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Conformational and Thermodynamic Properties of Macromolecules in Ternary Polymeric Systems

A.V.Gevorkyan

An account is given of the present state of knowledge on the properties of solutions of homopolymers and copolymers (having different distributions of monomer units in the chain) in binary mixtures of solvents. Several specific features of the hydrodynamic behaviour of macromolecules in such systems are discussed. Selective adsorption, which develops in mixed solvents, cannot be responsible for the lack of agreement between theory and experiment. Results reported here indicate that macromolecules retain a Gaussian structure ($[\eta]_\theta \propto M^{1/2}$) in several polymer-binary mixture systems. Conformational properties and transitions of macromolecules from a "segregated" to a random form are examined as functions of the composition of the mixed solvents. A list of 61 references is included.

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1. Introduction

Considerable attention has been paid during recent years [1-8] to investigating the properties of solutions of polymers involving ternary systems†. However, experimental information on this question is still inadequate and contradictory, perhaps owing to specific features of the hydrodynamic behaviour of copolymers in solution [9,10] or to the development of selective interactions (selective adsorption) in ternary systems comprising a polymer plus a binary mixture [11]. A final solution to the problem may be obtained from further special investigations, for the correlation of theory with experiment in ternary systems is still mainly qualitative.

The present paper gives a brief account of modern views on the thermodynamics of solutions of polymers in ternary systems. It considers also certain results obtained by the Reviewer when investigating the structure and the hydrodynamic behaviour of molecules of random chloroprene–isoprene and chloroprene–dichlorobutadiene copolymers and of the corresponding homopolymers in ideal mixed solvents [12-18]. In contrast to homopolymers, copolymers are inhomogeneous with respect not only to conformation but also to composition, but we shall not deal with the latter type of variability, and refer merely to the survey by Litmanovich and Izyumnikov [19].

2. θ-Conditions and Unperturbed Dimensions of Macromolecules in Ternary Polymeric Systems

According to modern views, "equilibrium dimensions" of macromolecules, whose structure is unperturbed by the solvent, are established under θ-conditions, when the osmotic forces of repulsion between the dissolved polymer macromolecules and the solvent molecules are balanced by coiling of the molecular chains because of the energetic unfavourability of the contacts between polymer and solvent [20]. In other words, the condition of zero second virial coefficient A_2 in the expansion of the osmotic pressure should correspond unambiguously to the absence of swelling of the molecular coil ($\alpha = 1$) and maintenance of the conditions $[\eta]_\theta \propto M^{\frac{1}{2}}$. However, recent results indicate that the Gaussian distribution may break down in ternary systems ($[\eta]_\theta \neq K_\theta M^{\frac{1}{2}}$).[9] Furthermore, the very concept of θ-point (and also α-point) now requires some elaboration, as indicated by results on the conformational transitions of macromolecules in the critical region of polymer–solvent mixing [21-23]. Attention must be paid also to the existence of both upper and lower critical temperatures for several rigid and semi-rigid macromolecules [24,25]. The Reviewer [26] has also observed phase separation with rise in temperature for aqueous solutions of poly(methyl vinyl ether)—"thermal denaturation" of the macromolecules—caused by rupture of polymer–solvent intermolecular hydrogen bonds [27].

It is noteworthy that Benoit and Dondos have recently suggested [28] that solutions of polymers in binary mixtures may have two θ-points, owing to the development of selective interactions (selective adsorption), which distort the Gaussian structure of the macromolecules even when $A_2 = 0$. From investigations of the temperature dependence of the unperturbed coil dimensions of several polymers in binary mixtures these workers concluded further that the present classical theory of solutions is unsuitable for strongly associated solvents [29]. It was found that K_θ in such solvents was smaller than $K_{\theta,\text{ideal}}$ and increased with rise in temperature (Fig. 1). Extrapolation of K_θ to the boiling point of the solvent, when association of solvent molecules disappears, yields the ideal value of K_θ. The decrease in the unperturbed dimensions of the macromolecules in associated solvents is explained [29] by intermolecular polymer–solvent interaction, leading to the formation of cyclic structures bound by hydrogen bonds of the solvent, which in turn produces a decrease in $(\overline{h^2})_\theta^{\frac{1}{2}}$ of the macromolecules.

However, the conclusions reached in the above papers are open to question, since they are based not on direct experiment but on extrapolation by the Stockmayer–Fixman method [30] far from the θ-point:

$$[\eta] \cdot M^{-1/2} = K_\theta + 0.51 \cdot \Phi_0 \cdot BM^{1/2}; \quad B = \bar{V}^2(1-2\chi_1)/V_1 N_A \qquad (1)$$

† We shall hencefore take a ternary polymeric system to imply solutions of copolymers (with different types of distribution of monomer units in the chain–random, block, and graft copolymers) and of homopolymers in binary mixtures of solvents.

where $\bar{V}$ is the partial specific volume of the polymer, V_1 the molar volume of the solvent, and χ_1 a thermodynamic parameter of intermolecular polymer–solvent interaction. Although Eqn. (1) is regarded as soundly enough based for estimating the unperturbed dimensions of macromolecules in solution [31], it is premature to consider that calculations using this equation establish a specific effect of the solvent.

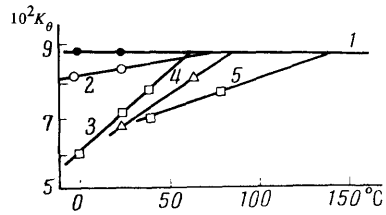


Figure 1. Temperature dependence [29] of K_θ for poly-2-vinylpyridine in dilute solution in: 1) chloroform; 2) ethanol; 3) methanol; 4) propan-2-ol; 5) cyclohexane.

On the other hand, Cowie [32], who investigated the unperturbed dimensions of a polystyrene fraction ($\bar{M}_w = 2.2 \times 10^6$) in binary solvent mixtures, demonstrated that selective adsorption cannot be responsible for the dependence of $(\overline{h^2})_\theta^{\frac{1}{2}}$ on the composition of the θ-solvent, since a unique relation between $(\overline{h^2})_\theta^{\frac{1}{2}}$ and the selective adsorption parameter λ' was not observed.

Several new results have been obtained [33,34] on selective adsorption in ternary polymeric systems, its thermodynamic interpretation, and also the effect on the conformation of the macromolecules. These workers state that a definite correlation exists between the swelling α of a macromolecule and selective adsorption in ternary systems, the change in the radius of inertia of the macromolecules $(R^2)^{\frac{1}{2}}$ being $\leq 10\%$ for solutions of non-polar polymers. Nevertheless, a quantitative relation is observed in the well known dependence on composition of the dimensions: $[\eta]_\theta$ and $(\overline{h^2})_\theta^{\frac{1}{2}}$ pass through a sharp maximum (this change in these parameters amounts to ~30% and 10% respectively).

Conformational transitions of cooperative character have been observed also for molecules of unionised polymethacrylic acid with change in composition of the θ-solvent [35,36].

The specific effect of θ-solvents on the structure of macromolecules observed by Poddubnyi et al. [37] in ternary systems was explained mainly by the considerable polarity of the copolymer examined. Other workers [11,38] attribute this effect to the thermodynamic interaction parameter χ_{AB} of the copolymer components in the given solvent. A linear relation is reported [38] between the values found for K_θ (extrapolated as in Ref. 30) and χ_{AB}, so that extrapolato $\chi_{AB} = 0$ (Fig. 2) will give the additive value of K_θ. The temperature variation in the parameter χ_{AB} is due also to the strong temperature dependence of the unperturbed dimensions.

Incidentally, analysis of the unperturbed coil dimensions of styrene–acrylonitrile and styrene–methyl methacrylate copolymers and of the corresponding homopolymers in solution shows that freedom of rotation about a single bond between unlike monomers is more strongly temperature-dependent than is that about similar bonds between units of the same type [39]. Considerable sensitivity of short-range action to variation in the θ-temperature has been established also by the Reviewer [15,16] for molecules of a random chloroprene–dichlorobutadiene copolymer, although additional short-range interactions between unlike monomer units in copolymer chains have a quite insignificant effect of $(\overline{h^2})_\theta^{\frac{1}{2}}$. [12,13] Fig. 3 shows that increase in the θ-temperature (by ~50 deg) leads to an average decrease of 15% in the unperturbed dimensions.

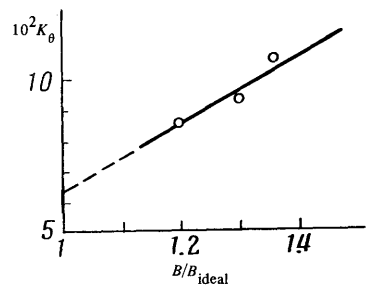


Figure 2. Variation in K_θ with the ratio of B to its "ideal" value: this relation represents the incompatibility of the components of the copolymer chain in solution [38].

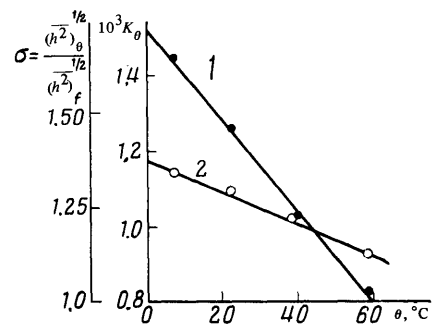


Figure 3. Variation with the θ-temperature, for a random chloroprene–dichlorobutadiene copolymer in solution, of the conformational parameters: 1) $K_\theta = \Phi_0(\overline{h_\theta^2}/M)^{\frac{3}{2}}$; 2) $\sigma = (\overline{h^2})_\theta^{\frac{1}{2}}/(\overline{h^2})_f^{\frac{1}{2}}$.

The above considerations do not exclude the possible preservation of the Gaussian structure of molecular coils in binary mixtures. In fact, the Reviewer has shown [18] (Fig. 4) that the nature of the θ-solvents (in this case their polarity) neither changes the Gaussian distribution in the chloroprene–dichlorobutadiene copolymer nor affects the values of $[\eta]_\theta$, although the influence of electrostatic

polymer–binary mixture interaction of $[\eta] \propto (\overline{h^2})_\theta^{\frac{3}{2}}$ is quite appreciable for molecular chains comprising monomer units of the same type[14]. The fact that it is not apparent in the above copolymer chains can probable be explained by the lower polarity of the dissolved copolymer molecules, caused by the predominance of *trans*-1,4-dichlorobutadiene units. An analogous dependence of unperturbed macromolecular dimensions on molecular weight (i.e. $[\eta]_\theta \propto M^{\frac{1}{2}}$) was obtained[40] for butadiene–nitrile copolymers, and was attributed to the impossibility of forming sufficiently long microblocks of units of the same type in the copolymer chains.

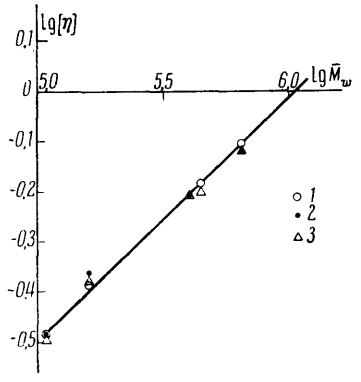


Figure 4. Dependence of $\lg[\eta]$ on $\lg\bar{M}_W$ for chloroprene–dichlorobutadiene copolymer fractions at $\theta = 25.4°C$ in binary solvent mixtures (by volume): 1) 1.33 : 1 chloroform + acetone; 2) 5.18 : 1 benzene + methanol; 3) 1 : 1 carbon tetrachloride + n-octane.

Nor is the Gaussian structure of the copolymer macromolecules distorted in the θ-state if the polymer–solvent interaction is almost the same for the chain components[10,41]. Results obtained by Inagaki et al. in a detailed study of the properties of solutions of block and random copolymers of styrene with methyl methacrylate show[41] that in cyclohexanol the θ-temperatures differ very little for block copolymers (with different styrene contents) and for the corresponding homopolymers, whereas for random copolymers the θ-temperature varies appreciably with different styrene contents, passing through a minimum in the vicinity of the equimolecular copolymer (Fig. 5). In 2-ethoxyethanol block copolymers have higher θ-temperatures than random copolymers of similar composition, probably as a consequence of intramolecular interaction between styrene and methyl methacrylate units. Nevertheless, the closeness of the conformational and thermodynamic properties of block copolymers to the average properties of homopolymers somewhat contradicts existing views[3].

Conformational analysis of macromolecules for a large number of copolymers differing in structure shows[42–46] that the unperturbed coil dimensions follow (with insignificant deviations) a simple additivity rule (i.e. short-range interactions in the copolymer chains are the same as in the corresponding homopolymers). A clear exception to this rule is provided by graft (particulate and block) copolymers, in which interactions between unlike units have a substantial effect of $(\overline{h^2})_\theta^{\frac{1}{2}}$ (or the thermodynamic flexibility). For example, the optical and hydrodynamic properties of solutions of graft poly(methyl methacrylate)–polystyrene copolymers show[47] that the rigidity of such a macromolecule, regarded by Tsvetkov and his coworkers as a persistent chain, exceeds the value usually obtained for carbon-chain macromolecules[20] by an order of magnitude. The greater rigidity of the graft copolymer chains is assumed[47] to be due to the interaction of side-groups, which form intramolecular structures, having a high degree of orientational order, this being responsible for the great optical anisotropy of the macromolecule.

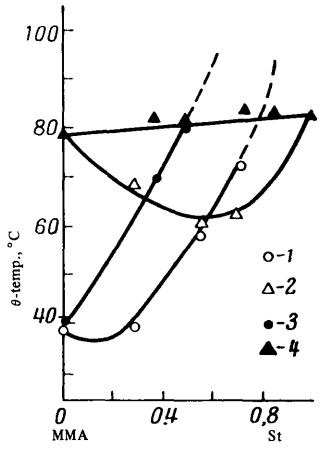


Figure 5. Dependence of θ-conditions on styrene (St) content for copolymers with methyl methacrylate (MMA):[41]
1) random copolymers in 2-ethoxyethanol;
2) random copolymers in cyclohexanol;
3) block copolymers in 2-ethoxyethanol;
4) block copolymers in cyclohexanol.

3. Ternary Polymeric Systems in Good Solvents

Several studies of ternary polymeric systems have demonstrated[50–53] that an intrachain phase separation of the copolymer (a "segregated conformation" of the coil) occurs in selective solvents, when the insoluble portion "settles out", being twisted "on itself", which diminishes to a minimum the interaction between unlike chain units (or the number of "heterocontacts"). In such a solution, therefore, intrachain and interchain interactions between segments differ markedly.

It has been reported[54] that the transition from the "segregated" to the random form corresponds to a definite composition of the binary solvent mixture: the "segregated conformation" exists above this transition composition (or temperature), and a random conformation below it, the former excluding and the latter permitting contact between unlike monomer units of the copolymer. These transitions are, of course, accompanied by great conformational changes (the dimensions of the copolymer chain and hence the viscosity of the solution either decrease or increase sharply). The presence of selective interactions in solutions of copolymers is responsible for their specific

thermodynamic and hydrodynamic behaviour. Fig. 6 [40] illustrates a peculiar effect associated with the development of such interactions for solutions of fractions of a random butadiene–acrylonitrile copolymer.

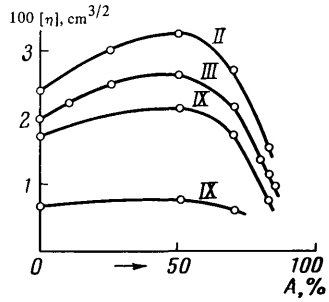


Figure 6. Dependence of intrinsic viscosity of butadiene–acrylonitrile copolymer fractions on composition of butan-2-one–cyclohexane mixtures (numbering of curves indicates that of the fractions [40]).

If we extend to solutions of copolymers the usual concepts applicable to homopolymers, and characterise the hydrodynamic behaviour of a molecular coil by the excluded segment volume

$$Z = \int_0^\infty \{1 - \exp[-U(r)/kT]\}\, 4\pi r^2\, dr \qquad (2)$$

where $U(r)$ is the potential interaction energy of two segments distant r apart, we obtain for a random copolymer [55]

$$\langle Z\rangle_{rand} = X^2 Z_{AA} + (1-X)^2 Z_{BB} + 2X(1-X) Z_{AB}, \qquad (3)$$

in which X is the proportion by weight of component A in the chain. The parameters representing interaction between A, B, and AB units are respectively

$$Z_{AA} = 2V_1\left(\frac{1}{2} - \chi_{A_1}\right);\ Z_{BB} = 2V_1\left(\frac{1}{2} - \chi_{B_1}\right);$$
$$Z_{AB} = \frac{Z_{AA} + Z_{BB}}{2} + V_1\chi_{AB}. \qquad (4)$$

(The subscript "1" denotes the solvent). Analogous deductions were made [55] for graft and block copolymers, but the formulae are too cumbersome to be considered here.

The above relations show that, when the θ-conditions are satisfied for a random copolymer and one of the corresponding homopolymers A (i.e. $\langle Z\rangle_{rand} = 0$ and $Z_{AA} = 0$), and χ_{AB} is positive, the other component may be somewhat below its θ-temperature ($Z_{BB} < 0$). This represents the so called "negative volume effect", which has actually been observed by several workers [9,53]. However, experimental results [9] show that Z_{BB} for the copolymers investigated is still so small that there is no appreciable "settling out" of monomer units of B, and hence no distortion of the Gaussian structure. In selective solvents, however, when the coefficients of Z_{AA}, Z_{BB}, and Z_{AB} become functions of the selectivity, the probability of contacts between units of the insoluble component is increased, which obviously leads to distortion of the conformation of the coil and ultimately its "stratification" [48–52,54]. With solvents and mixtures of cross selectivity (for a random copolymer of methacrylic acid with methyl methacrylate [53]) it becomes possible to trace a continuous transition from a secondary structure of one type to a structure of another type, through a stage involving the most uncoiled conformation, as a consequence of non-selective solvation of both types of monomer unit in the binary mixtures (Fig. 7).

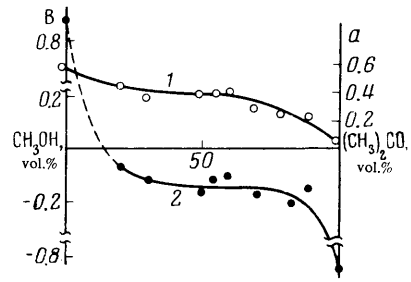


Figure 7. Effect of composition of mixed solvent (methanol + acetone) [49] on: 1) power of a in the Mark–Houwink equation; 2) the parameter B.

Since the literature frequently reports attempts to link the swelling coefficient α of copolymer molecules in solution with the thermodynamic parameter χ_{AB} of interaction between unlike monomer units of the copolymer one with the other and with the solvent [38,56], we must note a specific aspect of the thermodynamic properties of solutions of graft copolymers which was observed by Eskin and Baranovskaya [57,58]. These workers established that the second virial coefficient $A_2 \simeq 0$ for graft copolymers of polystyrene with poly(methyl methacrylate) ($X_A = 0.9$) having sufficiently high molecular weights ($\bar{M}_W > 10^6$). In fact calculation based on Flory's theory of polymer solutions [59]

$$A_2 = \frac{N_A Z}{2M^2} F(Z), \qquad (5)$$

(where $F(Z)$ is a function of the thermodynamic parameters of intermolecular polymer–solvent interaction), allowing for the hydrodynamic "non-flowability" of the coils [47], shows that the second virial coefficient A_2 for solutions of such graft copolymers [57] is of the order of 10% of that for solutions of the homopolymers, and decreases considerably more rapidly with molecular weight. This property of solutions of graft copolymers must, of course, be taken into account in determining the θ-conditions (e.g. by interpolating the temperature dependence of A_2 found by light scattering).

Experimental facts reported by Inagaki et al. [42] indicate, however, that long-range interactions between unlike monomer units do not disappear under any conditions, even when such interactions between units of the same type have absolutely no effect on the conformation of the macromolecules.

In conclusion we note that Dondos and Patterson [60] have examined the intrinsic viscosity of polymers in mixed solvents using theoretical results [61] on the effect of selective adsorption on the thermodynamic properties of polymer solutions. They find that the difference in the intrinsic viscosity of solutions of polymers in binary mixtures produced by taking selective adsorption into account is

$$\Delta[\eta] = \frac{1.02\bar{V}^2\Phi_0 M G^E(\varphi_2^0)}{N_A V R T}, \qquad (6)$$

where V is the molar volume of the mixed solvent, φ_2^0 the fraction by volume of the second component in the solvent, and G^E the excess free energy of mixing of the component with the solvent. Only qualitative agreement was obtained when this equation was tested on various ternary polymeric systems: the quantitative results differed by factors of $10-10^2$, a discrepancy between theory and experiment which could hardly be explained by selective adsorption, as the authors pointed out. Nevertheless, the theoretical slight temperature dependence of intrinsic viscosity in binary mixtures

$$-T\frac{\partial(\Delta[\eta])}{\partial T}=\frac{1{,}02V^{\frac{1}{3}}\Phi_0 MH^E(\varphi_2^0)}{N_A VRT}, \qquad (7)$$

where H^E is the heat of mixing of the binary solvent mixtures, agrees quite satisfactorily with experiment.

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All-Union Scientific Research
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