U.D.C. 678-19:532.77

# Structure and Properties of Polymer Mixtures in Solution

V.N.Kuleznev and L.S.Krokhina

Modern views on the solubility of two polymers in a common solvent are discussed, and the possibility of controlling the properties of polymer mixtures is examined. A list of 125 references is included.

CONTENTS


| | |
|---|---|
| I. Introduction | 570 |
| II. Thermodynamics of the mixing of polymers and their solutions | 570 |
| 1. Polymer-polymer system | 570 |
| 2. Solvent-polymer-polymer system | 572 |
| III. One-phase solutions of mixtures of polymers | 574 |
| IV. Factors influencing the limit of phase separation | 579 |
| V. Some aspects of the transition of a one-phase into a two-phase solution | 582 |
| VI. Two-phase solutions of polymer mixtures | 583 |


## I. INTRODUCTION

Mixtures of polymers are attracting increasing attention not only for the solution of applied problems but also in connection with the theory of the compatibility (mutual dissolution) of polymers, which in the amorphous state have the structure of highly viscous liquids. The high viscosity of polymeric liquids impedes the establishment of equilibrium, and macroscopic phase separation does not take place in mixtures of polymers even if the mixture actually comprises two phases, whose separation is determined thermodynamically. This fact is very useful for applied purposes, as it has led to the manufacture of materials from polymer mixtures. Nevertheless, the considerable difficulties involved in determining the phase constitution of a mixture of polymers have been responsible for broadening investigations of their properties in solution, where the phase composition can be easily established, and also means may be available for examining the structure of each phase separately and of the mixture as a whole. Many generalisations have already been made on polymer mixtures in solution, although they have been investigated systematically in effect during the past two decades.

The convenience of the rapid establishment of equilibrium in work with solutions is complicated by many difficulties, resulting from the presence of the solvent, in assessing interaction between the polymers themselves. For this reason results for polymer–polymer interaction in a polymer–polymer–solvent system cannot at present be confidently transferred to the polymer mixture in the absence of solvent or even to a solution of the polymers in a different solvent. Determining the interaction parameters of polymers and the structural parameters of their binary mixture from results obtained for their solutions constitutes a most important task for the future.

The present Review is concerned mainly to summarise work on solutions of polymer mixtures whose macromolecules contain neither ionogenic nor strongly polar groups. Reviews on this topic are lacking both in the Soviet and in the foreign literature.

## II. THERMODYNAMICS OF THE MIXING OF POLYMERS AND THEIR SOLUTIONS

### 1. Polymer–Polymer System

The spontaneous mixing of two liquids leads to the formation of a true, single-phase solution of one component in the other, provided that the process is accompanied by a decrease in the Gibbs function, i.e. that

$$\Delta G = \Delta H - T\Delta S$$

is negative. The spontaneous process ceases when $\Delta G = 0$, and the liquids then have limited miscibility. The direction of the change and the magnitude of $\Delta G$ are governed by the relation between $\Delta H$ and $T\Delta S$, the enthalpy of mixing $\Delta H$ being determined by the magnitude and sign of the heat of mixing, while the entropy of mixing $\Delta S$ represents the change in order of the system resulting from the intermingling of the molecules.

The change in the parameters can be calculated most easily for an idealised system. If the structure of the miscible liquids and that of the mixtures are regarded as completely similar, so that neither the volume nor the short-range order is affected by mixing, the change in entropy is determined by the increase in the number of ways in which the two kinds of molecules can be distributed in space. Calculation based on the lattice theory of solutions[1-3] yields the formula

$$\Delta S = -kn_1 \ln \frac{n_1}{n_1+n_2} - kn_2 \ln \frac{n_2}{n_1+n_2} \qquad (2)$$

where $k$ is Boltzmann's constant, for the change in entropy accompanying the mixing of $n_1$ molecules of one liquid with $n_2$ molecules of another liquid. According to this equation the entropy of mixing of the liquids decreases with increase in molecular weight. In fact, the higher the molecular weight the smaller the number of molecules ($n_1$ and $n_2$) in unit volume. Decrease in the number of molecules involves a decrease also in the number of combinations in which the molecules can be arranged: i.e. the entropy of mixing decreases.

If the molar volume of an ordinary liquid of low molecular weight is taken to be 100 cm³, and the molar volume of a polymer as 100 000 cm³, calculation using (2) for the mixing of 1 cm³ of one simple liquid with 1 cm³ of another gives[4] $T\Delta S$ = 8.3 cal/2 cm³; the corresponding value for the mixing of 1 cm³ of a polymer with 1 cm³ of the simple liquid is 4.5 cal/2 cm³, and for the mixing of the same quantities of two polymers $T\Delta S$ = 0.0083 cal/2 cm³. We are concerned here with the formation of an ideal mixture, in which molecules of one polymer are surrounded by those of the other, to give a molecularly disperse system, in which fluctuations of concentration are absent. These results show clearly that the entropy of mixing of polymers is so small that it can be disregarded in the calculation of $\Delta G$. The quantity $T\Delta S$ cannot affect the sign of $\Delta G$, so that the change in the Gibbs function is determined by the sign of the change in enthalpy (heat effect).

The same lattice model of a solution will yield a formula for the enthalpy of the mixing of $n_1$ solvent molecules with a volume fraction $\varphi_2$ of a polymer

$$\Delta H = kT\chi_1 n_1 \varphi_2 , \tag{3}$$

in which

$$\chi_1 = \frac{z\,\Delta\omega_{12} x_2}{kT} \tag{4}$$

is a dimensionless parameter representing the excess energy of interaction in the solution, where $\Delta\omega_{12}$ is the energy of interaction of a solvent molecule with a polymer segment of the same size, $z$ is the coordination number of the model lattice, and $x_2 = v_2/v_1$ (the molar volumes of polymer and solvent being $v_2$ and $v_1$).

On the basis of the Flory–Huggins theory[1-3] presented here, Flory[5], as well as Scott and Magat[6], obtained almost the same expression for the chemical potentials of the mixing of two polymers (2 and 3), which can be written

$$(\mu_2 - \mu_2^0) = \ln\varphi_2 + \left(1 - \frac{x_2}{x_3}\right)\varphi_3 + x_2\chi_{23}\varphi_3^2 , \tag{5}$$

$$(\mu_3 - \mu_3^0) = \ln\varphi_3 \left(1 - \frac{x_3}{x_2}\right)\varphi_2 + x_3\chi_{23}\varphi_2^2 , \tag{6}$$

where $\chi_{23}$ is a parameter of interaction of the polymers, $\mu$ the chemical potential of one polymer surrounded by the other, and $\mu^0$ the chemical potential of the same polymer surrounded by like molecules. The critical conditions for the mixing of two polymers (i.e. the concentration and the interaction parameter at which phase separation ensues) were determined by Scott[7], who obtained expressions for these critical values:

$$\chi_{23c} = \frac{1}{2}\left(\frac{1}{\sqrt{x_2}} + \frac{1}{\sqrt{x_3}}\right)^2 , \tag{7}$$

$$\varphi_{2c} = \sqrt{x_3}/(\sqrt{x_2} + \sqrt{x_3}) , \tag{8}$$

$$\varphi_{3c} = \sqrt{x_2}/(\sqrt{x_2} + \sqrt{x_3}) . \tag{9}$$

In the particular case of a mixture of polymers having molecules of the same length ($x_2 = x_3 = x$) we find that $\varphi_{2c} = \varphi_{3c} = \frac{1}{2}$ and $\chi_{23c} = 2$. Substituting $\chi_{23c} = 2$ in Eqn. (4) yields the condition

$$z\,\Delta\omega_{23}/kT = \frac{2}{x} \tag{10}$$

for a mixture of polymers at the consolute point. When $x$ is large, $\Delta\omega_{23}$ is small. With the high molecular weights of polymers, their already negligible interaction energy, i.e. negligible absorption of heat on mixing, will lead to phase separation. Thus in an ideal mixture of polymers phase separation occurs with the slightest endothermic change, and the insignificant positive change in entropy is unable to balance the increase in enthalpy. The mixing of polymers can take place only with considerable evolution of heat.

A systematic investigation of the heats of mixing of polymers was first undertaken by Slonimskii and his coworkers[8,9]. In only two of the twenty-one pairs of polymers that they examined (polybutadiene rubber mixed with polystyrene and with butadiene–styrene rubber) was the sign of the thermal effect inconsistent with the behaviour of the polymers on mixing. The evolution of heat on the mixing of these two segregating pairs of polymers was attributed to a change in volume accompanying mixing.

Subsequent work has shown that segregation of a mixture of solutions or melts occurs even when the polymers are closely similar[10-14]. Two-phase systems appear in a mixture of melts of linear and branched polyethylene[15], in a mixture of solutions of the butadiene–nitrile copolymers SKN-18 and SKN-40,[16] in a mixture of melts of copolymers of methyl methacrylate and butyl acrylate whose macromolecules differ by more than 10% in their content of the former monomer[17], and also in a mixture of butadiene–styrene copolymers differing in composition by ~20%.[18] Two-phase systems appear even in a solution of a mixture of isotactic and atactic poly(methyl methacrylate) (so called stereocomplexes)[19]. There are grounds for expecting incompatibility of fractions of the same polymer differing significantly in molecular weight, which has already been shown for a solution of fractions of polyethylene[20].

Allen et al.[21] determined several thermodynamic functions of the mixing of oligomeric polyisobutylene and polymethylsiloxane. They measured the heat of mixing of the polymers experimentally, and calculated the interaction parameter per segment $\alpha_{23} = \chi_{23}/v$ (where $v$ is the molar volume of the polymer) from the Flory–Huggins theory by means of Eqn. (3). The result was comparable in order of magnitude with that calculated on the basis of Hildebrand's theory from the difference between the solubility parameters $\delta_2$ and $\delta_3$ of the polymers. Since the latter theory assumes a random distribution of molecules, the result would correspond to a similar structure of the mixture. The value of $\alpha_{23}$ was equated to $\alpha_{23c}$, which according to Eqn. (7) defines the condition of critical separation of the mixture into two phases. This permitted the critical temperature of mixing of the polymers to be calculated. If the heat of mixing had alone been responsible for the phase separation of this mixture, separation would have occurred at a temperature almost 300 deg below the observed consolute temperature. It was concluded[21] that the entropy contribution to the term $\chi_{23}kTn_1\varphi_2$ in Eqn. (3) is quite large. The entropy of mixing which they calculated from the experimental results differed considerably from the theoretical value. This discrepancy, a consequence of some ordering of the system, was regarded as responsible for the deviation of calculated values from experimental data.

Flory[22] has recently used Prigogine's theory of solutions[23] to calculate the changes in thermodynamic parameters accompanying the mixing of polymers. The equilibrium properties of a liquid—its thermodynamic functions—depend on the fluctuation of its density: i.e. they are determined by its internal structure. Mixing may involve changes in structure, which influence the thermodynamic functions. The structure of a liquid was characterised in terms of the density, the free volume, and also the coefficient of thermal expansion. Experimental values of the thermodynamic functions for polyisobutylene and polymethylene were used to calculate the

thermodynamic parameters of the mixing of these polymers at temperatures above the melting point. Thus $\Delta H = 2.5$ cal/100 g mixture at 150°C, while $T\Delta S$ is negative (−5.4). Therefore $\Delta G$ is large and positive (7.9), which indicates that the polymers are incompatible. Flory did not indicate reasons for the decrease in entropy on mixing. A possible increase in the degree of order of the system—an increase in short-range order—probably increases the non-combinatorial component of the entropy[24], which will be discussed in Section III.

The considerable decrease in entropy observed when polymers are mixed above the glass point shows that phase separation can occur even with a small exothermic effect, as has been found experimentally[8,9]. From the above it is obviously illegitimate to estimate the mutual solubility (compatibility) of polymers from the difference in their cohesion energies[25], for this disregards the important part played by the entropy factor in the expression for the free energy of mixing of polymers.

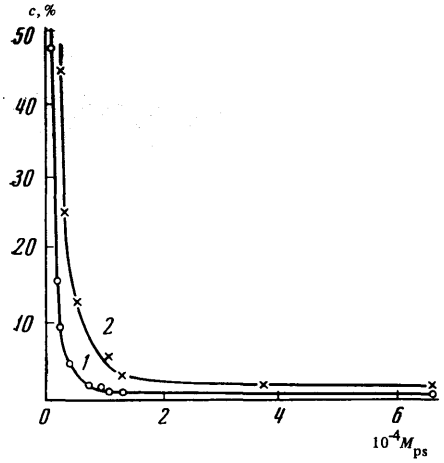



**Figure 1.** Solubility limit $c$ (%) as function of molecular weight of polystyrene (ps) in: 1) polyisoprene ($\overline{M}_W = 10^6$); 2) poly(methyl methacrylate) ($0.87 \times 10^5$).

The difficulty of the direct experimental measurement of the free energy of mixing demonstrates the importance of the direct determination of the mutual solubility of polymers[26,27] as a measure of their affinity. Fig. 1 shows that at high molecular weights the solubility of polymers is small (fractions of 1%) independently of their chemical nature: only at low molecular weights does the solubility increase. Polystyrene dissolves completely in polyisoprene of high molecular weight only when $M_W \leqslant 600$, and in poly(methyl methacrylate) when $M_W \leqslant 1500$.

These results are qualitatively consistent with those of other investigators. Thus Berek[28], while determining the variation in the critical separation concentration of polystyrene and atactic polypropylene in solution with polymers of different molecular weights, found by extrapolation that, in the absence of a solvent, complete miscibility was exhibited by polymers having molecular weights in the range 330—660. Kuhn and Cantow[29] found that poly(methyl methacrylate) of degree of polymerisation 17 ($M_W \simeq 1500$) should be a $\theta$-solvent for polystyrene. Oligomeric acrylates of various structures display considerable solubility in poly(methyl methacrylate)[30].

The above work together with that of Paxton[31], who established the limited miscibility of oligomers, disproves predictions[32] that polymers having $M_W \simeq 10^4$ are completely miscible. Fig. 1 indicates that $M_W = 10^4$ is the molecular-weight limit below which solubility increases rapidly with decrease in molecular weight.

Poly(vinyl chloride) and the butadiene—nitrile rubber SKN-40, which interact strongly owing to the polarity of their groups, probably constitute the only pair of polymers of high molecular weight that differ in chemical nature but yet are completely miscible[33].

Since mutual solubility increases markedly (up to complete miscibility) as the molecular weight of polymers falls below $M_W = 10^4$, segmental solubility of polymers was postulated[34] at their interface. This phenomenon is due to the dual nature of the macromolecules: they actually consist of segments, which accomplish the elementary act of thermal motion (displacement of the macromolecule). Mutual dissolution of the segments of unlike macromolecules can be assumed to occur[34] at the boundary of block polymers and especially in solution. Mutual solubility of the segments is well supported by the complete miscibility of the monomers (even when hydrogenated) of most polymers. Further confirmation is provided by the good miscibility of oligomers (Fig. 1). Hence most polymers are macromolecularly incompatible, but segmentally compatible in the interfacial layer[34]. The presence of such a transition layer, resulting from segmental solubility, is evidently responsible for the quite intense interaction of polymers in two-phase mixtures, i.e. when they are incompatible. Experimental determinations of the free energy of polymer mixtures, recently begun by Tager[35], show that $\Delta G$ is quite large and negative even for a mixture of incompatible polymers.

## 2. Solvent—Polymer—Polymer (1—2—3) System

Under certain conditions solutions of mixtures of two polymers in a common solvent, completely miscible with each of the polymers, separate into two phases each containing predominantly one polymer. Experience has shown that separation occurs not only in mixtures of polymers differing markedly in nature and structure, whose mutual insolubility is self-evident, but also in mixtures of polymers which are very similar in nature, such as polymeric *o*- and *p*-methylstyrenes[36], linear and branched polystyrenes[10], poly(methyl acrylate) and poly(ethyl acrylate)[11], poly(methyl acrylate) and poly(methyl methacrylate)[11], etc.

At infinite dilution, when the solution contains isolated macromolecules, the polymer—polymer—solvent system forms a single phase. Like any critical phenomenon, phase separation results from the interaction of macromolecules of the same kind and the consequent change in the supermolecular structure of the system. On increasing the concentration of solutions of polymer mixtures, therefore, we may expect phase separation only at a sufficiently high concentration, as follows from Eqns. (7)—(9), depending primarily on the interaction parameter of the polymers $\chi_{23}$ and on their degrees of polymerisation $x_2$ and $x_3$.

The conditions for the transition of a single-phase solution into two phases have been analysed thermodynamically mainly by Scott[7], Tompa[37], and Maron[38]. The calculations by Scott and by Tompa, which are complementary, are based on the Flory—Huggins theory, and have

been reported in detail in the books by Flory[39] and by Tompa[40].

If we assume that the polymers have the same degree of polymerisation and the same affinity for the solvent ($x_2 = x_3 = x$ and $\chi_{12} = \chi_{13} < 0.5$), the equality of the chemical potentials of the polymers and the solvent in the two phases of the separated solution will yield (Eqn. 5) the formula

$$\ln \varphi_2 + \chi_{23}(1 - v_1)\varphi_3^2 = \ln \varphi_2' + \chi_{23}(1 - v_1)\varphi_3'^2 \qquad (11)$$

where the volume fraction of polymer 2 in one phase is $\varphi_2 = v_2/(v_2 + v_3)$ and its volume fraction in the other phase

$$\varphi_2' = \frac{v_2'}{v_2' + v_3'} = \frac{v_2}{v_2 + v_3} = 1 - \varphi_2$$

so that $\varphi_3 = 1 - \varphi_2$ and $\varphi_3' = 1 - \varphi_2'$. Equation (11) is fundamental, giving the composition of the coexisting phases of the separated polymer—polymer—solvent (2—3—1) system.

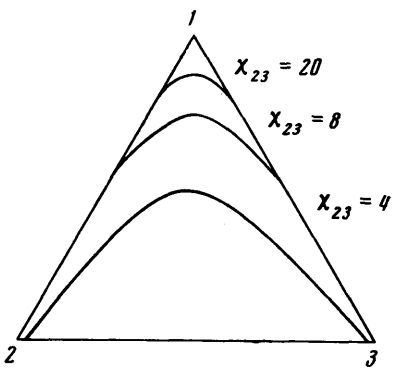



Figure 2. Diagram of solvent—polymer—polymer (1—2—3) ternary system with $x_2 = x_3 = x = 1000$ and the same interaction of the polymers with the solvent[7].

The "symmetry" of Eqn. (11) appears natural with the given initial conditions of equal degrees of polymerisation and the same affinity of the polymers for the solvent. Calculation of the phase diagram by means of Eqn. (11) yields symmetrical binodal curves separating the two-phase from the one-phase region (Fig. 2). In this case the position of the binodals is determined solely by $\chi_{23}$ and $x$.

By analogy with the binary system it is easy to determine the critical phase-separation concentration and the critical interaction parameter of the polymers in the ternary system:

$$\varphi_{2c} = \varphi_{3c} = (1 - \varphi_{1c})/2, \qquad (12)$$

$$\chi_{23c} = 2/(1 - \varphi_{1c}). \qquad (13)$$

Equation (13) shows that phase separation takes place only as a consequence of polymer—polymer interaction: the quantities $\chi_{12}$ and $\chi_{13}$, representing the interaction of each polymer with the solvent, do not even occur in the equations for the critical conditions. Comparison of the critical interaction parameters of the polymers in ternary and binary systems (Eqns. 13 and 7 respectively) indicates that stronger interaction is tolerable between the polymers, without causing phase separation, in the presence of a solvent than in the binary system. As in the binary system, however, interaction between the polymers at the consolute point is small, as follows from an analysis of Eqn. (13). Equating $\chi_{23}$ from Eqn. (4) to the critical interaction parameter from Eqn. (13), we obtain

$$\chi_{23c} = xz\,\Delta\omega_{23}/kT = \frac{1}{1 - \varphi_{1c}},$$

which can be more conveniently written $\chi_{23c}(1 - \varphi_{1c}) = 1/x$. Hence $\chi_{23c}$ is very small for compounds of high molecular weight, corresponding to large values of $x$. It was therefor concluded that mutual insolubility of polymers in solution is the rule rather than the exception. The equation shows also that the larger the interaction parameter the lower the phase-separation concentration (Fig. 2). No phase separation takes place when $1 - \varphi_{1c} \ll 1/x$. Hence solutions of mixtures of polymers in which $x$ is large should separate at very low concentrations, and the limit of separation should become lower with increase in the molecular weight of the polymers.

Scott showed[7] that a phase equilibrium diagram similar to Fig. 2 holds for a large class of ternary systems in which $\chi_{12}$ does not greatly differ from $\chi_{13}$, while the length of the molecular chains satisfy the condition $x_2^{1/2} < x_3 < x_2^2$. Most systems encountered in practice conform to this condition, so that mutual insolubility of polymers in solution is general in character.

The symmetry of the phase diagram is destroyed if the equality $x_2 = x_3 = x$ does not hold. Unsymmetrical diagrams have been obtained[40-42] in which the consolute point was displaced in the ternary diagram (Fig. 2) along the axis of the polymers towards the polymer of lower molecular weight.

An unsymmetrical phase diagram is obtained also when $\chi_{12} \neq \chi_{13}$. The macromolecules are solvated to different extents, so that the actual sizes of the coils of macromolecules of different polymers differ even when they have the same molecular weight. No detailed thermodynamic analysis has been made of the effect of the nature of the solvent on the critical conditions of phase separation. However, Tompa showed[37] that, when there is no interaction between one of the polymers and the solvent, the phase diagram is completely unsymmetrical.

Thermodynamic analysis shows that polymers possess little affinity for one another. Thus from the solubility parameters of polystyrene and polybutadiene Scott[43] found that mixtures of two butadiene—styrene copolymers should segregate if their styrene contents differ by only 8%.[18] Tompa[40,42] predicted from his theory of phase equilibria that fractions of the same polymer might separate if they differ significantly in molecular weight and are placed in a poor solvent for the given homologous series of polymers. This deduction has since been confirmed experimentally[20,44].

According to theory[7] a completely incompatible system, i.e. a system in which one phase consists of solvent plus polymer 2, and the other of solvent plus polymer 3, is in principle possible only where $\chi_{23}$ is very large or at high concentrations of the polymers, which is quite well confirmed experimentally.

We now realise that the theories of the phase composition of a polymer mixture in solution are oversimplified, representing idealised views on the behaviour of polymers in solution. Nevertheless, the theory gives a correct view of the main features of phase separation in the polymer—polymer—solvent system, as is indicated by several experimental investigations reported below.

The main conclusions from the Flory—Huggins theory are supported qualitatively by the work of Dobry and Boyer-Kawenoki[45], who examined 78 combinations in solution. They studied the effect of the nature of the polymers, their molecular weights and proportions in the mixture, and also the type of solvent on the miscibility of the polymers in solution by determining the phase-separation limit and analysing the composition of the coexisting phases.

Theory has been confirmed also by investigations of a mixture of homologous polymers in a common solvent. Sieglaff[10] observed the separation into two phases of a mixture of a linear polystyrene with its microgel in benzene. The best quantitative support for the theory was provided by Koningsveld and Staverman[20], who calculated, in conformity with Tompa's predictions[40,42], that a third phase must be expected at 119.0—121.7°C in a solution of a mixture of two polyethylenes having molecular weights $M_w$ of $1.2 \times 10^4$ and $5.4 \times 10^5$. Mixtures of these homologues in diphenyl ether actually separate into three phases in the range 120.4—121.6°C: the agreement with theory is entirely satisfactory. Shultz and Flory[46], who also investigated the phase separation of two polystyrene homologues ($x_2 = 770$ and $x_3 = 1100$) in cyclohexane, found that theoretical and experimental curves were of the same character, but the latter covered far wider ranges of composition and temperature. Koningsveld and Staverman[44] showed that the discrepancy was due to neglect, in Shulz and Flory's treatment of the experimental results, of the multimolecular character of the polymers.

Experimental work by Bristow[47] and by Berek et al.[28] provided quantitative confirmation of the theory. The former obtained symmetrical diagrams for the natural rubber—poly(methyl methacrylate)—benzene system and the latter for the polystyrene—polypropylene—toluene system; in both cases the polymers had the same molecular weights and a good solvent for both polymers was employed. The systems were analogous to the case examined by Scott[7] and characterised by the parameters $x_2 = x_3 = x$ and $\chi_{12} = \chi_{13}$. The consolute points calculated by Bristow did not lie on the experimental curves, which he attributed to inaccurate determination of molecular weights. The theoretical binoidal calculated by Berek by means of Scott's equation (11) coincided with the experimental curve. The symmetry was destroyed when polymers having different molecular weights were taken.

Allen et al.[32] made an interesting comparison of the Flory—Huggins and Hildebrand theories. They determined the interaction parameter $\alpha_{23} = \chi_{23}/v$ from the distribution of the polymers in the phases. The parameter found from the phase equilibrium was of comparable order of magnitude with the interaction parameters of other pairs of polymers, e.g. with that calculated by Scott[7] from Dobry and Boyer-Kawenoki's results and with that found by Stockmayer and Stanley[48] by light scattering. The interaction parameter was also calculated by means of Hildebrand's formula[49,50] $\alpha_{23} = (\delta_2 - \delta_3)/RT$. It is interesting to compare this work[32] with that of Paxton[31], who determined the interaction parameters of polymers by means of an equation, obtained by him on the basis of Maron's theory[38,51,52], for a mixture of two polymers of low molecular weight in a common solvent. This theory modifies the usual Flory—Huggins formula for the free energy by including a term representing the variation in the effective volume of the polymer in solution, as a consequence of which the interaction parameter varies with the concentration of the solution.

Table 1 assembles values of the interaction parameters, calculated on the basis of various theories, for polystyrene and polybutadiene in solution. The difference in the results given by the Flory—Huggins and Hildebrand theories is to some extent understandable. As already mentioned, Hildebrand assumed a completely random distribution of the molecules. The low results given by the Flory—Huggins theory indicate some ordering of the system and a decrease in entropy. This is confirmed by Flory's calculations for a binary system[22]. Nevertheless, the excessively high values of $\alpha_{23}$ obtained from Maron's theory, which already allows for some orientation of the molecules in the mixture, are completely incomprehensible, and Paxton's explanations of the discrepancies in $\alpha_{23}$ in terms of the polydispersity of the specimens are unconvincing.

Table 1. Polystyrene—polybutadiene interaction parameter calculated on basis of different theories.

| Theory | $\alpha_{23}$, litre$^{-1}$ | Ref. |
|---|---|---|
| Flory-Huggins | 0.1 | 32 |
| Hildebrand | 0.15 | 32 |
| Maron | 28—29 | 31 |

The results surveyed show that the Flory—Huggins theory provides the most complete description of the behaviour of ternary systems, although certain discrepancies are found, mostly concerning estimates of the interaction parameter of polymers in solution. According to the theory $\chi_{23}$ represents the energy of contact between segments of the two polymers, and is constant for a given pair of polymers, independently of the composition of the mixture and the temperature. Experiment shows that the interaction parameter depends on the mixture composition[32] and on the total concentration of polymers in solution[28]. Theory indicates also that $\chi_{23}$ is independent of the solvent, although in several cases it has been found to vary with the nature of the latter[36,53].

A need has undoubtedly grown in this field for general papers that will show, on the basis of comprehensive experimental data, the dependence of the limit of phase separation, the composition of the layers after separation, and ultimately the dependence of the structure of the polymer mixture after removal of solvent on the interaction parameter calculated by any available method.

## III. ONE-PHASE SOLUTIONS OF MIXTURES OF POLYMERS

Nuclei of a second phase appear in any system long before the phase transition takes place. This should apply also to solutions of polymer mixtures, where corresponding changes in the supermolecular structure of the solution must be expected at concentrations below the phase-separation limit.

Association complexes of the macromolecules appear in a polymer solution at a certain concentration[24,54]. In a solution of a polymer mixture there are two theoretical

possibilities: either molecules of polymer A and those of polymer B can associate separately; or mixed adducts, each containing macromolecules both of A and of B, can be formed. In the former case increase in size of the association complexes with increase in concentration can reasonably be expected, terminating in the formation of an interface between unlike aggregates and the separation of droplets of a new phase. In the latter case increase in size of adducts of unlike macromolecules can hardly lead to separation of the solution into two phases, since experiment shows that, after a solution has separated into layers, each phase contains predominantly one of the polymers, so that adducts of unlike molecules must have broken down at the instant of phase separation, after which separation into layers occurs with the formation of association complexes of like molecules in each phase. The second type of structural changes at the instant of phase separation is illogical to the extent that formation of adducts of unlike macromolecules can probably be assumed only in cases in which the polymer mixtures do not separate into layers at all (at least in solution).

Although these suggestions on the mechanism of structure formation appear convincing, they require experimental verification, and the present Section is devoted to the relevant results.

When the concentration of a very dilute solution of a polymer is increased, a point may be reached at which isolated coils of macromolecules come into mutual contact. This ensues at a critical concentration $c_1$, indicated by a break on the property—concentration curves for the polymer solution[55,56] or determinable, following Debye, from the reciprocal of the intrinsic viscosity, the latter having the dimensions of a specific volume and characterising the density with which the solution is filled with macromolecule segments[57].

A critical concentration has been detected experimentally in solutions of polymer mixtures[58-60]. Cragg and Bigelow[58,59] determined the intrinsic viscosity and the intrinsic asymmetry ($[\eta]_A$ and $[\varepsilon]_A$) of a polymer A from light-scattering data in a solvent—a solution of polymer B of concentration $c_B$—and observed at the critical concentration a discontinuity—a peak or a dip—in the dependence of $[\eta]_A$ and $[\varepsilon]_A$ on $c_B$. Kuleznev and his coworkers[60] compared the intensity of scattering $R_{90}{}''$ by a mixture of polystyrene and polyisobutylene in toluene with the scattering by polystyrene in pure toluene, and found that, up to a certain concentration $c_1$, polystyrene scatters with the same intensity in the mixture as in pure toluene, after which its scattering in the mixture increases sharply. Such comparison was made possible by the isorefractivity of polyisobutylene and toluene, as a consequence of which the former was optically invisible in the latter. The critical concentration $c_1$ was easily determined from the break in the linear dependence of $c/R_{90}{}''$ on $c$. The considerable increase in intensity of scattering by polystyrene in mixtures having $c > c_1$ is attributed by the Reviewers to the fact that, in the presence of another polymer, the polystyrene macromolecules are constrained to associate to a greater extent than in the pure solvent (excess association).

The results reveal at least two characteristic concentrations in solutions of polymer mixtures, separating concentration ranges differing in structure. The first and lowest concentration may be $c_1$, at which the macromolecules come into mutual contact; at the second concentration $c_2$, termed the phase-separation limit, the solution divides into two layers. The concentration range $c_1$—$c_2$ gives solutions with a definite extent of association of the macromolecules: association begins at $c_1$, and at $c_2$ the size of the aggregates reaches a limit at which an interface appears (Fig. 3). Let us examine the changes in structure undergone by solutions of polymer mixtures within these concentration ranges.

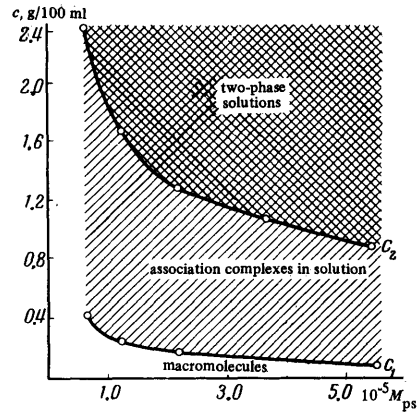



**Figure 3.** Concentration limits of solutions of polystyrene—polyisobutylene (7 : 3) mixtures in three structural states as function of molecular weight of polystyrene.

In 1964 we first proposed[61] the "polymeric" (isorefractive) solvent method for investigating such structures. The method consists essentially in choosing a solvent in which the increment of the refractive index of one polymer is zero, and a solution of this polymer of given concentration is used as the "polymeric" solvent, e.g. a solution of polyisobutylene in toluene. This permits the preparation of solutions of polymer mixtures, e.g. with different concentrations of polystyrene and a constant concentration of polyisobutylene. Such solution may be concentrated with respect to the polymer mixture, but dilute with respect to polystyrene, which permits the theory of dilute solutions and the usual methods of processing experimental results to be applied to the solution of polystyrene. The Debye or Zimm method can be used to determine the molecular weight of polystyrene, the size of its coil, and the second virial coefficient in a polymeric solvent at a different concentration. This principle has since been applied by several workers in investigating light scattering[29,62-65] and viscosity in solutions of polymer mixtures[53].

Using a very dilute polymeric solvent, Eskin[64] and Kuhn[62,63] observed a contraction of the polymer coil relative to its size in the pure solvent, but Kuhn noted that the coil is larger in a polymeric $\theta$-solvent than in a $\theta$-solvent of low molecular weight. Eskin[66] also remarked on the lack of identity between the two types of $\theta$-solvents. The coil contracted with increase in concentration of the polymeric solvent, but, as already noted, the concentration remained low. Similar results were obtained in viscosimetric measurements[53], when a decrease in intrinsic viscosity with increase in the concentration of the polymeric solvent was established. However, these results are inconsistent with those of Hyde and Tanner[65], who found that the size of the polymer coil was independent of the concentration of the polymeric solvent, and attributed

this to the almost zero interaction parameter of the polymers. The Reviewers have shown[60] that the size of the coil of one polymer in a solution of another polymer remained constant over a certain concentration range of the polymeric solvent not exceeding the concentration at which association begins. At higher concentrations the coil size increases while the molecular weight remains constant. The Reviewers offer the explanation that, at solution concentrations below $c_1$, unlike macromolecules may be sufficiently far apart not to interact strongly enough to increase the extent of association or change the shape of the coil. If the concentration of the polymeric solvent comes to exceed $c_1$, the molecular coils of unlike macromolecules may interpenetrate. This is entirely possible, for the solution is a single phase at these concentrations, so that there is no physical boundary between coils of unlike molecules or their association complexes in contact. Thus a considerable concentration of segments of one polymer may be produced within a coil of the other polymer in a single-phase solution of a polymer mixture. Because contacts between like segments are preferred, the interaction of unlike segments will be equivalent to repulsion. As a consequence of the presence of polyisobutylene segments both outside and inside the polystyrene coil, the latter may either uncoil or contract depending on whether the resultant effect is directed inside or outside the coil. In the present case the polystyrene coil unwinds, becoming larger, a prerequisite for the association of such an "uncoiled" molecule with similar molecules, as occurs at high polystyrene contents in the solution. In other cases[62-64] the polymer coil became smaller with increase in concentration of the "polymeric" solvent.

The partial straightening (uncoiling) of coils with increase in solution concentration is characteristic of all individual solutions of polymers (see e.g. Ref. 57, p. 102). If, however, a solution of one polymer is diluted with a fairly concentrated polymeric solvent (total solution concentration close to the phase-separation limit of the mixture), the solution of the first polymer will not break down into individual coils of macromolecules, as Kuhn and Cantow showed[62,63], but the polymeric solvent will contain aggregates of degree of association ~55. It is obvious that data on the variation in size of the coil give limited information on possible association processes, for almost all the experiments mentioned were made at high dilutions of the polymer whose molecular association was being investigated.

The 1964 paper already mentioned reported the determination of the second virial coefficient $A_2$ of polystyrene from light-scattering data in a polymeric solvent (a solution of polyisobutylene). It was found that $A_2$ for polystyrene dropped sharply, approaching zero, with increase in the polyisobutylene concentration[61]. Kuhn has since found[29] that $A_2$ may not only reach zero but even assume negative values. The higher the molecular weight of the polymer in the polymeric solvent, the lower its concentrations at which $A_2$ becomes zero.

A decrease in $A_2$ indicates deterioration of the solvent. Hence a solution of one polymer is a thermodynamically poor solvent for another polymer. In poor solvents the association of polymers is large, which sometimes may even lead to separation of the polymer as a new phase. It can reasonably be assumed that macromolecules of one polymer will show a greater tendency to associate in the presence of another.

The scattering of light has been used to investigate association phenomena[60]. With simple liquids the composition variation of the scattering is often non-additive. A positive deviation in the intensity of scattering above the additive value indicates[67] excess molecular association relative to the mean degree of association of the two liquids.

The polymer–polymer–solvent system is more complicated than a mixture of two liquids. It would have been completely unjustified to apply the additivity principle here, and therefore the investigation was made in the polystyrene–polyisobutylene–toluene system, in which the latter two compounds had almost the same refractive indices, so that scattering in the mixture was due mainly to polystyrene, whose scattering $R_{90°}''$ was compared with its scattering in toluene. The dependence of $R_{90°}''$ on the composition of the polymer mixture (Fig. 4) at constant solution concentrations in the range $c_1$–$c_2$ passes through a maximum. The increased scattering by polystyrene in the mixture, relative to its scattering in toluene, depends on the proportions of the polymers, the molecular weight, and the concentration of the solution. The excess scattering $\Delta R_{90°}''$, obtained by subtracting the intensity of scattering by polystyrene in toluene from the intensity of scattering by the mixture, increases linearly with the concentration of the solution (Fig. 5), which separates into layers at concentration $c_2$.

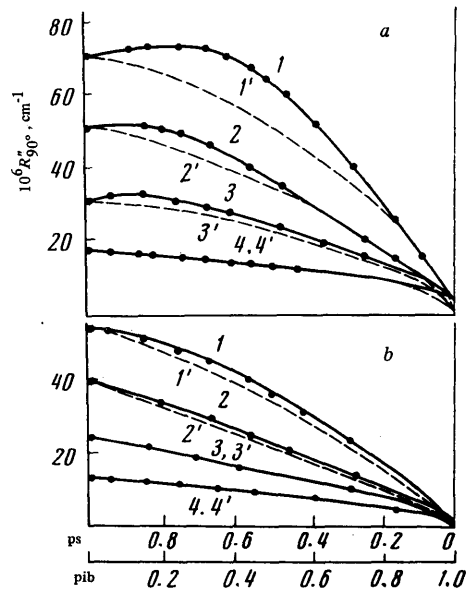



**Figure 4.** Dependence of $R_{90°}''$ ratio of polymers for polystyrene–polyisobutylene (ps–pib) mixtures in toluene solutions of constant concentration (g/100 ml): *a*) 0.5; *b*) 0.2 on molecular weight of polystyrene ($\times 10^{-5}$): 1) and 1') 5.5; 2) and 2') 2.2; 3) and 3') 1.2; 4) and 4') 0.65. The full (unprimed) curves represent solutions of mixtures, and the broken (primed) curves solutions of polystyrene.

The above results show that, in a solution of a mixture of polymers, like molecules begin to associate at a concentration $c_1$, and the association complexes reach their limiting size and density at point $c_2$, when the system separates into two phases. At the concentration $c_2$ the

density of association complexes of polymer A and polymer B is such that they acquire the properties inherent in particles of a new phase: in particular, a physical interface appears. It may be suggested that a polymer of given chemical nature will have a critical degree of association, independent of the molecular weight of the polymer, at which an interface is formed. This hypothesis was tested[60] by determining the excess scattering $\Delta R_{90°}''$ by polystyrene of various molecular weights in mixtures having the same ratio of polymers (Fig. 5).

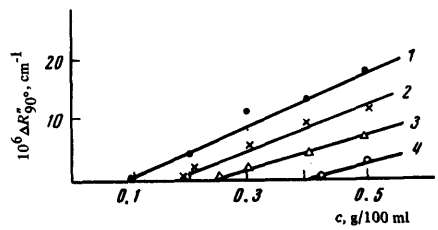



**Figure 5.** Concentration dependence of excess scattering $\Delta R_{90°}''$ of polystyrene in mixture with polyisobutylene (7 : 3) in comparison with individual solution of polystyrene in toluene for different molecular weights ($\times 10^{-5}$) of polystyrene: 1) 5.5; 2) 2.2; 3) 1.2; 4) 0.65.

The excess light scattering can be regarded as the same in solutions of mixtures of polystyrene and polyisobutylene independently of the molecular weight of the former, provided that the solutions are in a corresponding state, i.e. that their concentrations are equidistant from $c_1$ and $c_2$. A dimensionless parameter—the reduced concentration $c^* = (c - c_1)/(c_2 - c_1)$, where $c$ is the concentration of the solution of the polymer mixture in the usual weight units—was taken as measure of a corresponding state. The experiment showed that the dependence of $\Delta R_{90°}''$ on $c^*$ is represented by a single straight line for all solutions of mixtures of the two polymers in toluene, independently of the molecular weight of the polystyrene (Fig. 6). In the precritical range $\Delta R_{90°}''$ is the same for all polystyrene fractions independently of their molecular weight.

It is hardly justifiable to assert that mixtures of different pairs of polymers will be represented by the same linear plot of $\Delta R_{90°}''$ against $c^*$, since an interface is apparently formed at different densities of association complexes with different polymers. In any case, comparison of the tendency of polymers to associate in a mixture must obviously be made at equal values of $c^*$, whose calculation requires a knowledge of $c_1$ and $c_2$.

Thus a solution of a mixture of two polymers has a fairly specific "cellular" structure. Segments of polymer A are concentrated in individual microvolumes, and segments of polymer B in others; the intermediate spaces are filled with a mixture of segments of A and B in the absence of a physical interface. Light-scattering data show that microvolumes containing like segments (association complexes) are more densely packed than the corresponding homophase fluctuations in individual solutions of polymers A and B at the same concentrations by weight. Microvolumes containing a mixture of segments, on the other hand, would be loosened, for, in a system of incompatible polymers, the A—A and B—B segment interactions are more intense than the A—B interaction. Such a structure affects the properties of the solution, and also provides an explanation of certain aspects of the properties of polymer mixtures in bulk. Examples are given below.

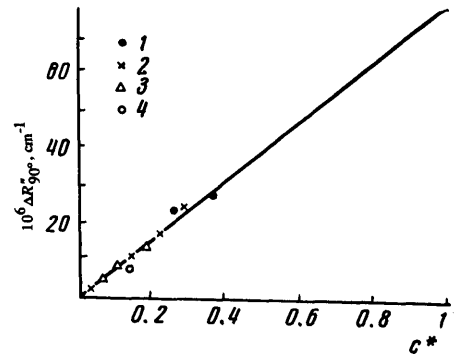



**Figure 6.** Dependence of excess scattering $\Delta R_{90°}''$ by polystyrene in mixture with polyisobutylene on reduced concentration $c^*$ for different molecular weights ($\times 10^{-5}$) of polystyrene: 1) 5.5; 2) 2.2; 3) 1.2; 4) 0.65.

The presence of microregions with a loosened structure leads to a considerable increase in solubility of a third polymer in a solution of a binary polymer mixture. If solutions are prepared of a mixture of polyisobutylene, polybutadiene, and polystyrene in chloroform having a total concentration of 4.0 g/100 ml but with different proportions of the polymers, the range of proportions in which the mixture is transparent defines the region of mutual solubility of the polymers. With the above total concentration of polymers in solution the solubility of polyisobutylene in polybutadiene and in polystyrene is ~1.4%, but its solubility in a 3 : 1 mixture of the latter polymers is 13%. Fig. 7 shows as example the solubility diagram for the polyisoprene—polyisobutylene—polystyrene system, where the effect is still more clearly evident.

A mixture of polyethylene and polypropylene illustrates the increase in order of arrangement of segments in each polymer phase when polymers are mixed in the melt[69]. The temperature range between the melting point and the crystallisation point in each polymer phase in the mixture is smaller than in the individual polymers. The fact that each molten polymer crystallises at higher temperatures in the mixture indicates a high degree of order in the molten mixture.

Research on solutions of polymer mixtures was first made by physicochemical methods, and the composition dependence of viscosity was studied initially. This approach was not altogether fruitful, for it was necessary to compare the viscosity—composition curve with the calculated or experimental curve for the same components forming an ideal mixture. The experimental curve then differs from the theoretical curve (ideal mixture), and the interaction of the components can be assessed from the magnitude and character of the deviations. Such approach is known to be fruitful for investigating the vapour pressure over mixtures of liquids of low molecular weight.

The situation is more complicated with polymer mixtures in solution, since in several cases the theoretical property—composition curve can be plotted only for very dilute solutions. For a long time the experimental curves were compared with straight lines connecting the properties of the individual components, which cannot be accepted as justified, since most properties—especially mechanical—are not represented by these lines even in ideal mixtures[70].

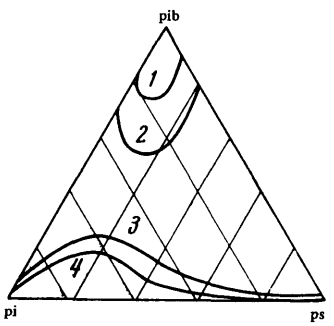



Figure 7. Miscibility diagram at 25°C for solutions of polyisobutylene (pib), polyisoprene (pi), and polystyrene (ps) in chloroform with different total concentrations (g/100 ml) of polymers in solution: 1) 2.5; 2) 2.25; 3) 2.25; 4) 2.5.[68]

It is very important here to examine the units in which the composition of the mixture is expressed and the quantity used to measure the given property. In fact Arrhenius long ago suggested, for the viscosity of binary liquid mixtures, the empirical formula[71]

$$\ln \eta = N_1 \ln \eta_1 + N_2 \ln \eta_2 \qquad (14)$$

where $N_1$ and $N_2$ are the mole fractions of the components, and $\eta_1$ and $\eta_2$ the corresponding viscosities. Although this formula is quite approximate, it nevertheless shows that viscosity is not an additive function of composition, but its logarithm varies linearly with mixture composition. For a polymer mixture this formula agrees with experiment only in the region of small concentrations[72].

Calculation of the composition dependence of a particular property can sometimes be usefully based on its dependence on molecular weight, since the molecular weight of a mixture is the mean of those of the components. Thus the calculation[73] of the dependence of the specific viscosity of a solution on the ratio of the polymers showed that mixtures of solutions of polyethylene fractions are not "ideal" even at low concentrations.

The intrinsic viscosity of solutions of polymer mixtures is given by the simple formula[74-78]

$$[\eta]_{m.} = x[\eta]_1 + (1-x)[\eta]_2 \qquad (15)$$

where $x$ is the fraction of component 1 by volume[74-76] or by weight[77,78].

The specific interaction in solutions of polymer mixtures of finite concentration, at which unlike macromolecules interact, could be estimated if the ideal behaviour of the mixture were known. Thus several attempts were made to describe the theoretical specific viscosity $\eta_{spm}$ of a solution of a mixture[73,79-81]. Krigbaum and Wall[79] suggested the formula

$$\eta_{spm} = [\eta]_1 c_1 + [\eta]_2 c_2 + b_{11} c_1^2 + 2\sqrt{b_{11} b_{22}}\, c_1 c_2 + b_{22} c_2^2 , \qquad (16)$$

$$b_{12} = \sqrt{b_{11} b_{22}} , \qquad (17)$$

where $b_{11}$ and $b_{22}$ are parameters of interaction between the like macromolecules, and $b_{12}$ is the parameter of interaction between unlike macromolecules. An analogous equation, differing only in the expression for $b_{12}$, was proposed by Catsiff and Hewett[80]:

$$\eta_{spm} = [\eta]_1 c_1 + [\eta]_2 c_1 + b_{11} c_2^2 + (b_{11} + b_{22}) c_1 c_2 + b_{22} c_2^2 , \qquad (18)$$

where

$$b_{12} = \frac{b_{11} + b_{22}}{2} . \qquad (19)$$

Cragg and Bigelow[81] obtained a theoretical formula for the Huggins constant $k'$ for a binary polymer mixture in solution and a theoretical value for the viscosity of the mixture:

$$\frac{\eta_{spm}}{c} = \frac{[\eta]_1 c_1 + [\eta]_2 c_2 + k_1' [\eta]_1^2 c_1^2 + k_2' [\eta]_2^2 c_2^2 + 2\sqrt{k_1' k_2'}\,[\eta]_1 [\eta]_2 c_1 c_2}{c_1 + c_2} . \qquad (20)$$

If the interaction parameter is taken to be $b = k'[\eta]^2$, this relation proves to be analogous to the Krigbaum—Wall equation.

These workers[79,80] propose that the difference between experimental and theoretical values of the parameter $\Delta b_{12} = b_{12,\,exp} - b_{12,\,theor}$ should be taken as a measure of the affinity of the polymers in solution.

Wright and Williamson[82] compared the two methods for calculating $b_{12}$, and considered that far better agreement between theory and experiment is obtained by substituting the arithmetic mean value of $b_{12}$ in the appropriate equations.

The parameter $\Delta b_{12}$ has recently been used to assess the compatibility of polymers in solution, and results have been obtained[41] coinciding with the estimate obtained from phase separation. Other workers[83] have shown that the range of compatibility of polymers can be established by means of $\Delta b_{12}$, but they regard the possibilities of the method as limited.

It is still impossible to calculate the composition dependence of viscosity (or a related quantity) at sufficiently high mixture concentrations. In some cases definite information can be obtained on the structure of a mixture of polymers in solution and on the intensity of their interaction by analysing the viscosity—composition curve itself, without comparing it with the curve for an ideal mixture[84,85].

Finally, it must be borne in mind, when plotting a property—composition graph, that the polymer macromolecules have different effective volumes in the solvent and in the mixed solutions. Mixing solutions of polymers in a common solvent usually involves an increase in the coil volume of that polymer which has the greater affinity for the solvent. It is then obvious that the true volume fraction of this polymer in the mixture will be larger than that calculated from the ratio of the initial volumes of solutions of equal concentration. The real volume ratio of polymers in a solution of their mixture has recently been allowed for[86].

## IV. FACTORS INFLUENCING THE LIMIT OF PHASE SEPARATION

The more highly concentrated the solution of a polymer mixture at which it separates into layers, the broader the range of existence of thermodynamically stable single-phase systems. Although a polymer mixture is stable for an unlimited time in the absence of a solvent, and phase separation is prevented by the high viscosity of the components, the viscosity of solutions is usually sufficiently low for phase separation to occur quite rapidly and to be easily noticeable. Therefore study of the dependence of the phase-separation limit on various external and internal factors is an indirect method for assessing the effect of these factors on the compatibility of polymers in the block (in the absence of a solvent), where such estimates are very difficult. An investigation of this type is also of intrinsic scientific value in connection with the use of polymer mixtures as a common solution[87] for subsequent processing. The phase-separation limit of a solution of a polymer mixture can in principle be affected by the factors—(*a*) nature and structure of macromolecules, (*b*) proportions of polymers in mixture, (*c*) molecular weights of polymers and molecular-weight distribution, (*d*) type of solvent, (*e*) temperature, (*f*) shear stress, and (*g*) additives—which will be examined below.

### (*a*) Nature and Structure of Macromolecules

A pair of polymers in solution can be regarded as compatible or incompatible depending on the concentration. The higher the phase-separation limit the higher the mutual affinity of the polymers, as is shown by experience, and the greater the compatibility of the polymers, it is usually supposed. However, the phase-separation limit of a mixture in solution is only a particular qualitative indication of the mutual solubility (compatibility) of the polymers. No comparison has been made of this limit or of its variation with the true solubility of the polymers in the absence of a solvent.

Analysis of published information shows[45,88,89] that solutions of polymers are usually mixed to establish the actual fact of their compatibility or incompatibility, without relating the phase-separation limit with their nature and structure. Polymers of apparently similar polarity, whether a mixture of two polar or two non-polar polymers, and also those differing strongly in polarity—a combination of polar and non-polar polymers—have been found to be incompatible[88,89]. Moreover, the incompatibility has been established of polymers of the same chemical nature, differing in the stereochemistry of the monomer units (the position of substituents[11,13]) or in the degree of chain branching[10,90]. Thus Kern[13] found that polymeric *o*- *p*-, and *m*-methylstyrenes were incompatible. Rylov and Karpov[12] observed mutual insolubility of natural rubber and gutta-percha, which are *cis*- and *trans*-isomers. Attempts were made to correlate the phase-separation limit with the structure of the polymers. Dobry and Boyer-Kawenoki[45] were unfortunately unsuccessful: no definite rule could be established.

In order to elucidate the effect just of the structure of the polymers, all factors influencing the phase-separation limit must be maintained constant, and only the chain structure of the macromolecules varied. This is an extraordinarily complicated task, since it is especially difficult to select polymers of the same molecular weight. Fuchs[11] was faced with this problem in studying the effect of the structure of polymethacrylates and polyacrylates on the limit. He determined the limit in benzene of solutions of mixtures of polyacrylates (methyl, ethyl, and n-butyl) with one another, mixtures of polymethacrylates differing in the length of the alkoxyl side-chain (methyl, ethyl, n-butyl, isobutyl, and hexyl), and also mixtures of polyacrylates with polymethacrylates, and compared the results with the difference in the number of carbon atoms in the monomer units of the mixed polymers. Unfortunately, the molecular weights were not always the same or even close, but nevertheless a general tendency could be established. A difference of one carbon atom, whether in the main chain or in a side-chain, was sufficient for the polymers to become incompatible. Thus poly(methyl acrylate) separated from poly(ethyl acrylate) and from poly(methyl methacrylate) in solution. Moreover, solutions of mixtures of poly(isobutyl methacrylate) with poly-(n-butyl methacrylate) separated into layers. The phase-separation limit fell with increase in the difference in the numbers of carbon atoms in the monomer units of the mixed polymers. Unfortunately, these rules were not verified on binary mixtures of two polymers in the absence of a solvent.

The effect of the degree of branching of the macromolecules on the phase-separation limit has also been studied[90].

### (*b*) Proportions of Polymers in Mixture

The theoretically calculated binoidal separating the single-phase from the two-phase region in Fig. 2 shows that increasing the content of one of the components raises the phase-separation limit. This applies also to unsymmetrical diagrams. Regions having a low content of one of the polymeric components have in general been little investigated. Moreover, it has been noted several times[70,85,91] that phase separation does not take place when the mixture contains 10% of one of the polymers. This conclusion is probably due to the technique used to study the phase separation of solutions: solutions of the same concentration, deliberately exceeding the phase-separation limit for a 1 : 1 mixture, were always mixed in various proportions. But this concentration might be insufficient for the mixture to separate into layers when the content of one of the polymers is small.

A correct choice of technique enabled the Reviewers[92] to observe phase separation in a mixture of polyisobutylene with only 0.4% of polystyrene. It is quite obvious that the compatibility of a solution of one polymer with a solution of another depends on the total polymer concentration, and diminishes with increase in the total concentration of the solutions taken.

### (*c*) Molecular Weights of Polymers

Dobry and Boyer-Kawenoki[45] were long ago able to establish qualitatively that the higher the molecular weight the lower the concentrations at which solutions separate into layers. Theory also predicts a decrease in mutual solubility with increase in the molecular weight of polymers.

The effect of molecular weight on the phase-separation limit has repeatedly been examined experimentally, and this usually ended in establishing empirical relations

unconnected with theory. Berek et al.[93] found the relation—later confirmed[94]—between the critical phase-separation concentration $c_c$ and the molecular weights of the polymers

$$c_c = A(\bar{M}^+)^{-2/3} + c_\infty , \quad (21)$$

where $\bar{M}^+ = (M_i M_j)^{0.5}$ is the geometric mean of the molecular weights, $M_i$ and $M_j$ are the molecular weights of polymers $i$ and $j$, and $A$ and $c_\infty$ are constants for a given pair of polymers. This equation applies in effect both to monodisperse and to relatively polydisperse polymers. Only when a combination of polymers is investigated whose molecular weights differ very markedly, and for which the conditions $\chi_{12} - \chi_{13} < 1$ and $x_2^{0.5} < x_3 < x_2^2$ are not satisfied, do the values of $c_c$ depart from a linear dependence on $(\bar{M}^+)^{-2/3}$.

Berek's equation is similar to an equation proposed by Kuhn et al.[95]. Later results[29] indicate that the dependence of $c_c$ on the molecular weight of polystyrene in the ternary system with poly(methyl methacrylate) and benzene is given by the equation

$$1/[\eta]_{nc} = a_1 \ln(c_c v_{av.}) + f(\bar{M}_{w_{nc}}) , \quad (22)$$

where $v_{av}$ is the mean specific volume of the polymer, and $a_1$ and $f$ are constants. An analogous equation can be written for the dependence of $c_c$ on the molecular weight of the poly(methyl methacrylate).

On the assumption that the phase-separation limit should depend on the molecular weight and the type of solvent, Fuchs[96] suggested the empirical relation

$$\left(\frac{\eta_2}{P_2} + \frac{\eta_3}{P_3}\right) b = k c_3 , \quad (23)$$

where $\eta_2$ and $\eta_3$ are the specific viscosities of solutions of the polymers ($c$ = 1 g/100 ml), $P_2$ and $P_3$ are the degrees of polymerisation of the polymers, and $b$ and $k$ are constants. The validity of this relation was confirmed on several pairs of polymers.

Analysis of the above results shows that decrease in molecular weight of the polymers (over the range investigated) was always accompanied by a rise in the phase-separation limit: i.e. the concentration range in which the solution consisted of a single phase increased.

### (*d*) Type of Solvent

Theory regards the solvent as a simple diluent, which merely shifts the phase-separation limit.

Experimentally, Bristow's choice of solvents[47] was very unfortunate, one being a good solvent for both polymers, whereas the other was in our opinion a poor solvent, again for both polymers. He did not explain the effect of this quality on the symmetry of the phase diagrams, because he did not evaluate the quality, but simply started from the similarity in structure between solvent and polymers. At the present time no definite criterion of solvent quality is available, although certain properties of the solution have been correlated with solvent quality by Schulz[97] and by Tager[98,99]. As a consequence of the lack of a sensitive criterion for estimating the affinity of a solvent for a polymer, each worker has used his own criterion for assessing the quality of a solvent in investigating the effect of type of solvent on compatibility.

Kern[36] judged the quality of a solvent from its solubility parameter $\delta$. He compared the parameters of various solvents with those of the mixed polymers, and observed maximum compatibility in solvents whose solubility parameters were closely similar to those of the polymers.

Fuchs[96] investigated the compatibility of polystyrene with poly(vinyl acetate) in eighteen solvents, in whose choice he was guided by the solvating power assessed from the viscosity of solutions of concentration 1 g/100 ml, which introduces some arbitrariness, as it would have been more reliable to base the comparison on the intrinsic viscosity. He determined the empirical relation (23), which indicates that the poorer the solvent (the lower the viscosity) the lower the concentration at which solutions separate into layers. This conclusion has been confirmed[27] on mixtures of widely varying composition, the quality of a solvent with respect to the polymers being judged from the intrinsic viscosity.

An explanation for the phase separation of a polymer mixture at lower solution concentrations the poorer the solvent is that polymer—solvent interaction is slight in poor solvents, so that polymer—polymer interaction increases. Deterioration in the quality of the solvent in the solvent—polymer—polymer (1—2—3) system involves an increase in the size of 2—2 and 3—3 polymeric association complexes. This size must probably reach a certain critical value for phase separation to ensue, and this occurs at a lower concentration in poor solvents because of the greater tendency of polymers to associate in such solvents.

Hugelin et al.[53] proposed that the affinity of a solvent for a polymer should be assessed by the constant $\alpha$ in the Kuhn—Mark—Houwink equation $[\eta] = kM^\alpha$, characterising the shape of the polymer coil, which varies with swelling. The phase-separation limit rises as the difference between the constants of the mixed polymers becomes smaller, except in poor solvents for both polymers. This is inconsistent with the results[27,96] indicating that the compatibility of polymers in solution diminishes as the quality of the solvent becomes worse. A poor solvent for both polymers should correspond to a small difference $\alpha_2 - \alpha_3$ and a low phase-separation concentration. Hugelin's equation evidently applies only to systems containing a good solvent for one or both polymers.

Sometimes homogeneous films can be obtained from a mixture of incompatible polymers by suitable choice of solvent. Thus Thies and his coworkers[100,101] obtained transparent and turbid films respectively of a mixture of polystyrene and poly(methyl vinyl ether) from solutions in toluene and in chloroform. The temperature dependence of the slope of the mechanical-loss curve indicates some microheterogeneity of the transparent films (one intermediate loss peak), but from the results there is no doubt about the strong effect of the nature of the solvent on the structure of the film.

### (*e*) Temperature

Varied views have been published on the effect of temperature on phase separation. Several workers state that temperature has either almost no effect[62,63] or a very slight effect[28,45] on the phase-separation limit of solutions. Flory's theoretical calculation[22] of the thermodynamic functions of the mixing of polymers has also shown their independence of temperature. Other work[36,100] shows that temperature plays a considerable part, influencing the flexibility of the polymer molecules and also their solvation. Thus Kern[36] found that a mixture of polystyrene and poly(methyl methacrylate) in *o*-xylene separates into

layers at 25°C, and becomes a single phase at 85°C. In methoxybenzene, however, this mixture was homogeneous at 25°C, and separated at 85°C. A similar phenomenon was observed by Purcell[100] with a mixture of chlorinated rubber and an ethylene—vinyl acetate copolymer: the mixture was compatible at 25°C, but separated into layers with rise in temperature.

Available experimental results show that both lower and upper temperatures of mixing can exist in solutions of polymer mixtures, as in solutions of individual polymers. The more distant a solution from both consolute temperatures the less marked the effect of temperature on its phase constitution. Systems having a lower consolute temperature are evidently not a rarity among solutions of polymer mixtures. The desirability of further experimental investigation in this field is self-evident.

### (*f*) Shear Stress

The phase-separation limit of solutions of polymer mixtures has been found experimentally to depend on the rate of stirring of the solution. Detailed studies have been made[86,102-104] of the effect of the rate of shear on the phase composition of a mixture of polymers in solution.

Silberberg and Kuhn showed[102] that, if the polystyrene—ethylcellulose—benzene system is subjected to shear, solubility of the phases equivalent to 15% dilution can be achieved at a certain rate of shear. The changes observed under the influence of a shearing force are completely reversible, in contrast to those occurring on dilution: the system again separates into layers immediately stirring ceases. Drops of an emulsion undergo deformation and breakdown in a field of mechanical shear stresses. Diminution in the size of the drops is associated with the accumulation of free energy in the system. The reverse phenomenon—coalescence and enlargement of the drops—accompanies the tendency of the free energy to decrease. Homogenisation depends on the relative rates of the two processes—destruction of the drops and their coalescence.

A more detailed investigation has shown[86,103] that, with increase in the shear stress, the phase-separation limit rises only to a certain limiting value, after which it ceases to depend on the shear stress. Thus $c_2$ in the polystyrene—polyisoprene—decalin system at 20°C increases from 10.5% to 12.5% with increase in the shearing stress ($\lg \tau$) from 1.2 to 2.9 dyn cm$^{-2}$, after which it ceases to depend on the stress.

Any pair of polymers can in principle be combined under shear, i.e. converted into a single-phase system, provided that the supermolecular structures in both polymers can be destroyed. Under these shear conditions in solutions of polystyrene and polyisoprene, however, the viscosity did not even reach that with limiting breakdown of the structure, which is indirect evidence of association of the macromolecules of each polymer in the system. This gave rise to the following explanation.

Previous Sections of the Review have mentioned that the macromolecules of polymers are incompatible, while their segments may be compatible, so that an intermediate layer is present at the boundary between the polymer phases. This layer is quite large in the absence of a solvent[105], and obviously becomes larger on addition of a solvent. As a consequence of the subdivision of droplets of a two-phase system under shear, their radius becomes close to the thickness of the transition layer even in the presence of comparatively coarse drops (according to Kuhn[102] amounting to micrometres or fractions of a micrometre). The system thus becomes a single phase while association of like macromolecules is preserved.

The above results must be taken into account in determining consolute temperatures and concentrations. Stirring the solution may lead to a change in the critical parameters, especially in very viscous systems.

### (*g*) Additives

The compatibility of polymers in their mixed solutions can be influenced by additives of low molecular weight[84,91,106-108]. There is no generally accepted view on the mechanism of their action. Voyutskii et al.[84] attributed the action of polar additives—alcohol and acetone—on a mixture of solutions of poly(vinyl chloride) and a butadiene—styrene copolymer to the blocking of polar groups in the polymers by the additives. But this explanation did not fit the observed effect of methanol and acetone on a mixture of non-polar polymers[91]. Lipatov[106] explained the elimination of phase separation in solutions of polystyrene and poly(vinyl acetate) on the introduction of acetone by aggregation of the molecules and a change in their shape. However, Hunyar and Weisner[107], who investigated the effect of several simple substances on the poly(vinyl chloride)—cellulose nitrate—acetone system, found that phase separation was delayed by substances of higher surface tension than acetone or whose solutions in acetone possessed a higher surface tension than acetone itself. No quantitative relation was established between the concentration of additive eliminating phase separation and its surface tension.

Kuleznev and Igosheva[108] examined the effect of 23 additives representing various classes of chemical compounds on a polystyrene—poly(methyl methacrylate)—benzene mixture, and found that the phase separation of 9% solutions is completely eliminated by dimethylaniline, heptanol, and pentanol. There was no direct relation between the action of the additive and its surface tension, dipole moment, dielectric constant, or heat of evaporation.

We conclude by considering the action of copolymers and block copolymers on the phase separation of a mixture of the corresponding homopolymers[109,110]. There are no data to show that random copolymers or block copolymers raise the phase-separation limit of a mixture of homopolymers in solution. Block copolymers are stabilisers of the incipient emulsion of type "polymer A solution—polymer B solution". The size of the blocks controls that of the emulsion droplets[109,110]. Molau considers that a block copolymer acts as an emulsifier, forming a protective layer preventing adhesion of the drops of emulsion. We can hardly regard such explanation as satisfactory. Unlike blocks of the copolymer most probably form in a solution distinctive domains or, by analogy with soaps, micelles, in which the corresponding homopolymers undergo solubilisation, as is observed in the solubilisation of hydrocarbons in solutions of surface-active substances. Because the blocks are chemically combined in the block copolymer, and it is obviously impossible to separate the whole quantity of the latter into two macrophases, the emulsion remains stable. In our opinion it is also wrong to think that the effectiveness of a block copolymer is due merely to lowering the surface tension of drops of solutions of the homopolymers: the interfacial tension here by itself is negligible[111,112].

## V. SOME ASPECTS OF THE TRANSITION OF A ONE-PHASE INTO A TWO-PHASE SOLUTION

The transition of a one-phase into a two-phase system has always been a central problem of colloid chemistry. Such a transition can conveniently be investigated on solutions of polymer mixtures, because the transition is produced by increasing the solution concentration: when a certain concentration $c_2$ is reached, the system separates into two layers—a solution of the less dense polymer above a solution of the denser polymer. The transition takes place here without change in chemical composition of the system, in particular without the addition of surface-active agents.

Very scanty data are at present available on the properties of a solution of a polymer mixture in the region of phase separation. In effect they relate only to the investigation of viscosity and light scattering[72,103,104,113].

The optical density of a system usually increases sharply in the vicinity of the phase-separation point, to reach a maximum at the instant of separation. After this the light scattering diminishes appreciably owing to the increase in size of the scattering particles and the non-monotonic variation in scattering with particle size.

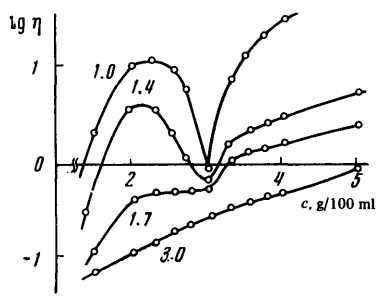



**Figure 8.** Dependence of viscosity on concentration of toluene solution of 1 : 1 polystyrene—polyisoprene mixture. The numerals on the curves indicate the shear stress ($\lg \tau$, dyn cm$^{-2}$) at which the solution was deformed.

The viscosity—concentration curve passes through a maximum before phase separation ensues. Fig. 8 shows such relations for different shear stresses[104]. Minimum viscosity corresponds to transition into a two-phase system. The minimum levels out with increase in shear stress, and at high stresses the viscosity increases monotonically with concentration: transition into a two-phase system is accomplished gradually over a wide concentration range.

The Reviewers accept the explanation that a polymer mixture may pass through a metastable region during the transition from a true solution into a rapidly separating two-phase system[57]. The region of metastable states may evidently be quite large in polymers, especially in view of their broad molecular-weight distribution. The structure of a polymer or its solution in the critical region has not yet been finally elucidated, and we can only make certain suggestions here. It is entirely possible that such compression of macromolecular coils or ordering of supermolecular structures occurs in this region that the viscosity decreases considerably. The possibility of such rearrangement is mentioned by Eskin[114], who calculated that the size of the macromolecular coils of a polymer is smaller by factors of 1.5—7 at the consolute point than at the $\theta$-point.

Thus the most probable cause of the decrease in the viscosity of a solution of a polymer mixture in the region of phase separation is evidently the transition of the system into a special critical metastable state[115]. With increase in the variation in the shear stress, of course, fluctuating structures break, and separation of the solution into phases takes place gradually over a wider concentration range.

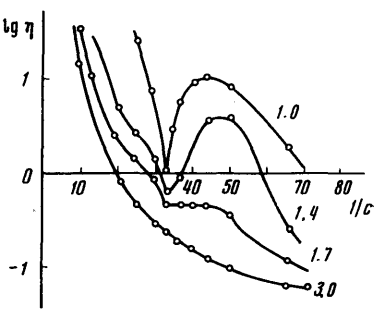



**Figure 9.** Dependence of viscosity of toluene solution of 1 : 1 polystyrene—polyisoprene mixture on the dilution $1/c$. The numerals on the curves indicate the logarithms of the shear stresses at which the solution was deformed.

It is interesting that the dependence of the logarithm of the effective viscosity on the dilution of the solution is represented by a family of curves (Fig. 9) resembling the isotherms of a real gas. The dilution axis expresses the volume occupied by 1 g of polymer, and the ln $\eta$ axis can, though very arbitrarily, be compared with the pressure axis in a gas: like the pressure, the viscosity of a solution reflects the intensity of interaction of solute molecules. The function of different temperatures is filled here by different shear stresses, which, like the temperature in a gas, lead to the breakdown of association complexes. The greater the shear stress in a solution (or the temperature in a gas), the closer is the system to ideal. It is curious that the whole isostress line (line of equal shear stress), including the portion along which viscosity increases with dilution, can easily be obtained for a solution: the isotherm of a gas in the corresponding region (rise in pressure with increase in volume) cannot be obtained experimentally.

A decrease in the viscosity of a solution of a polymer mixture in the precritical region can be obtained also when the volume of one of the separating phases is very small. Thus the viscosity of a solution of a mixture of polystyrene and polyisoprene in decalin falls in the precritical range even when the quantity of polystyrene phase being formed is 2% of the total volume of the solution. This shows how specific is the interaction of polymers. This phenomenon can appropriately be compared with the effect of interstructural plasticisers on the viscosity of polymer melts[116]. It is significant that, in contrast to such plasticisers, the

addition of a solution of another polymer more viscous than the original solution may lower its viscosity. This is not due to a plasticising effect in the usual sense, but to the creation of conditions for transition into a special pre-critical state, in which the system as a whole has diminished viscosity.

## VI. TWO-PHASE SOLUTIONS OF POLYMER MIXTURES

Insufficient study has been made of the structure and properties of solutions of polymer mixtures above the phase-separation concentration, which is easily understood from the instability of such systems with time. Two lines of information—the distribution of polymers and solvent in the separating phases and the rules of variation in interfacial tension between these solutions—are worthy of attention in this field.

Mixing solutions of different polymers in a common solvent, at a concentration above the phase-separation limit, produces a turbid emulsion of a solution of one polymer in a solution of the other polymer. The mixture is unstable: with time it gradually becomes clearer, and ultimately the mixture separates into two layers, between which a distinct boundary is visible. One of the layers is frequently more turbid than the other, and retains a cellular structure. The cause of the enhanced turbidity of one of the layers has not been studied. Each layer contains predominantly one polymer—the denser polymer in the lower layer, and the less dense in the upper layer.

The stability of a two-phase mixture of polymer solutions depends on the total concentration of polymers in solution, the composition of the mixture, and the temperature, as has been studied in detail by Mikhailov and his coworkers[117-119]. The stability was assessed visually from the appearance of an interface. The mixture became more stable with increase in concentration of the solutions, owing to the increase in viscosity. It had early been shown[45] that temperature has the opposite effect: it increases the rate of phase separation.

Theory predicts that each layer should contain predominantly one polymer, except in the vicinity of the critical phase-separation concentration. Each layer must contain a small amount of the second polymer. According to Scott's theory[7] complete incompatibility is possible only with very large interaction parameters or at high solution concentrations. At high concentrations, however, the kinetic stability, which is due to the high viscosity, increases strongly, and the establishment of equilibrium is retarded.

A detailed study of the composition of the layers was made on the polystyrene—atactic polypropylene—toluene system by Berek[28], who determined the concentration dependence of the polypropylene content of the mainly polystyrene lower layer, beginning from tenths percent above the critical concentration. Near the consolute concentration the polystyrene layer contained ~50% of polypropylene. With increase in concentration of the solutions the polypropylene content of the layer dropped sharply, to reach a value (4—5%) which remained almost unchanged with further variation in concentration. Calculation of the interaction parameter by means of Scott's equation showed that $\chi_{23}$ fell asymptotically with increase in concentration.

At first glance this contradicts Alekseenko's observation[120], on the system comprising polyethylene and a butadiene—styrene copolymer in a common solvent, that both polymers pass into the lower layer, only 4.8% of the copolymer remaining in the upper layer, whereas theoretically the latter should contain polyethylene. The probable reason is that polyethylene, which is sparingly soluble in the solvent at low temperatures, becomes insoluble in the presence of the second polymer, and is precipitated into the lower layer. The action of a second polymer in worsening the quality of a solvent for an initial polymer is well known[29,61-63].

On the basis that each layer contains predominantly one polymer, a method was proposed for determining the molecular weight of a polymer from the ratio of the volumes of the solutions resulting from separation of its mixture with a polymer of known molecular weight[45,106]. It was assumed that, when the two separated solutions are in equilibrium, the two phases have the same osmotic pressure. If each phase contains only one polymer, and the osmotic pressure is proportional to concentration, the molecular-weight ratios should approximate to the ratio of the concentrations of the polymers in the layers or to the ratio of the layer volumes. However, this method has not found application, since it does not allow for incomplete separation of the polymers, especially appreciable with polydisperse systems, and also disregards the effect of the nature of the solvent on the volume ratio. However, it may be of interest for a systematic estimation of molecular weight for a homologous series of polymers.

Lautout-Magat[121] made a general calculation of the partition coefficient of the solvent between the phases. The calculation was tested only on two polymer mixtures in solution.

Little study has been made of the establishment of equilibrium between the phases and of their composition. Available experimental results often concern only isolated aspects, and do not cover the phenomenon as a whole. For example, it was found[111] that, when solutions of the same concentration were mixed, the equilibrium concentration of the upper layer far exceeded those of the lower layer and of the initial solutions. However, no analysis was made of the composition of the polymer layers.

Hyde and Tanner[65] made an extremely interesting observation on the stability of the separated solutions resulting from mixing solutions of polystyrene and polyisobutylene in cyclohexane at 30°C, which is 4—5 deg below the $\theta$-point of polystyrene in this solvent. Solutions of the mixtures were stable for several hours, and more concentrated solutions for several days. The polystyrene molecules were regarded as retaining the same ability to aggregate and be precipitated as in the absence of the other polymer, but their aggregation occurred extremely slowly in the mixture, as the solution contained polyisobutylene molecules.

The most important parameter characterising the properties of any two-phase system is its interfacial tension. As early as 1952 it was suggested[102] that a polymer—polymer—solvent system has a low value, because droplets of a solution of one polymer break down in a solution of another polymer at very low velocity gradients.

Among the first experimental determinations[111,112] were measurements of the interfacial tension between solutions of poly(vinyl acetate) and poly(vinyl chloride) in ethyl oxalate[111]. Two capillaries of different diameters were placed at the interface, and the tension was calculated from the difference in liquid levels in them. The extraordinarily low value of $10^{-3}$ dyn cm$^{-1}$ was observed.

Interfacial tension has been determined also by the sessile drop method[112]. A drop of a solution of one polymer was forced out on to a solid support into a solution of

the other polymer. The interfacial tension could be calculated from the shape of the drop. At the interface between polystyrene and polyisobutylene solutions the tension was so small that the drop spread all over the support, and a considerable proportion was spontaneously dispersed in the surrounding solution of the other polymer.

Vrij[122] calculated the surface tension theoretically. The calculation of interfacial tension is formally similar to Debye's calculation of the scattering of light by polymer solutions near the consolute temperature. Vrij confirms directly that the two phenomena—separation of an individual solution of a polymer into layers at a critical temperature and phase separation of a mixture of solutions of incompatible polymers—are similar. The equation which he deduced is valid only for a symmetrical system, containing polymers of the same molecular weight. The calculated[122] interfacial tensions were of the same order of magnitude as the experimental values[111].

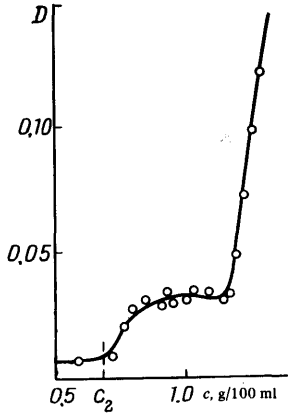



Figure 10. Dependence of optical density $D$ on concentration $c$ of toluene solution of polystyrene—polyisobutylene mixture.

The earlier work[112] was later continued[92] by measurements of the interfacial tension between solutions of polystyrene and polyisobutylene by means of two capillaries. With this pair of non-polar polymers, as with polar polymers[111], the interfacial tension tended to zero at $c_2$, and increased with increase in the concentration of the solution and in the molecular weight of the polymers. Values fluctuated within the range 0.01—0.001 dyn cm$^{-1}$ depending on these two factors. Extrapolation to 100% concentration (absence of solvent) gave the interfacial tension between polystyrene and polyisobutylene as ~1 dyn cm$^{-1}$, the first experimental value of the interfacial tension between non-polar polymers of high molecular weight.

The low surface tensions can easily be explained by the presence of a considerable transition layer at the interface, resulting from the segmental solubility of polymers discussed in Section II.

Liquids of low interfacial tension are capable of spontaneous emulsification[123,124], when the increase in entropy of the system produced by dispersion exceeds the increase in surface [free] energy, so that the process occurs under the influence of the thermal motion and terminates in the formation of a thermodynamically stable two-phase system. This requires that the interfacial tension must have been <0.1—1.0 dyn cm$^{-1}$. Spontaneous mutual emulsification of polymers obviously cannot be observed in the absence of a solvent, owing to the high viscosity of the mixture. Nevertheless, the low polymer—polymer interfacial tension is one of the main reasons for the high operational compatibility of polymers[125].

Spontaneous emulsification of a drop of a solution of one polymer in another was observed as long ago as 1967,[112] and has since been studied in greater detail[92] on solutions of polystyrene and polyisobutylene. If a layer of a solution of the latter polymer is carefully placed on a solution of polystyrene, after a few weeks the upper layer will contain not only polyisobutylene but also 4.5—5% of polystyrene. The layer has become cloudy, and under a microscope drops of diameter 0.5—3 μm are visible. However, if the solutions are mixed, the concentration of the emulsion of the polystyrene solution in the upper layer is about 10% (weight of polystyrene to weight of polyisobutylene) after phase separation. Formation of a stable spontaneous emulsion in a polymer—polymer—solvent system can be observed also from the concentration dependence of optical density (Fig. 10), where the appearance of a stable emulsion corresponds to a horizontal portion on the curve.

The results explain the turbidity[45] of one layer after phase separation of a solution of a polymer mixture: it is due to formation of a stable emulsion of one solution in the other. It is interesting that, for a given pair of polymers in a common solvent, the cloudiness of the layer is determined by the viscosity ratio of the solutions: after phase separation the more viscous layer is turbid (Table 2).

**Table 2.** Phase separation of mixtures of solutions of polystyrene (ps) and poly(methyl methacrylate) (pmma) in a common solvent.

| Mol. wt. $M_w$ | | Solvent | Parameters of true solutions | | | Cloudy layer |
|---|---|---|---|---|---|---|
| ps | pmma | | c, g/100 ml | $\eta$, cP | $\eta$, cP | |
| $3.9 \cdot 10^5$ | $0.87 \cdot 10^5$ | benzene | 20.0 | 604.4 | 37.5 | upper |
| $3.9 \cdot 10^5$ | $0.87 \cdot 10^5$ | chloroform | 20.0 | 536.8 | 33.0 | upper |
| $3.9 \cdot 10^5$ | $0.87 \cdot 10^5$ | butyl acetate | 20.0 | 495.2 | 27.2 | upper |
| $3.9 \cdot 10^5$ | $30.9 \cdot 10^5$ | benzene | 17.0 | 31.2 | 9 978 | lower |
| $3.9 \cdot 10^5$ | $30.9 \cdot 10^5$ | chloroform | 7.0 | 34.5 | 22 962 | lower |
| $3.9 \cdot 10^5$ | $30.9 \cdot 10^5$ | butyl acetate | 4.0 | 5.3 | 5 008 | lower |

The upper (polystyrene) layer is cloudy if its viscosity exceeds that of the poly(methyl methacrylate) solution; the lower layer becomes turbid if, owing to increase in molecular weight of the poly(methyl methacrylate), its viscosity exceeds that of the polystyrene solution. The effects of viscosity and the structural parameters of the polymers on the formation of stable emulsions is of great interest and requires further investigation.

Thus the vast majority of polymers are incapable of unlimited mutual dissolution, either in the presence or in the absence of a solvent. Segmental solubility occurs at the interface in their mixture, with a fall in interfacial tension to a negligible value. The low interfacial tension results in the spontaneous dispersion of a solution of one polymer in a solution of another; this is responsible for the high operational stability of a binary mixture of polymers. Within a certain concentration range below

the phase-separation limit, polymers in solution form a single-phase system generated by association complexes of macromolecules of the same chemical nature, the degree of association being greater than in a solution of the individual polymers of the same concentration. The association of macromolecules begins at the concentration $c_1$ and reaches a limit at the phase-separation point $c_2$; the degree of association is determined by the reduced concentration in the range $c_1-c_2$. The value of $c_2$ can be varied, and the concentration limits of single-phase mixtures increased, by varying the temperature, shear stress, nature of solvent, etc. The structural peculiarities of solutions of polymer mixtures lead to a sharp drop in viscosity in the concentration range directly preceding phase separation.

Further development of research on the theoretical and experimental thermodynamics of polymer mixtures is required, as a basis for comparing the interaction parameters of unlike polymers in solution and in the block.

REFERENCES


1. P. J. Flory, J. Chem. Phys., 9, 660 (1941); 10, 51 (1942).
2. M. L. Huggins, J. Chem. Phys., 9, 440 (1941); J. Phys. Chem., 46, 1 (1942).
3. V. N. Tsvetkov, V. E. Eskin, and S. Ya. Frenkel', "Struktura Makromolekul v Rastvorakh" (Structure of Macromolecules in Solutions), Nauka, 1964.
4. G. Gee, Quart. Rev. Chem. Soc., 1, 265 (1947).
5. P. J. Flory, J. Chem. Phys., 12, 425 (1944).
6. R. L. Scott and M. Magat, J. Chem. Phys., 13, 172 (1945).
7. R. L. Scott, J. Chem. Phys., 17, 279 (1949).
8. G. V. Struminskii and G. L. Slonimskii, Zhur. Fiz. Khim., 30, 1941 (1956).
9. G. L. Slonimskii, J. Polymer Sci., 30, 625 (1958).
10. C. L. Sieglaff, J. Polymer Sci., 41, 319 (1959).
11. O. Fuchs, Angew. makromol. Chem., 6, 79 (1969).
12. E. E. Rylov and A. A. Karpov, Zhur. Fiz. Khim., 27, 579 (1953).
13. R. L. Kern and R. I. Scolombe, J. Polymer Sci., 15, 183 (1955).
14. R. L. Kern, J. Polymer Sci., 33, 524 (1958).
15. T. Sato and M. Takahashi, J. Appl. Polymer Sci., 13, 2665 (1969).
16. S. V. Orekhov, Candidate's Thesis, Yaroslavl Institute of Technology, 1968.
17. F. Kollinsky and G. Markert, Multicomponent Polymer Symposium, Washington, D. C., 1971, pp. 175–188.
18. G. Kraus and K. W. Rollmann, Multicomponent Polymer Symposium, Washington, D. C., 1971, pp. 189–210.
19. S. Fujishige, P. Coeldi, and H. G. Elias, J. Macromol. Sci., A5, 1011 (1971).
20. R. Koningsveld and A. J. Staverman, Kolloid-Z., 210, 151 (1966); 220, 31 (1967).
21. G. Allen, G. Gee, and J. P. Nicolson, Polymer, 2, 8 (1961).
22. P. J. Flory, B. E. Eichinger, and R. A. Orwoll, Macromolecules, 1, 287 (1968).
23. J. Prigogine, "The Molecular Theory of Solution", New York, 1957.
24. A. A. Tager, "Fiziko-khimiya Polimerov" (Physical Chemistry of Polymers), Khimiya, Moscow, 1968.
25. A. G. Shvarts, Kolloid. Zhur., 18, 755 (1956).
26. V. N. Kuleznev, L. S. Krokhina, Yu. G. Oganesov, and S. S. Voyutskii, IUPAC International Symposium on Macromolecules, Leiden, 1970, Book of Abstracts, Vol. 1, p. 239.
27. V. N. Kuleznev, L. S. Krokhina, Yu. G. Oganesov, and L. M. Zlatsen, Kolloid. Zhur., 33, 98 (1971).
28. D. Berek, D. Lath, and V. Dudovič, J. Polymer Sci., C5, 659 (1967).
29. W. Kuhn, H. J. Cantow, and W. Burchard, Angew. Macromol. Chem., 2, 146 (1968).
30. T. I. Radbil', I. N. Razinskaya, and B. P. Shtarkman, Vysokomol. Soed., C9, 692 (1967).
31. T. R. Paxton, J. Appl. Polymer Sci., 7, 1499 (1963).
32. G. Allen, G. Gee, and J. P. Nicolson, Polymer, 1, 56 (1960).
33. Yu. G. Oganesov, V. N. Kuleznev, and S. S. Voyutskii, Vysokomol. Soed., B12, 691 (1971).
34. V. N. Kuleznev, V. D. Klykova, and B. A. Dogadkin, Kolloid. Zhur., 30, 255 (1968).
35. A. A. Tager, M. I. Shelokhovich, and M. V. Tsilipotkina, Vysokomol. Soed., A14, 1423 (1972).
36. R. L. Kern, J. Polymer Sci., 21, 19 (1951).
37. H. Tompa, Trans. Faraday Soc., 45, 1142 (1949).
38. S. H. Maron and N. Nakajima, J. Polymer Sci., 47, 169 (1960).
39. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953.
40. H. Tompa, "Polymer Solutions", Butterworths, London, 1956.
41. B. Bohmer, D. Berek, and S. Florian, European Polymer J., 6, 471 (1970).
42. H. Tompa, Trans. Faraday Soc., 46, 970 (1950).
43. R. L. Scott, J. Polymer Sci., 9, 423 (1952).
44. R. Koningsveld and A. J. Staverman, J. Polymer Sci., A6, 305 (1968).
45. A. Dobry and F. Boyer-Kawenoki, J. Polymer Sci., 12, 90 (1947).
46. G. V. Schulz and P. J. Flory, J. Amer. Chem. Soc., 74, 4760 (1952).
47. G. M. Bristow, J. Appl. Polymer Sci., 2, 4, 120 (1959).
48. W. H. Stockmayer and H. E. Stanley, J. Chem. Phys., 18, 153 (1950).
49. J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Reinhold, New York, 1950.
50. J. H. Hildebrand and R. L. Scott, "Regular Solutions", Prentice-Hall, Englewood Cliffs, N. J., 1962.
51. S. H. Maron, J. Polymer Sci., 38, 329 (1959).
52. S. H. Maron and N. Nakajima, J. Polymer Sci., 40, 59 (1959); 42, 327 (1959); 54, 587 (1961).
53. C. Hugelin and A. Dondos, Makromol. Chem., 126, 206 (1969).
54. B. A. Dogadkin, "Uchenie o Kauchuke" (Science of Rubber), Mashgiz, 1938, p. 182.
55. R. E. Boyer and R. S. Spencer, J. Polymer Sci., 5, 375 (1950).
56. P. Doty and R. Steiner, J. Polymer Sci., 5, 383 (1950).
57. S. Ya. Frenkel', G. K. El'yashevich, and Yu. N. Panov, in "Uspekhi Khimii i Fiziki Polimerov" (Advances in the Chemistry and Physics of Polymers), Khimiya, Moscow, 1970, p. 88.
58. L. H. Cragg and C. C. Bigelow, J. Polymer Sci., 24, 427 (1958); 32, 187 (1958).
59. L. H. Cragg and C. C. Bigelow, Canad. J. Chem., 36, 199 (1958).
60. V. N. Kuleznev and L. S. Krokhina, Vysokomol. Soed., A15, 906 (1973).

61. V. N. Kuleznev, L. S. Krokhina, Yu. I. Lyakin, and B. A. Dogadkin, Kolloid. Zhur., 26, 475 (1964).
62. H. J. Cantow, R. Kuhn, and W. Burchard, Internat. Symposium Chem., Toronto, 1968, Prepr. Sci. Papers, A1, 14.
63. R. Kuhn and H. J. Cantow, Makromol. Chem., 122, 65 (1969).
64. V. E. Eskin and A. E. Nesterov, Kolloid. Zhur., 28, 904 (1966).
65. A. J. Hyde and A. G. Tanner, J. Colloid Sci., 28, 179 (1968).
66. V. E. Eskin and I. A. Baranovskaya, Kolloid. Zhur., 31, 924 (1969).
67. G. P. Roshchina, in "Termodinamika i Stroenie Rastvorov" (Thermodynamics and Structure of Solutions), Izd. Akad. Nauk SSSR, Moscow, 1959, p. 233.
68. Yu. P. Miroshnikov, Candidate's Thesis, Moscow Institute of Fine Chemical Technology, Moscow, 1971.
69. G. V. Vinogradov, Yu. G. Yanovskii, V. N. Kuleznev, and T. A. Ivanenko, Kolloid. Zhur., 28, 640 (1966).
70. V. N. Kuleznev and B. A. Dogadkin, Kolloid. Zhur., 24, 632 (1962).
71. Ya. I. Frenkel', "Sobranie Izbrannykh Trudov" (Selected Works), Izd. Akad. Nauk SSSR, Moscow—Leningrad, 1959, Vol. 3, p. 422.
72. L. S. Krokhina, Candidate's Thesis, Moscow Institute of Fine Chemical Technology, Moscow, 1971.
73. V. E. Gul', E. A. Penskaya, and V. N. Kuleznev, Kolloid. Zhur., 27, 341 (1965).
74. H. G. Bungenberg de Jong and W. A. L. Dekker, Biochem. Z., 212, 318 (1929).
75. H. G. Bungenberg de Jong and C. C. Ong, Biochem. Z., 221, 166 (1930).
76. W. Philippoff, Ber., 70, 639 (1937).
77. K. Atsuki and M. Ishiwara, J. Soc. Chem. Ind. Japan, 33, 5080 (1930).
78. W. Philippoff, "Viscosität der Kolloide", Dresden, 1942.
79. W. R. Krigbaum and T. F. Wall, J. Polymer Sci., 5, 550 (1950).
80. E. H. Catsiff and W. A. Hewett, J. Appl. Polymer Sci., 6, 830 (1962).
81. L. H. Cragg and C. C. Bigelow, J. Polymer Sci., 16, 177 (1955).
82. G. R. Williamson and B. Wright, J. Polymer Sci., A3, 3885 (1965).
83. C. Vasile and J. A. Schneider, Macromol. Chem., 141, 127 (1971).
84. S. S. Voyutskii, A. D. Zaionchkovskii, and R. A. Reznikova, Kolloid. Zhur., 18, 515 (1956).
85. N. V. Mikhailov and S. G. Zelikman, Kolloid. Zhur., 19, 465 (1957).
86. L. B. Kandyrin, Candidate's Thesis, Moscow Institute of Fine Chemical Technology, Moscow, 1971.
87. S. P. Papkov, "Fiziko-khimicheskie Osnovy Pererabotki Rastvorov Polimerov" (Physicochemical Foundations of the Processing of Polymer Solutions), Khimiya, 1971.
88. L. Bohn, Kolloid-Z., 213, 55 (1966).
89. K. Friese, Plaste und Kautschuk, 12, 90 (1965).
90. I. Mladenov, P. Nikolinski, V. Gul', and N. Petrov, Compt. rend., Belge, 14, 615 (1961).
91. B. A. Dogadkin, V. N. Kuleznev, and S. F. Pryakhina, Kolloid. Zhur., 21, 483 (1961).
92. V. N. Kuleznev, L. S. Krokhina, and B. A. Dogadkin, Kolloid. Zhur., 31, 853 (1969).
93. D. Berek, B. Böhmer, and D. Lath, Plaste und Kautschuk, 14, 556 (1967).
94. J. Györgyi-Edelenyi and E. Wolfram, Ann. Univ. Sci. Budapest, Sect. chim., 11, 125 (1969).
95. F. Burkhardt, H. Majer, and W. Kuhn, Helv. Chim. Acta, 43, 1192 (1960).
96. O. Fuchs, Makromol. Chem., 90, 253 (1966).
97. G. V. Schulz, Angew. Chem., 14, 553 (1952).
98. A. A. Tager, Uspekhi Khim., 27, 481 (1958).
99. A. A. Tager and V. E. Dreval', Uspekhi Khim., 36, 888 (1967) [Russ. Chem. Rev., No. 5 (1967)].
100. A. Purcell and C. Thies, Amer. Chem. Soc., Polymer Prepr., 9, No. 1, 115 (1968).
101. M. Bank, J. Leffingwell, and C. Thies, Macromolecules, 4, 43 (1971).
102. A. Silberberg and W. Kuhn, Nature, 170, 450 (1952); J. Polymer Sci., 13, 21 (1954).
103. V. N. Kuleznev and L. B. Kandyrin, Kolloid. Zhur., 31, 245 (1969).
104. V. N. Kuleznev, L. B. Kandyrin, L. S. Krokhina, and E. F. Bukanova, Kolloid. Zhur., 33, 539 (1971).
105. S. S. Voyutskii, A. N. Kamenskii, and N. A. Fodiman, Mekhan. Polimerov, 446 (1966).
106. S. M. Lipatov, Kolloid. Zhur., 22, 639 (1960).
107. A. Hunyar and E. Weisner, J. Polymer Sci., 30, 649 (1958).
108. V. N. Kuleznev and K. M. Igosheva, Kolloid. Zhur., 24, 306 (1962).
109. G. Molau, J. Polymer Sci., A3, 1267, 4235 (1965).
110. G. Molau, Kolloid-Z., 238, 493 (1970).
111. G. Langhammer and L. Nestler, Makromol. Chem., 88, 179 (1965).
112. V. N. Kuleznev, L. S. Krokhina, and B. A. Dogadkin, Kolloid. Zhur., 29, 170 (1967).
113. V. N. Kuleznev and V. M. Andreeva, Vysokomol. Soed., 4, 1851 (1962).
114. V. E. Eskin and A. E. Nesterov, Vysokomol. Soed., 8, 1045 (1966).
115. V. N. Kuleznev, L. B. Kandyrin, and V. D. Klykova, Kolloid. Zhur., 34, 231 (1972).
116. G. P. Andrianova, N. F. Bakeev, and P. V. Kozlov, Vysokomol. Soed., A13, 266 (1971).
117. N. V. Mikhailov, "Tezisy Dokladov na IV Vsesoyuznoi Konferentsii po Kolloidnoi Khimii, Tbilisi" (Abstracts of Papers at Fourth All-Union Conference on Colloid Chemistry, Tiflis), Izd. Akad. Nauk SSSR, 1958, p. 243.
118. N. V. Mikhailov, Z. V. Ukhanova, and T. I. Karetina, Khim. Volokna, No. 3, 18 (1959).
119. N. V. Mikhailov, T. I. Karetina, and N. B. Pokrovskaya, Khim. Volokna, No. 1, 24 (1961).
120. V. I. Alekseenko, Vysokomol. Soed., 2, 639 (1960).
121. M. Lautout-Magat, J. Chim. phys., 57, 528 (1960).
122. A. Vrij, J. Polymer Sci., 6, 1919 (1968).
123. P. A. Rebinder, "Trudy III Vsesoyuznoi Konferentsii po Kolloidnoi Khimii" (Proceedings of the Third All-Union Conference on Colloid Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1956, p. 7; Kolloid. Zhur., 20, 527 (1958).
124. E. D. Shchukin and P. A. Rebinder, Kolloid. Zhur., 20, 645 (1958).
125. V. E. Gul', E. A. Penskaya, V. N. Kuleznev, and S. G. Arutyunova, Dokl. Akad. Nauk SSSR, 160, 154 (1965).


Lomonosov Moscow Institute of
Fine Chemical Technology