi(a_s\phi_p)$ for graft copolymers], calculated from the Scott, Patterson, and Krause equations using the Flory–Huggins and Flory–Scott theories are directly related to the average free energies of the blending of the polymers Δg_x determined by Tager's method.[91] Numerous determinations of the Δg_x for polymer blends have been published—by Tager and co-workers[43–45,92,93] for block copolymers, while for the graft copolymers a series of investigations have been made by Tashmukhamedov and coworkers.[62,86,87,90,94] Tager and co-workers[43–45] demonstrated for the first time the possibility of applying Tager's method in the estimation of the thermodynamic stability of blocks in block copolymers and established that the presence of chemical bonds between the blocks of the system investigated impairs their compatibility. However, the influence of molecular weight and of the number of and ratio of the blocks on their compatibility, which would make possible a detailed analysis of the thermodynamic criteria of the compatibility of block copolymers, was not investigated in the above studies.

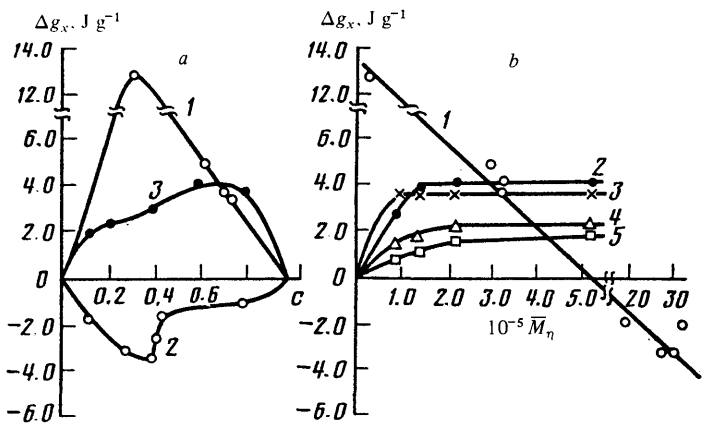


Figure 3. Dependence of the average free energy of mixing of the polymers Δg_x on the content c (a) and the molecular weight of PMMA (b) in methylene chloride:[65] a) CTA–PMMA graft copolymers having grafted branches with relatively low values of $\bar{M}_\eta$ (3.30×10^4–3.30×10^5) (curve *1*), CTA–PMMA graft copolymers having grafted branches with high values of $\bar{M}_\eta$ (1.95×10^6–3.30×10^6) (curve *2*), and CTA–PMMA mixtures (curve *3*); b) CTA–PMMA graft copolymers (curve *1*) and mixtures of CTA and PMMA polymers in which the proportions of PMMA are 0.6 (curve *2*), 0.8 (curve *3*), 0.2 (curve *4*), and 0.1 (curve *5*).

Graft copolymers have been studied in detail in a number of investigations[62,63,65,68,95,96] where a study was made of the relation between the molecular structure and the thermodynamic properties of solutions of graft copolymers. It was shown that $\Delta g_x > 0$ for CTA–PMMA graft copolymers with relatively low molecular weights and that the degree of incompatibility is much greater than for polymer blends (Fig. 3). For higher molecular weights of the grafted branches, the Δg_x assume low negative values; under these conditions, curve *2*, representing the variation of Δg_x with the content of the grafted PMMA branches, shows

a rise, which indicates microlayer formation in the system; this was later confirmed by electron microscope investigations.

The different character of the changes in Δg_x with increase in the molecular weight of the second component in polymer blends and in graft copolymers is especially remarkable. Whereas the thermodynamic stability of polymer blends is impaired with increase of the molecular weight of PMMA, for graft copolymers Δg_x diminishes to negative values as the molecular weight of the grafted branches rises (Fig. 3*b*, curve *1*). Such behaviour of graft copolymers can be accounted for by the "segregated" conformation of the macromolecules for low molecular weights of grafted branches and by the complete suppression of the segregation effect with increase of the molecular weight of such branches. It is noteworthy that the mean square radii of inertia and the intrinsic viscosities are higher for copolymers with a relatively low molecular weight of the grafted branches compared with those where the molecular weights of such branches are high.[95-97]

V. THE INFLUENCE OF VARIOUS FACTORS ON THE PROPERTIES OF SOLUTIONS OF GRAFT COPOLYMERS

1. The Influence of the Nature of the Solvent

In the case of selective solvents the macromolecules of graft copolymers form monomolecular micelles in dilute solutions; with increase in solvent selectivity or the concentration of such a solution, polymolecular micelles are produced. Strong interactions (of the acid–base type) of the solvent with one of the components of the graft copolymer are fairly distinctly manifested in the character of the structure formation in graft copolymers in solution, in their viscosity properties {there is the sharp increase of $[\eta]$ and its weak temperature dependence} and by an increase of A_2 for the solutions.

2. The Influence of the Nature of the Polymer

On the basis of the available literature data, one cannot visualise what is the decisive factor governing the compatibility or incompatibility of the polymer pairs and the conformational, thermodynamic, and other physicochemical properties of graft copolymers which follow from this. Polymers having very similar chemical structures may split into separate layers and conversely polymers differing in chemical nature are sometimes compatible.

The nature of the grafted components influences the solubility of the copolymer as a whole, which is due to a change in the absolute chemical potential of the solvent (in some cases a change in the energy component of the chemical potential and in others in the enthalpy component). The change in the solubilities of graft copolymers based on cellulose acetates is determined mainly by the energy component of the chemical potential. The impairment of the dissolving power of the solvent in relation to the graft copolymer is a consequence mainly of the unfavourable changes in the enthalpy component of the thermodynamic potential.

The discrepancy between the type of consolute temperature and the signs of the thermodynamic functions ΔH^m and ΔS^m has been observed in certain graft copolymers, which is due to the sharp difference between the properties of the main and grafted chains of the copolymer.

3. The Influence of the Compatibility of the Components

In the case of incompatible components, microseparation is observed in good solvents or a preferential interaction may take place between chemically homogeneous segments, favouring the formation of microgels and the precipitation of the graft copolymer.[65]

The conformational properties and structure formation in graft copolymers depends on the compatibility of the components.[65,87] An increase in compatibility entails a decrease of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and A_2 for the solution. In incompatible systems structure formation depends on the nature of the solvent to a greater extent than in compatible systems.[91] The determination of the molecular parameters and the study of the inhomogeneity of the compositions of the CPVC–PS graft copolymer showed that the graft copolymers become inhomogeneous both as regards the chemical composition of the macromolecules and the molecular weight of the components constituting the copolymers.[98]

4. The Influence of the Number of Grafted Branches

It has been shown[22] that an increase in the number of grafted branches hinders the formation of polymolecular micelles and that in such cases monomolecular micelles are formed. An increase in the number of grafted branches promotes the formation of a segregated conformation, i.e. microseparation.[65] The intrinsic viscosity $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ diminish for graft copolymers with a small number of grafted branches on microseparation, while in the case of comb copolymers an increase of $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ may be observed.

5. The Influence of the Molecular Weight of the Grafted Branches

With increase in the length of the grafted branches, $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ for solutions of the graft copolymers both increase.[62] A marked increase in the molecular weight of the grafted branches can promote the suppression of the segregation effect. It has been shown[65] that graft copolymers with relatively low molecular weights of the grafted branches and a large number of the latter proved to be incompatible and that, when their molecular weight increases considerably, the components become incompatible and the macromolecules assume a more compact form. The second virial coefficient for the solution diminishes with increase in the molecular weight of the grafted branches.[65,95-98] There are no literature data on the influence of the molecular weight of the grafted branches on micelle formation.

6. The Influence of Polydispersity and Inhomogeneity of Composition

The graft copolymers employed by Akbarov[65] had grafted branches with a narrow molecular weight distribution. The increments in the refractive indices of the copolymer components proved to be very similar in many solvents, which precluded the determination of the inhomogeneity of their composition and of its influence on the properties of the solutions.

Micelle formation by PVAC–PS graft copolymers in different solvents has been investigated[99] and it has been concluded that the nature of the solvent does not influence the size of the micelles and that the relatively broad distribution of the

micelles with respect to size is a consequence of the polydispersity of the initial copolymers. It has been shown for CPVC and CDA graft copolymers with certain vinyl polymers that, for the copolymers with a marked inhomogeneity of composition and polydispersity, the degree of incompatibility is greater and the values of A_2 for the solutions are smaller.[98] The polydispersity of the grafted component leads to a greater incompatibility of the copolymer and the homopolymer in a blend and to an impairment of the solubilisation and the homopolymer by the copolymer.[100]

Thus analysis of studies on the thermodynamic and conformational properties of solutions of graft copolymers has shown that the principal features of the behaviour of the macromolecules of graft copolymers in solution have now been quite adequately characterised on the basis of the quantitative compatibility data. Detailed investigations have been made of the thermodynamics of mixing as a function of the composition and the molecular structure of the graft copolymers. The data obtained have been interpreted in the light of modern views on the nature of polymer solutions taking into account the Flory–Prigogine–Patterson theory. Attention has been concentrated on thermodynamic properties which are most important for the understanding of the interaction of the graft copolymers with solvents of different nature.

At the same time many publications are descriptive in character, because there is so far no rigorous theory of solutions of graft copolymers.

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