THERMODYNAMIC ASPECTS OF POLYMER COMPATIBILITY

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ABSTRACT

Polymer compatibility, to be understood here in the sense of thermodynamic stability, depends in a subtle way on molecular parameters. Some of these are traceable with the aid of model calculations based upon Flory and Huggins' expression for the free enthalpy of mixing. It appears that, in oligomeric mixtures in particular, the average chain lengths and the distributions of chain lengths in the two constituents markedly affect the location and shape of the miscibility gap. The entropy of mixing tends to shift the gap towards the composition region in which the constituent with the smaller average chain length dominates.

The interaction parameter, if depending on concentration, can outweigh this effect. Examples, taken from literature and our own data, indicate that this situation does occur in practice. Hence, the lattice-based free enthalpy expression is an accurate tool for describing actual phase relations; however, it cannot quantitatively predict their temperature, chain length, and concentration dependence. In the last respect Flory's equation of state theory appears to be very superior. This was recently shown by McMaster, who analysed Flory's new free enthalpy function and found that small differences *inter al.* in the thermal expansion coefficients of two compatible polymers will cause the system to become incompatible upon a rise in temperature. The latter phenomenon is known to occur; examples are given. Compatibility being a subtle phenomenon, the question seems to be justified whether two samples of the same polymer of widely differing chain length might be immiscible. For linear polyethylene and anionic polystyrene the available data point to chain length compatibility. Two methods for the determination of compatibility are discussed, viz. the mutual solvent method and a light-scattering technique.

INTRODUCTION

Polymer compatibility is a comprehensive subject which has been treated from quite different angles. If one has to deal with practical production problems the processability of a polymer blend naturally offers itself as a useful measure of compatibility. This criterion, however important, does not necessarily coincide with other standards. From the viewpoint of equilibrium thermodynamics, for instance, compatibility means miscibility on a molecular scale, and we cannot say off-hand whether such a state goes with easy processing.

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In view of the high viscosity of the constituents it seems obvious that one should not expect polymer mixtures prepared by the usual technological procedures to be in an equilibrium state, and kinetic effects will doubtless have a good deal to do with differences in judgment on polymer compatibility. It is of considerable importance to recognize the parameters that determine the equilibrium state of mixed polymers. In those cases where the mixture has not yet reached equilibrium such insight will be needed, or at least be helpful, in understanding the change of properties with time.

A mixture of two miscible polymers will gradually increase its degree of dispersion so as eventually to become a one-phase system. On the other hand, thermodynamically incompatible polymers will in course of time reduce the degree of dispersion. This illustrative example was given by Gul', Penskaya, Kuleznev and Arutyunova[1] who suggested use of the conditions of thermodynamic stability as a criterion for compatibility. We follow their line of
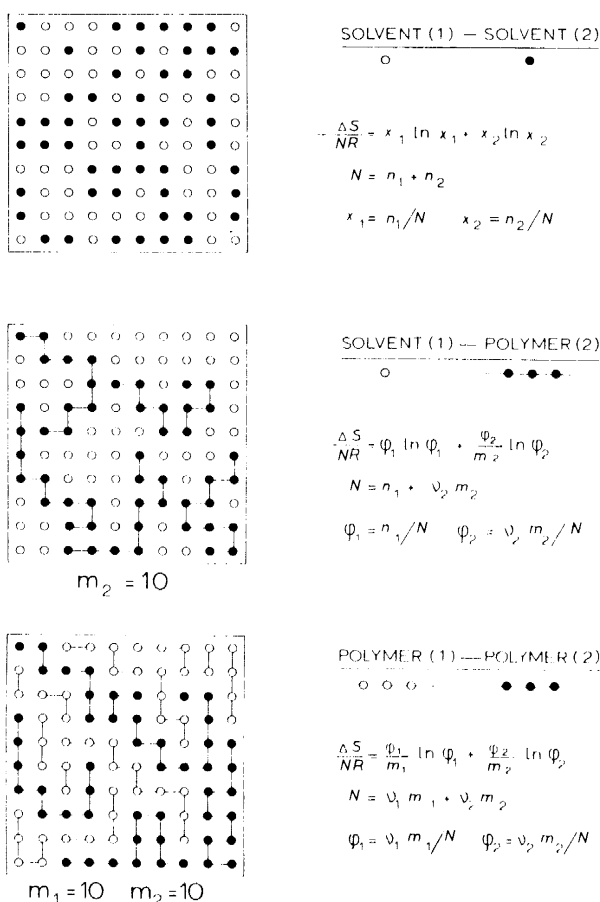

SOLVENT (1) — SOLVENT (2)

$$-\frac{\Delta S}{NR} = x_1 \ln x_1 + x_2 \ln x_2$$

$$N = n_1 + n_2$$

$$x_1 = n_1/N \qquad x_2 = n_2/N$$

SOLVENT (1) — POLYMER (2)

$$-\frac{\Delta S}{NR} = \varphi_1 \ln \varphi_1 + \frac{\varphi_2}{m_2} \ln \varphi_2$$

$$N = n_1 + \nu_2 m_2$$

$$\varphi_1 = n_1/N \qquad \varphi_2 = \nu_2 m_2/N$$

$m_2 = 10$

POLYMER (1) — POLYMER (2)

$$-\frac{\Delta S}{NR} = \frac{\varphi_1}{m_1} \ln \varphi_1 + \frac{\varphi_2}{m_2} \ln \varphi_2$$

$$N = \nu_1 m_1 + \nu_2 m_2$$

$$\varphi_1 = \nu_1 m_1/N \qquad \varphi_2 = \nu_2 m_2/N$$

$m_1 = 10 \qquad m_2 = 10$

Figure 1. Schematical illustration of the numbers of possible arrangements in a small-molecule mixture (top), a polymer solution (middle) and a polymer mixture (bottom). The polymer chains each contain 10 segments of the size of the solvent molecules.

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thought here and restrict ourselves to a discussion of the various parameters that determine polymer compatibility in thermodynamic equilibrium. The reader is referred to the literature for more comprehensive reviews[2-7].

Thermodynamic considerations in this field are often limited to the qualitative statement that the free enthalpy (Gibbs free energy) of mixing (ΔG) must be negative for a system to be thermodynamically stable. This involves a balance between the enthalpy and entropy of mixing, and a boundary between stable and unstable states determined by the condition $\Delta G = 0$. The usual molecular picture is a lattice representation of the system, illustrated schematically in *Figure 1*. In equal volumes, the number of possible arrangements in the binary small-molecule mixture (top) is much larger than that in a polymer solution (middle), obtained by partly stringing the molecules of one species together to chain molecules. A similar treatment of the molecules in the other component yields a representation of a polymer mixture, and is accompanied by a further drastic decrease of the number of arrangements (bottom). The number of nearest neighbour contacts is only slightly affected in the process so that the energy and, hence, the heat of mixing do not differ much between the three cases. This simple model is very illustrative and reveals the principal reason why polymer solutions are less resistant to demixing than representative small-molecule mixtures. We also understand that polymer mixtures have so little entropy of mixing to match energy effects, that very small positive heats of mixing suffice to bring about incompatibility.

Slonimskii *et al.*[8-11] measured heats of mixing in a series of polymer pairs and found most of them to mix endothermally, i.e. $\Delta H > 0$. An exception to this expected behaviour was provided by the system polystyrene–polybutadiene which sets heat free upon mixing and yet shows partial miscibility. Slonimskii *et al.* concluded that the actual situation is obviously not at all covered comprehensively by the simple molecular picture outlined above and that entropy of mixing terms other than combinatorial ones are involved. They thought the non-combinatorial entropy terms to be related to molecular packing and, hence, to volume changes accompanying the mixing process. In this way they foreshadowed more recent approaches to improve the theory of liquid mixtures, among which the 'equation of state' treatment by Flory and his co-workers[12-14] and its application to polymer mixtures by Mc-Master[15] are particularly noteworthy.

Alekseyenko[16] also considered the packing density of mixed polymers and suggested the packing coefficient K, defined as the ratio of the actual and additive (calculated) volumes of the mixture, to be a useful criterion for compatibility. Expansion ($K > 1$) would then point to incompatibility, contraction ($K < 1$) to miscibility. Gul' *et al.*[1,17] used the independence of a property of the blend from the path by which it is attained as a criterion for thermodynamic stability. They measured optical densities of mixed films as an illustration.

It is evident that heats and volumes of mixing, as well as optical properties, are important parameters for thermodynamic stability but they are not wholly determinative. The free enthalpy of mixing unambiguously determines equilibrium states and we therefore prefer to base discussions of compatibility on this quantity. A consideration of the dependence of ΔG on composition immediately shows that the boundary condition $\Delta G = 0$ mentioned above

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arises from much too crude a picture. Mixtures can be and often are unstable at negative ΔG (though not, of course, relative to the pure components), and can diminish ΔG still further by separating into two phases.

Figure 2 illustrates this situation for a strictly-binary mixture. The stability of the system is determined by the curvature of $\Delta G(\varphi_2)$[18-20] and the stability limit, also called spinodal, is given by

$$(\partial^2 \Delta G / \partial \varphi_2^2)_{p, T} = 0. \tag{1}$$

where φ_2 is the volume fraction of the second component. The slight ripple in the $\Delta G(\varphi_2)$ curve which goes with partial miscibility may be caused by the heat
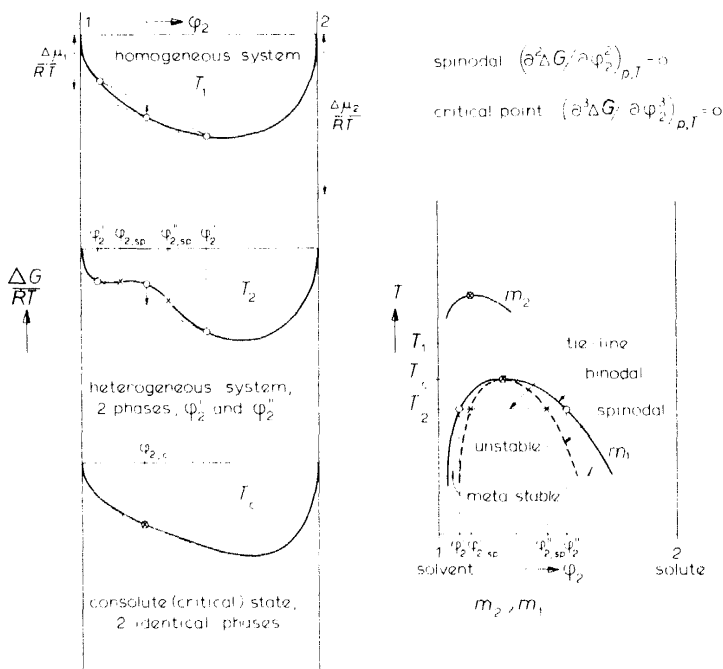
Figure 2. Free enthalpy (Gibbs free energy) of mixing as a function of concentration in a binary liquid system showing partial miscibility.

of mixing, but could equally well spring from a deviation of the entropy of mixing from mere combinatorial terms. In the latter case one may have partial miscibility even if ΔH is negative. Wolf recently reviewed entropically and enthalpically induced demixing[21].

A free enthalpy of mixing expression that has proved useful in describing liquid–liquid phase relations is that by Flory[22,23] and Huggins[24,25], based on the lattice model of the liquid state. For quantitative descriptions it must be slightly extended[23,26-28] by a semi-empirical correction term. Further, the fact that actual polymers are generally characterized by a chain-length distribution rather than a single species must be taken into account[22,26,29]. Leaving chain-branching and copolymerisation out of consideration we can

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write

$$\Delta G_\varphi/RT = \sum_i \varphi_{1,i} \, m_{1,i}^{-1} \ln \varphi_{1,i} + \sum_j \varphi_{2,j} m_{2,j}^{-1} \ln \varphi_{2,j} + \Gamma(p, T, \varphi_2) \quad (2)$$

where ΔG_φ is the free enthalpy of mixing per mole of lattice sites, $\varphi_{1,i}$ and $\varphi_{2,j}$ are the volume fractions of species i in polymer 1 and species j in polymer 2, and $m_{1,i}$ and $m_{2,j}$ are the relative chain lengths of the same, expressed in the number of lattice sites they occupy. RT has the usual meaning, and p stands for pressure.

The correction term Γ can be written as

$$\Gamma = g(p, T, \varphi_2) \, \varphi_1 \varphi_2 \quad (3)$$

where φ_1 and φ_2 are the volume fractions of the whole polymers 1 and 2, i.e. $\varphi_1 = 1 - \varphi_2$. For the moment we ignore a possible chain-length dependence of interaction parameter g. If g goes not depend on concentration we have the familiar Van Laar interaction term[30].

Using the multicomponent version of equation (1) one finds for the stability limit of a system obeying equation (2)[31–33]:

$$\bullet \qquad -(\partial^2 \Gamma/\partial \varphi_2^2)_{p,T} = (1/m_{w,1}\varphi_1) + (1/m_{w,2}\varphi_2) \quad (4)$$

where $m_{w,1}$ and $m_{w,2}$ are the weight-average chain lengths of the two polymers. Within the range of validity of equation (2) the stability limit of a two-polymer mixture is determined by the concentration dependence of Γ (or g), and the chain length distributions of the polymers reveal themselves in terms of the two weight averages only. In some of the cases we shall discuss presently this simple approach seems to work satisfactorily even though relatively small chain lengths are involved.

The simple lattice theory supplies descriptive expressions for g in terms of temperature, concentration and chain lengths[33–35], but it cannot *predict* how g will depend on pressure and temperature. For that purpose the theory by Flory and his co-workers[12–14] and Patterson and Delmas[36–38] have proved to be powerful tools. A striking example of the usefulness of Flory's theory has recently been given by McMaster who applied it to mixtures of two polymers[15]. Both Flory's and Patterson's free enthalpy expressions are very complicated and contain many parameters that, although readily obtainable from independent measurements on the constituents of the mixture, make these expressions less suitable for the present purpose. Moreover, they are mainly concerned with the dependence of Γ on temperature, pressure and concentration and attribute the effect of the chain length distributions to the same two combinatorial entropy terms that are used in the lattice theory [first two terms in equation (2)]. Since we are primarily interested here in the effect molecular weight distributions have on the location of miscibility gaps in polymer mixtures we prefer the simpler expressions (2) and (3). The implications of 'equation of state' parameters will be discussed briefly on the basis of McMaster's results.

Very recently, Derham, Goldsbrough and Gordon[39] expressed serious doubts about the adequcy of equation (2), in as much the influence of the molecular weight distribution is concerned. They carried out very accurate measurements of stability limits in the system cyclohexane–polystyrene, using

the pulse-induced critical scattering method developed in their institute. The spinodals were found to depend on the molecular weight distribution of polystyrene in an intricate manner, much more complicated than is suggested by equation (4) which restricts the influence of the distribution to the weight average alone. It is possible to introduce an arbitrary, empirical dependence on the chain length distribution into equation (3), and work out the stability limit[33, 35]. An improved theoretical treatment of the free enthalpy, however, would be preferable. With the systems on hand in particular we are not yet in a position to discuss such subtleties and we shall have to proceed on the basis of the simple expression (2) for the time being.

It has been noted before[40-42] that the stability condition (1) supplies a convenient means of investigating phase behaviour of liquid systems. This is because all ΔG functions in current use allow equation (1) to be worked out and the result be written in closed form. This is not possible with the equilibrium conditions for the concentrations of the two coexisting phases (*Figure 1*), φ_2' and φ_2''. The latter conditions (arising from the equality of the chemical potential of each component in the two phases) lead to implicit equations that must be solved with numerical methods. Every miscibility gap, however, comprises a spinodal and the occurrence of such a limit of stability is therefore indicative of a range of two-liquid-phase equilibria in the system. In case of doubt one might use the sign of the curvature of $\Delta G(\varphi_2)$ to decide on which side of the spinodal the unstable states are located.

Changing from a heterogeneous to a homogeneous mixture by a change in temperature or pressure, the system passes through the consolute or critical state in which the points of inflection as well as the double tangent points of $\Delta G(\varphi_2)$ coincide (*Figure 2*). The critical state is characterized by equation (1) in conjunction with

$$(\partial^3 \Delta G / \partial \varphi_2^3)_{p, T} = 0 \tag{5}$$

The multicomponent version of this condition leads to

$$-(\partial^3 \Gamma / \partial \varphi_2^3)_{p, T} = (m_{z, 1}/m_{w, 1}^2 \varphi_{1, c}^2) - (m_{z, 2}/m_{w, 2}^2 \varphi_{2, c}^2) \tag{6}$$

where m_z stands for the z-average chain length, and φ_c is the critical concentration. Equation (6) is subject to the assumptions underlying equation (4).

A critical point is located on the spinodal. It coincides with the latter's maximum in a strictly-binary system and shifts away from the maximum if one of the constituents or both contain more than one component[32]. Estimations of the shape of miscibility gaps are greatly helped if the location of the critical point on the spinodal, calculated with equation (6), is included.

In the following discussions the experimental evidence will mainly be derived from literature and our own data on mixtures of low-molecular-weight polymers. Allen, Gee and Nicholson[43], who studied the system poly-isobutene–poly(dimethylsiloxane), realized that, owing to their relatively low viscosity, oligomeric systems allow investigation of phase equilibria with the usual means, and yet have some of the properties characteristic for long-chain constituents. For related reasons McIntyre, Rounds, and Campos-Lopez[44] investigated the system polyisoprene–polystyrene to which data we have added some of our own.

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Many experimental methods are in use for establishing the miscibility. of polymers[2-7]. We limit ourselves to some general remarks which might justify the choice of the methods discussed here in some detail. Alekseyenko warns against methods using solutions of the mixed polymer in a common solvent (mutual-solvent method)[16]. We agree with him that reliable conclusions about the properties of the solvent-free polymer mixture cannot be drawn from its behaviour in more or less dilute solution, no matter whether the solvent is good or poor.

Procedures based upon solvent-free mixtures are not without danger of misinterpretation either. It has been established that polymer mixtures can sometimes follow temperature changes with an amazing speed. Direct observation of blends with the light microscope has shown that demixing of even high-molecular-weight constituents can set in quite rapidly upon a change of temperature[15,45,46]. Hence, if the sample has to be frozen in, as for instance in the preparation for the electron microscope, the picture taken is not necessarily representative of the system at room temperature but may be determined by what happened during the heat treatment.

Similarly, mechanical loss peaks, in wide use to detect the number of glass transitions (number of separate phases) in a blend, have only significance in the temperature range where the peaks occur and may easily not be representative for the system at other temperatures. In this connection the system natural rubber–SBR might offer an interesting example. Mechanical loss measurements reveal two peaks below $0\,^{\circ}C$[47], yet microscopic investigation at room temperature shows transparent films only. One could conclude that the system exhibits upper critical solution behaviour upon cooling below room temperature. This conclusion however depends entirely on whether the refractive indices of the constituents differ enough to make the microscopic observation significant. This is the main limitation of the microscopic determination of compatibility.

Scholte[48,49], Chu et al.[50,51] and others have shown that light-scattering measurements provide direct access to the stability limit and thus yield basic thermodynamic information. As in light microscopy, the constituents should have sufficiently different refractive indices for the method to be applicable but the amount of information is much greater. This, however, seems to be the only limitation of the light-scattering method which, in particular in the elegant variation by Gordon et al. (pulse-induced critical scattering[39,52]), will doubtless prove to be of great value in thermodynamic studies of polymer compatibility.

MISCIBILITY GAPS IN MIXTURES OF POLYDISPERSE POLYMERS

1. Concentration-independent interaction parameter

If g in equation (3) depends on p and T only, we have

$$-(\partial^2 \Gamma / \partial \varphi_2^2)_T = 2g = (1/m_{w,1}\varphi_1) + (1/m_{w,2}\varphi_2) \tag{7}$$

(spinodal). The location of the critical points on the spinodal is determined by

$$-(\partial^3 \Gamma / \partial \varphi_2^3)_{p,T} = (m_{z,1}/m_{w,1}^2 \varphi_{1,c}^2) - (m_{z,2}/m_{w,2}^2 \varphi_{2,c}^2) = 0. \tag{8}$$

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Equation (8) can be solved for $\varphi_{2,c}$, which yields

$$\varphi_{2,c} = 1/[1 + (m_{w,2}a_1/m_{w,1}a_2)^{\frac{1}{2}}] \qquad (9)$$

where a_k stands for $m_{z,k}/m_{w,k}$. For $m_{w,1} = m_{z,1} = 1$, equation (9) reduces to the critical concentration of a quasibinary polymer solution (polydisperse polymer in a single, small-molecule solvent), first derived by Stockmayer[53].

In this study we are only interested in properties at atmospheric pressure. Further, we leave the temperature dependence of g unspecified for the time being. Thus we have a g axis instead of T in *Figure 3* which shows some
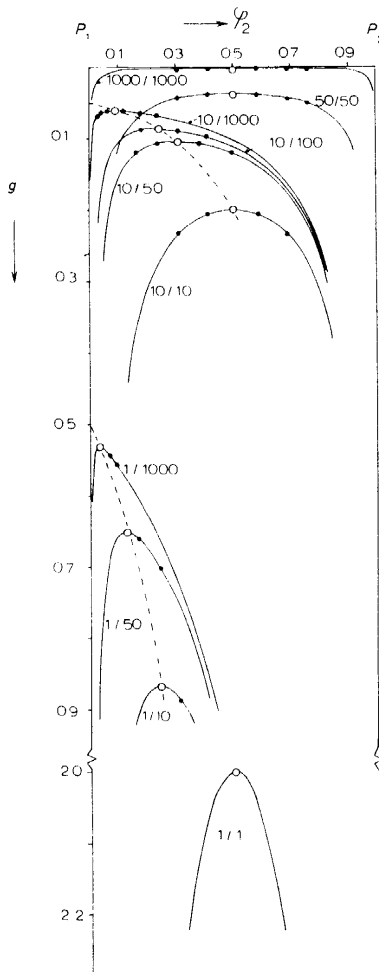
Figure 3. Stability limits for various polymer 1–polymer 2 systems for indicated $m_{w,1}/m_{w,2}$ values. Critical points for strictly-binary systems and for mixtures of polydisperse polymers with identical m_z/m_w (○). If the m_z/m_w values differ the critical point shifts away from the maximum towards the axis of the constituent wlth the larger m_z/m_w ratio (●). The dashed lines are loci of critical points at equal m_z/m_w.

spinodals and critical points calculated with equations (7) and (9). Concentrating on the stability limits in polymer solutions first (systems $1/m_{w,2}$) we note the well known asymmetry of the unstable region (and, hence, of the miscibility gap), and the equally familiar shifting of the critical point towards the solvent axis with an increase of $m_{w,2}$. At constant $m_{w,2}$, the critical point travels down the right-hand branch with a broadening of the molecular weight distribution of the polymer (increasing a_2)[54]. A truly binary polymer solution ($a_2 = 1$) has its critical point at the maximum of the spinodal.

A similar, but less pronounced, asymmetry is seen if the solvent (constituent 1) is also a polymer, but with a smaller average chain length than constituent 2. The stability limit is shifted towards smaller g values because the entropy of mixing per unit volume is less than in the ($1/m_{w,2}$) mixtures. A peculiar situation arises if the two polydisperse polymers have equal a values. Then, the critical point coincides with the maximum of the spinodal and, no matter how broad the distributions, the system behaves in this respect as if it were a truly binary one. However, it is only in this respect that polymer mixtures may look like binary systems, all other features of phase behaviour differ[55].
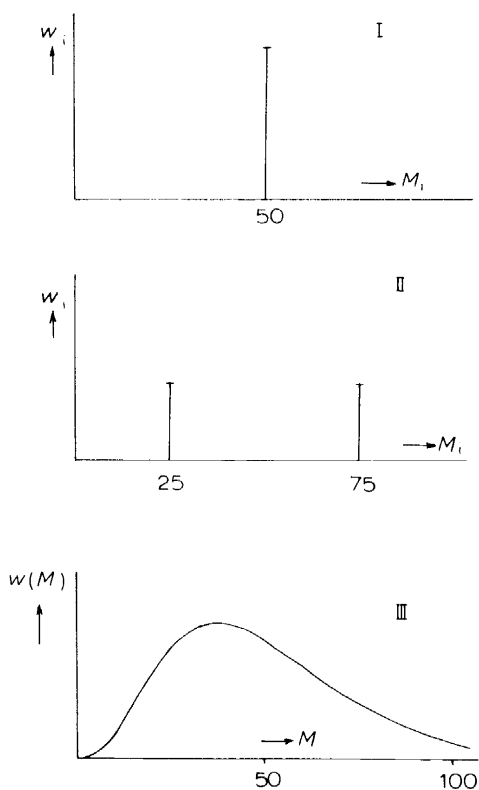

Figure 4. Molecular weight distributions with equal m_w ($=50$). I: monodisperse; II:binary polymer ($m_z = 62.5$); III: exponential weight distribution ($m_z = 62.5$).

To appreciate this we must turn to the shape of the miscibility gap which is wider than the unstable region comprised by the spinodal (see *Figure 2*). Numerical methods have been developed to calculate the location of the two-phase region. They are based on the equilibrium conditions mentioned above (equality of chemical potentials). Multicomponent systems present some problems, since there are as many equations as there are components. Methods to deal with them are described in the appendix.

To elucidate the peculiar situation when the critical point in a non-binary system coincides with the maximum of the spinodal we compare miscibility gaps calculated for mixtures of two polymers with identical molecular weight distributions (*Figure 4*). We have: I, a strictly binary mixture ($m_{w,1} = m_{w,2} = m = 50$) of two monodisperse polymers; II, two binary polymers ($m_{w,1} = m_{w,2} = 50$; $m_{z,1} = m_{z,2} = 62.5$); and III, two polydisperse polymers, each with an exponential distribution and m_w and m_z values equal to
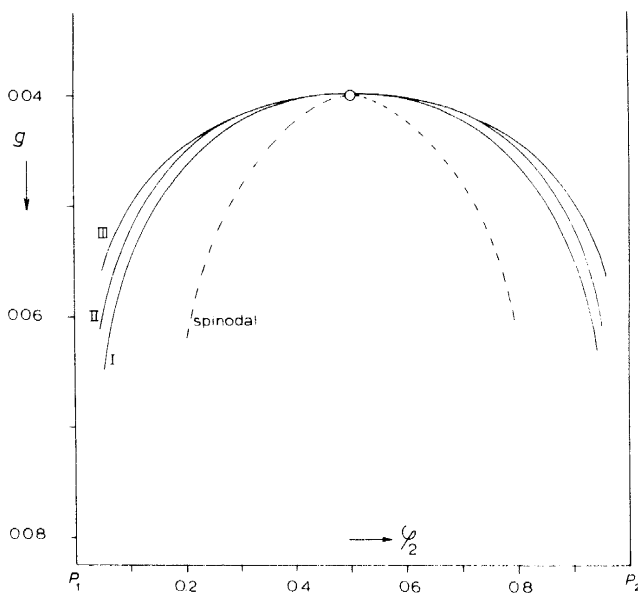

Figure 5. Miscibility gap calculated for a mixture of two polymers (P_1, P_2) with identical molecular weight distributions. The three cases refer to the distributions in *Figure 4*.

those of case II. Distributions II and III also have identical number-average chain lengths m_n ($m_w/m_n = 4/3$). In accordance with equation (7) these three systems share the same spinodal, and have the critical point at its maximum [equation (9), $a_1 = a_2$], but they differ with regard to the extension of their miscibility gaps. The mixture of monodisperse polymers has the narrowest gap, and increasing polydispersity appears to widen the gap, i.e. decrease the miscibility. Although the average chain lengths m_n, m_w and m_z are identical in cases II and III, the continuous distribution III contains appreciable amounts of very high molecular-weight material which presumably is responsible for the smaller compatibility.

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Figure 6 shows that a decrease of the average chain lengths of the smaller constituent shifts the miscibility gap towards the latter's axis, in accordance with *Figure 3*. In the examples 35/46.4 and 27.5/31.8 the critical point is
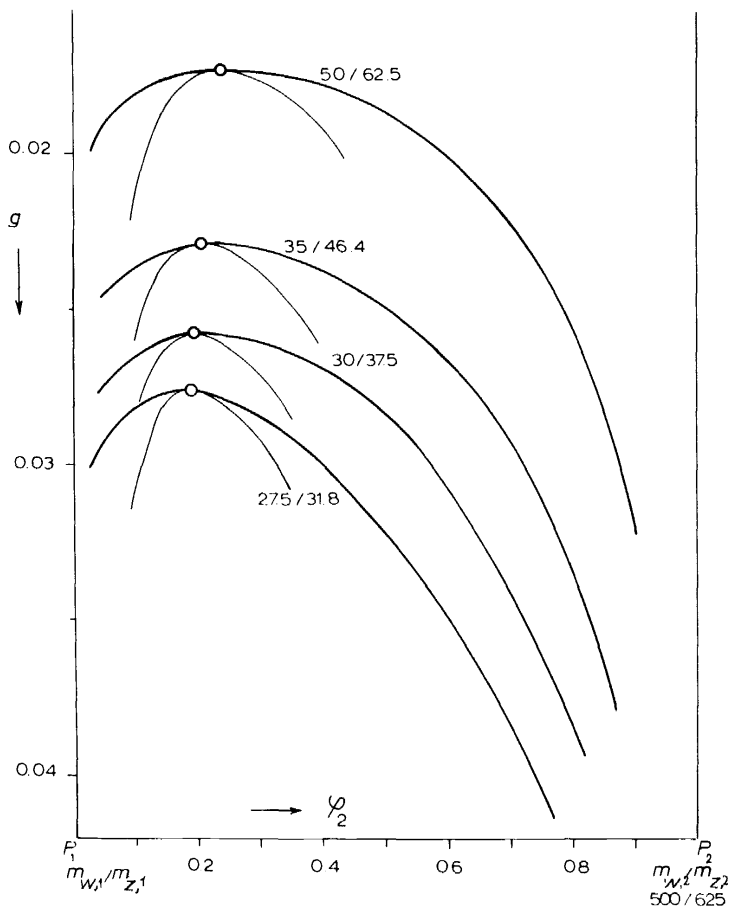

Figure 6. Calculated miscibility gaps (———), spinodals (———) and critical points (O) for mixtures of two polydisperse polymers showing the effect of a variation of the average chain length in polymer 1; $m_{w,1}/m_{z,1}$ values are indicated; g independent of concentration (φ_2).

shifted away a little from the maximum of spinodal and cloud-point curve owing to slight variations in a_1.

2. Concentration-dependent interaction parameter

Many studies on thermodynamic properties of polymer solutions have established beyond doubt that the interaction parameter generally depends on the polymer concentration. It seems therefore worthwhile to check the influence of a possible concentration dependence of g on polymer compatibility. In polymer solution work a linear dependence on φ_2, although not

sufficient for quantitative purposes, qualitatively describes observed deviations from behaviour predicted by a concentration-independent g. We assume

$$g = g_0 + g_1\varphi_2 \qquad (10)$$

and, for convenience, take only g_0 to be temperature-dependent. This involves that g_1 is a correction factor for the entropy of mixing.

It was shown elsewhere that such a correction may have a considerable effect[32]. A positive value of g_1, for instance, may even give rise to a correction term outweighing the first two (combinatorial entropy) terms in equation (2), and thus shifting the miscibility gap over to the 'wrong' side of the phase diagram. *Figure 7* gives some further examples, calculated for the same molecular weight distributions as used in *Figure 6*.
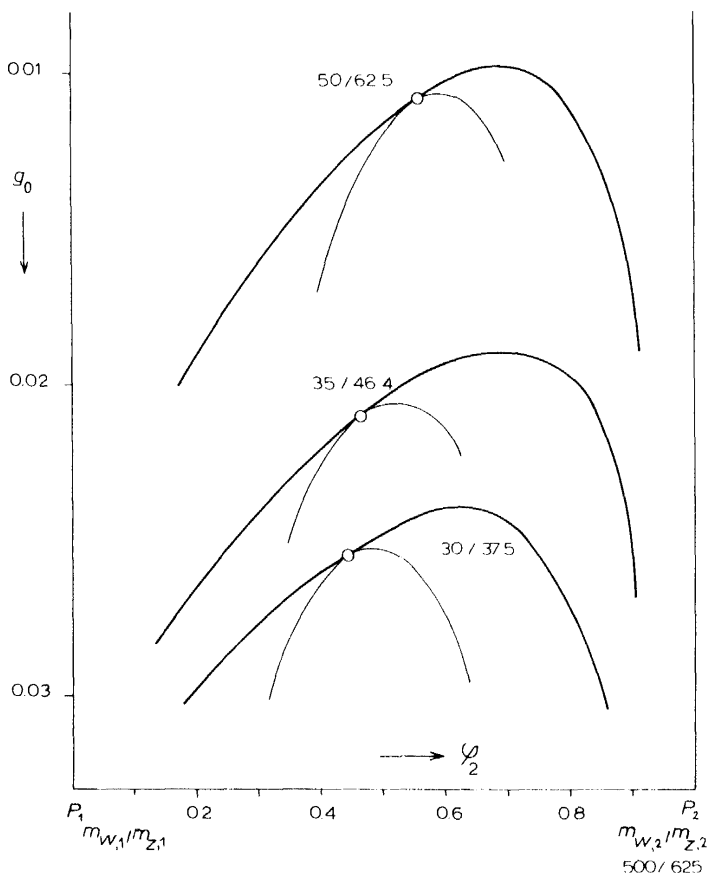
Figure 7. Caption as Figure 6, $g = g_0 + g_1\varphi_2$; $g_1 = 0.02$.

An increase of the average chain length in constituent 1 involves a decrease of the combinatorial entropy of mixing. As a consequence we observe the shift towards the axis of constituent 2 to become more pronounced as $m_{w,1}$

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increases. We observe also that the location of the critical point relative to the maximum of the spinodal is more sensitive to differences in the average chain lengths than in the case of a concentration-independent g (*Figure 6*).

The concentration dependence of g may well have been responsible for the remarkable location of miscibility gaps in the system polyisobutene–poly(dimethylsiloxane), reported by Allen, Gee and Nicholson[43]. These authors found cloud-point curves in the silicone-rich region of the phase diagram; the silicones, however, had the larger average chain lengths.

POLYISOBUTENE–POLY(DIMETHYLSILOXANE)

The extensive data by Allen, Gee and Nicholson[43] (*Figure 8*) deserve a more detailed analysis, in particular because these authors took the considerable trouble to measure heats of mixing in addition to could-point curves. Heats of mixing data can supply useful additional information on the interaction parameter, in particular on its dependence on concentration.
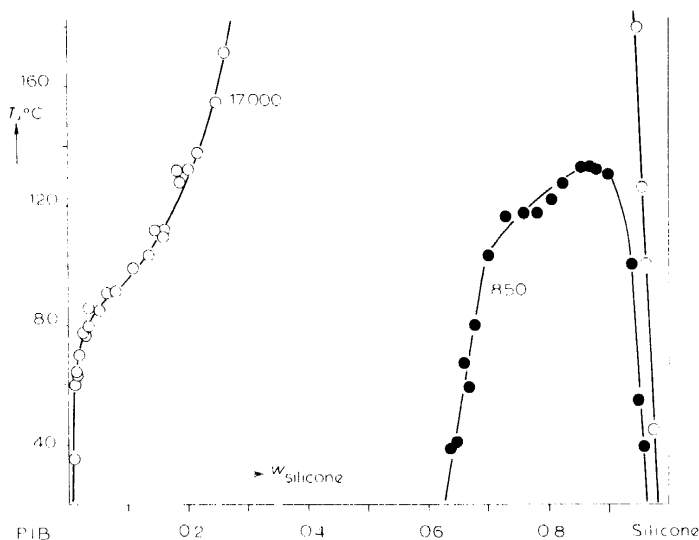

Figure 8. Two of the cloud-point curves in the system polyisobutene (PIB)–polydimethylsiloxane (silicone) measured by Allen, Gee and Nicholson[43]. Average molecular weights: PIB: 250, silicones: 850; 17000; $w_{silicone}$ = weight fraction of silicone.

If we assume the first two terms in equation (2) to be independent of temperature we have

$$\Delta H = -T^2 \partial(\Delta G/T)/\partial T = -RT^2 \varphi_1 \varphi_2 \partial g/\partial T \tag{12}$$

Extending the concentration dependence of g [equation (10)] to a power series in φ_2, and taking every coefficient to show the usual linear dependence on $1/T^{56}$), we can write

$$g = g_0 + g_1\varphi_2 + g_2\varphi_2^2 + \dots \tag{13}$$

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where

$$g_k = g_{k,1} + g_{k,2}/T \tag{14}$$

Application of equation (12) yields

$$\Delta H/\varphi_1\varphi_2 = R(g_{0,2} + g_{1,2}\varphi_2 + g_{2,2}\varphi_2^2 + \ldots) \tag{15}$$

Allen *et al.* plotted $\Delta H/\varphi_1\varphi_2$ data, taken at two temperatures, against φ_2, and found the same significantly curved line with a minimum at $\varphi_2 \approx 0.2$ for the two temperatures. This implies the feasibility of the description by equations (13) and (14) and calls for at least a quadratic dependence of g on
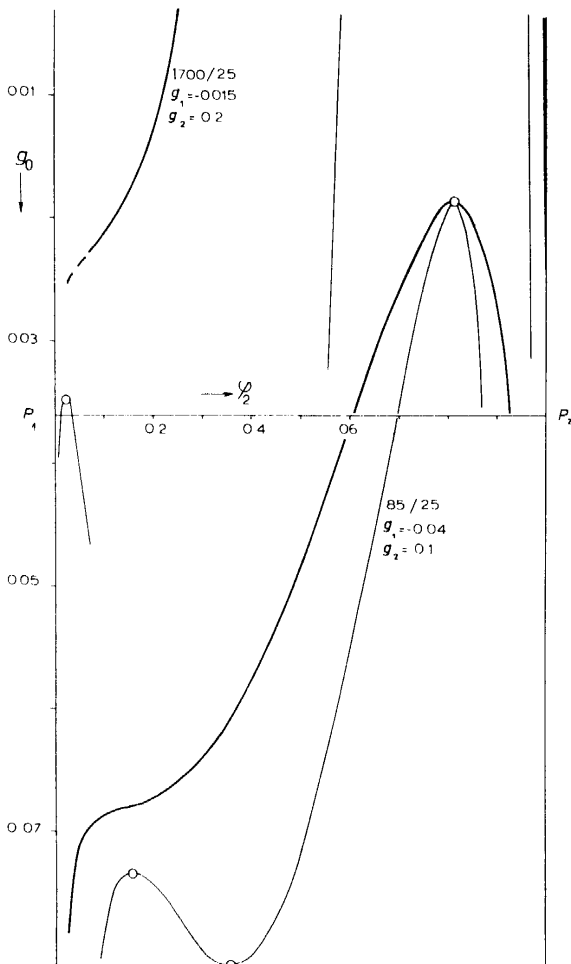
Figure 9. Cloud point curves (———), critical points (○) and spinodals (· · ·) calculated with the indicated values of g_1 and g_2 for two sets of m_2/m_1 values, qualitatively representative for the systems in *Figure 8.* In the 1700/25 system problems of computational accuracy prevented calculation of the full curve at higher g_0 values. The existence of the shoulder, however, is well established.

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φ_2. Then, the occurrence of a minimum reveals that $g_{1,2}$ and $g_{2,2}$ are related

$$\varphi_{2,\text{min}} = -g_{1,2}/2g_{2,2}(g_{1,2} < 0; g_{2,2} > 0)$$

If we assume the signs of the coefficients in equation (15) also to be valid for the complete expression (13) we may attempt to calculate miscibility gaps for the various mixtures investigated by Allen *et al. Figures 9* and *10* demonstrate that inclusion of an appropriate concentration function greatly
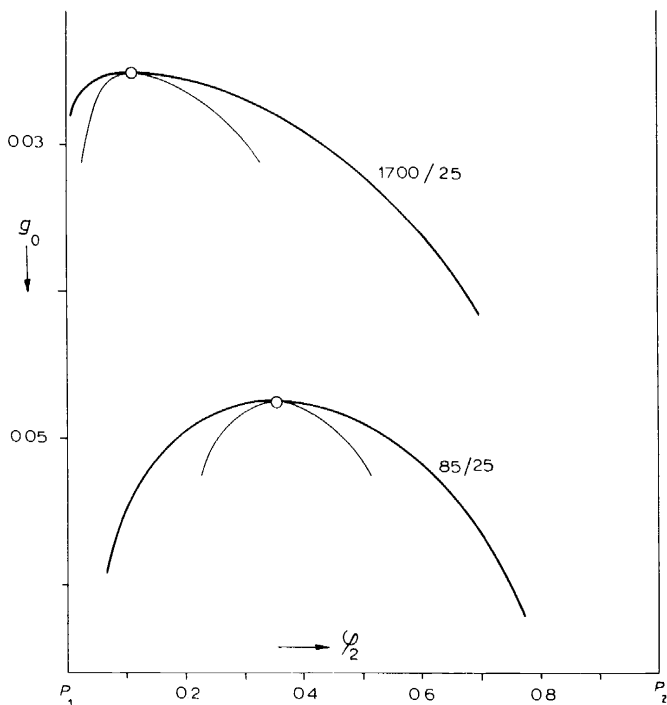

Figure 10. Caption as *Figure 9, g* independent of concentration.

improves the similarity between calculated and measured cloud-point curves. The combinatorial entropy terms are clearly outweighed by terms which cause the miscibility gap to be shifted into the region of compositions rich in silicone, the constituent with the larger average chain length.

Using the $g(\varphi_2)$ function (13) we do not only describe the shift but also recover the remarkable shape of the cloud-point curve of the 250/17 000 system. The upper part of the calculated curves in *Figure 9* refers to the experimental data, the lower part suggests that the 250/850 system would have shown a similar shoulder at $\varphi_2 \approx 0.1$ if the measurements would have been extended to lower temperatures. Evidently, the shoulder has to do with the minimum in the $\Delta H/\varphi_1 \varphi_2$ curve.

The use of different g_1 and g_2 values in the calculations for the 250/17 000 and 250/850 systems was prescribed by Allen *et al.*'s observation that

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ΔH, although not being affected significantly by temperature in each of the systems, did differ between the two systems. This indicates that g depends on chain length. The calculated cloud-point curves refer to strictly binary mixtures so that the chain length problem (difficult to deal with in multi-component systems) could be circumvented simply by using different sets of g_1 and g_2 values. In multicomponent calculations this would have been incorrect.

The measured cloud-point curves (*Figure 8*) reveal that the location and extension of the miscibility gap are very sensitive to changes in chain length in one constituent or both. For instance, a twentyfold increase of the silicone chain length shifts the maximum over several hundred °C. We should note that the simple description by means of equations (2), (12) and (13) can allow for this phenomenon without need of introduction of unreasonable values of g_0 (see *Figures 3, 5–7*).

If the concentration dependence of g is ignored, we have the usual asymmetry towards the polyisobutene axis (*Figure 10*). This was noted by Allen *et al.*, who also suggested that a possible concentration-dependence might have something to do with the discrepancy. This conjecture is supported by the calculated curves in *Figure 9*. The agreement, however, is only qualitative for which we can advance two reasons—(*a*) polydispersity was ignored, and does affect the detailed shape of cloud-point curves and (*b*) the temperature dependence of g was restricted to g_0 (for sake of convenience), whereas equations (13), (14) and (15) indicate that this premise cannot be quite adequate for the system on hand.

The fact that nevertheless qualitative agreement is obtained suggests that the main cause of the phenomenon has been located. Improved agreement could doubtless be achieved if the polydispersities were known, and if additional information on the ΔG function itself were obtained, for instance by measuring critical points and spinodals.

Spinodals in particular could be very informative. The calculated curves in *Figure 9* indicate that a shoulder on the cloud-point curve seems to be accompanied by a second maximum in the spinodal. The latter maximum also represents a critical point, but this is metastable, like the critical point located at the minimum of the spinodal. It can be shown[35, 41] that, by a suitable change of the values of g_1 and g_2, the second maximum in the spinodal can be emphasized to an extent that the cloud-point curve eventually becomes bimodal too (see next section).

POLYSTYRENE–POLYISOPRENE

McIntyre *et al.*[44] studied miscibility gaps in oligomeric mixtures of polystyrene and polyisoprene in order to collect thermodynamic data that might be helpful in understanding properties of triblock copolymers of styrene and isoprene. We used the same system to gain insight into the parameters that determine location and shape of a two-phase region. *Figure 11* shows our data for two quasi-binary systems containing anionic polymers: polyisoprene ($M_n \approx 2\,700$) and two polystyrenes ($M_n \approx 2\,100$ and $2\,700$).

As in the system polyisobutene–silicone, changes in chain length bring
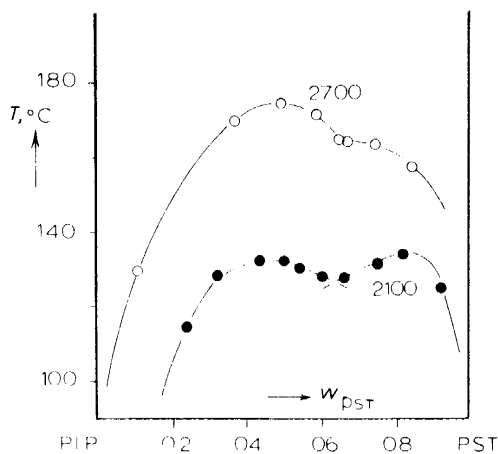
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Figure 11. Measured cloud-point curves in the system polyisoprene (PIP: $M_n = 2\,700$)–polystyrene (PST, M_n values indicated): w_{PST} = weight fraction polystyrene.
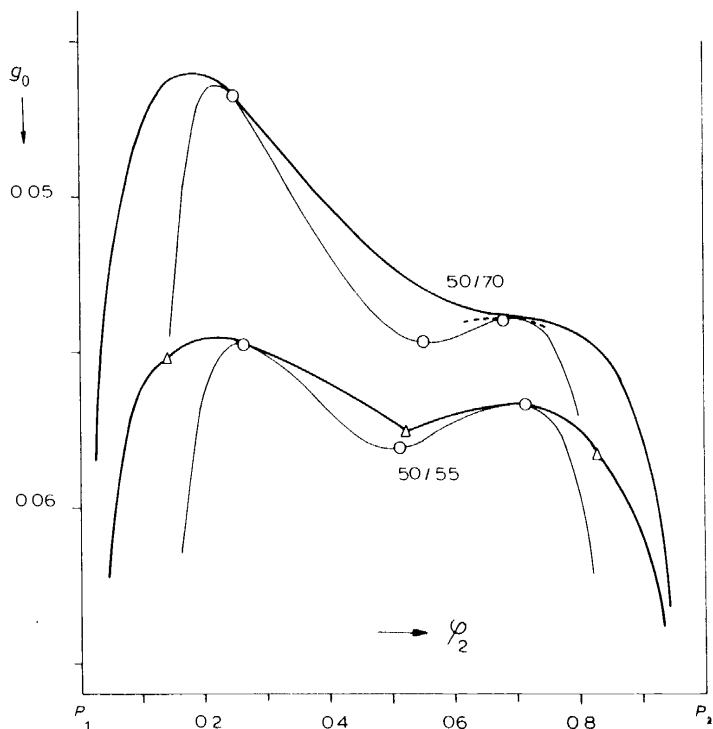

Figure 12. Cloud-point curves (——), critical points (O) and spinodals (----), calculated with $g = g_0 - 0.04\varphi_2 + 0.04\varphi_2^2$, for indicated $m_{w,1}/m_{w,2}$ values. Corners of three-phase triangles (△), metastable cloud-point curve: (-----) (see ref. 35).

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about vast variations in location of the miscibility gap. A decrease of the polystyrene molecular weight from 2 700 to 2 100 goes with a temperature shift of about 50 °C. Judged from the data of McIntyre *et al.* the sensitivity is even greater towards the chain length of the polyisoprene, the maximum of their cloud-point curve (PIP 2000; PST 2 700) occurs at 56 °C.

The system 2 700/2 100 in *Figure 11* is particularly interesting because its miscibility gap has two maxima. After the preceding considerations it is obvious to assign this behaviour to the concentration dependence of g. Model calculations on a system that is only a very rough representation bring out that a qualitatively correct description can be obtained with a $g(\varphi_2)$ function similar to that used for polyisobutene–silicone mixtures (*Figure 12*). The shift with chain length is now achieved with the combinatorial terms alone, and no variation in g_1 and g_2 with molecular weight is needed. Again, further attempts at improving the description would call for knowledge of polydispersity and for measurements of stability limits and critical points.

The bimodality of a cloud-point curve might be thought to be caused by polydispersity in one of the polymers or in both. It has been shown elsewhere that this is not necessarily so, a strictly binary polymer mixture may also show a two-peaked cloud-point curve[35]. The phenomenon can be attributed to a particular dependence of g on φ_2 (at least quadratic).
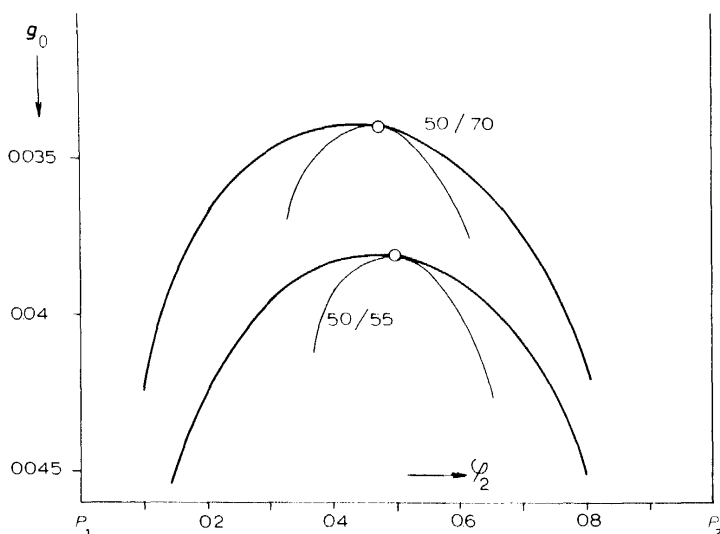

Figure 13. Caption as *Figure 12*, g independent of concentration.

Another objection might be raised in view of the relatively short chains considered here. End-group effects, leading to g being dependent on m_n, cannot off-hand be ruled out as possible causes of unusually shaped miscibility gaps. It is possible to derive the stability limit for an arbitrary m_n-dependence of g at the cost of some lengthy algebra which we shall not repeat here[33-35]. Some model calculations for oligomeric mixtures indicate that two maxima can artificially be brought about in spinodals by end-group

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effects, but only for values of the interchange free enthalpies that are un-acceptably large. The two maxima vanish upon introduction of reasonable values. Hence, end-group effects are not likely to be the origin of bimodality in cloud-point curves of these oligomeric mixtures[46].

It hardly needs verification that the observed behaviour cannot at all be described with g independent of φ_2 (*Figure 13*).

EQUATION OF STATE APPROACH

We have seen that the lattice theory is capable of supplying a satisfactory but after-the-fact description of liquid–liquid phase relations in polymer compatibility. For predictive purposes, however, it is inadequate. For in-stance, the sensitivity of the cloud point to relatively small variations in chain length is reflected in the relation between g_0 and T, which can be described but not predicted. The marked influence of the exact form of the $g(\varphi_2)$ function is another example.

Very recently it was shown by McMaster[15] that Flory's equation of state theory[12] is superior to the lattice treatment in that it does not only predict the extreme sensitivity of the cloud point to variations in chain length, but also reveals the marked influence of thermal expansion and pressure co-efficients. McMaster's model calculations show that lower critical miscibility (phase separation upon an increase of T) must be expected to be a normal phenomenon in polymer mixtures. This is a particularly strong point for the theory; Flory and his co-workers[13, 57] predicted lower critical demixing of polymer solutions, consistent with experimental findings. McMaster predicts that a difference by a factor of two in the average chain length of one of the polymers may shift the cloud point more than 100 °C. Similar shifts may be brought about by quite acceptable differences between the thermal expansion or pressure coefficients of the two polymers. Further, the value of Flory's interaction parameter X_{12} is also sensitively determinative, the merging together of two separate miscibility gaps (upper and lower miscibility type) in the same system into a single hour-glass shaped two-phase region calls for
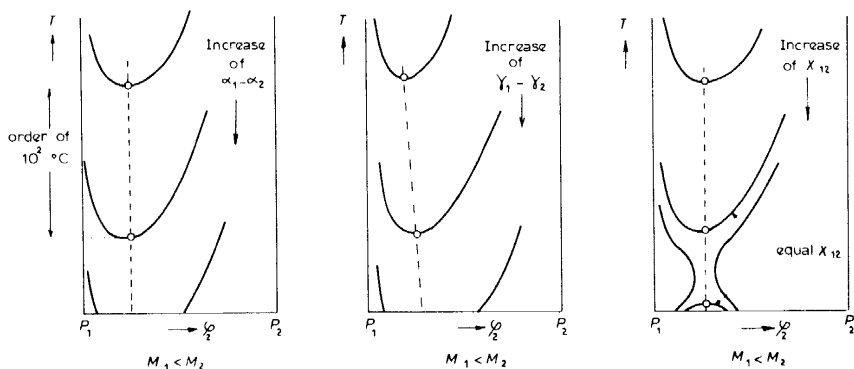

Figure 14. Dependence of the location of the miscibility gap in two-polymer mixtures on equation of state parameters (α = thermal expansion coefficient; γ = thermal pressure coefficient) and interaction energy parameter (X_{12}). Cloud-point curve: ——; critical point: O. Schematical, from McMaster[15].

subtle changes in X_{12} only. *Figure 14* schematically summarizes some of McMaster's results; we refer the reader to the original paper for details.

In order to support the general conclusion of his calculations, McMaster presented two examples of miscible polymer pairs that demix upon heating. His systems are polystyrene–poly(methyl vinyl ether) and styrene–acrylonitrile copolymer–polycaprolactone. From our own experience we can add the system butyl-rubber–EPDM terpolymer which is also compatible at room temperature and becomes immiscible when heated[46].

The lattice treatment of the oligomeric systems showed that a well-defined concentration dependence of the interaction parameter g must be introduced for quantitative descriptions of phase relations to be feasible. The form of the $g(T, \varphi_2)$ function, however, is rather peculiar and cannot be derived from lattice considerations. The equation of state theory defines $g(T, \varphi_2)$ to a considerable extent in terms of fundamental parameters. It should be noted, however, that, at least within the range of values McMaster attached to these parameters, the irregular asymmetry of miscibility gaps reported by Allen *et al.*[43] cannot be described. All of McMaster's calculated and measured cloud-point curves have the normal asymmetry and are located in that part of the phase diagram which represents systems rich in the constituent with the shorter chains. Further, McMaster's extensive data do not suggest the possibility of describing a bimodal cloud-point curve with his equation of state treatment in unmodified form. Although tremendous progress had been made by this application of Flory's equation of state theory it is obvious that further improvements are needed in order to achieve a completely quantitative prediction of phase relations in polymer compatibility, which proves to be a very subtle phenomenon indeed.

CHAIN LENGTH COMPATIBILITY

Polymer compatibility evidently being governed by subtleties in the enthalpy and/or entropy of mixing, the question does not seem to be altogether superfluous whether a mixture consisting of two chemically identical homopolymers with widely varying chain lengths might show incompatibility. If, for instance, the interaction energy between end and middle groups differed enough from that between end–end and middle–middle contacts, one might have a positive heat of mixing of the two samples. Assuming Flory and Huggins' expression for the entropy of mixing to be valid, one can estimate that the energy difference, necessary for samples with chain lengths of 10 and 10000 to be partially miscible, is only a fraction of RT. Hence, the phenomenon would seem physically possible[58].

There is some controversy in the literature as to the question whether polyethylene might show this behaviour[6]. Orwoll and Flory[13] made a thorough analysis of heat of mixing data on binary mixtures of n-alkanes of various chain lengths in terms of the equation of state theory. They were remarkably succesful in describing the data and, in addition, the phenomenon of lower critical miscibility in alkane polyethylene solutions, which does occur. From the heat of mixing data one could roughly deduce that the mixing of two polyethylene samples with widely differing chain lengths will presumably go with a negative heat of mixing at temperatures above *ca.*

$120\ ^\circ C^{58}$. However, this is no guarantee for chain length compatibility, because the entropy of mixing may also bring about a ripple on the $\Delta G(\varphi_2)$ curve. Hamada *et al.*[59] considerably extended the existing data in this field by measuring cloud-point curves for linear polyethylenes with various average chain lengths in alkanes (C_5–C_8). They found the miscibility to increase with increasing chain length of the solvent.

In view of all these data one is inclined to accept the compatibility of polydisperse polyethylene.

Buchdahl and Nielsen[60] reported a secondary maximum in the mechanical loss as a function of temperature for a 1/1 mixture of two polystyrenes with weight-average molecular weights of 2×10^3 and 1.2×10^6. The occurrence of two peaks points to the existence of two phases, each with its own glass temperature. Buchdahl and Nielsen are somewhat vague in their discussion of the polystyrene mixture and we thought it worthwhile to repeat their
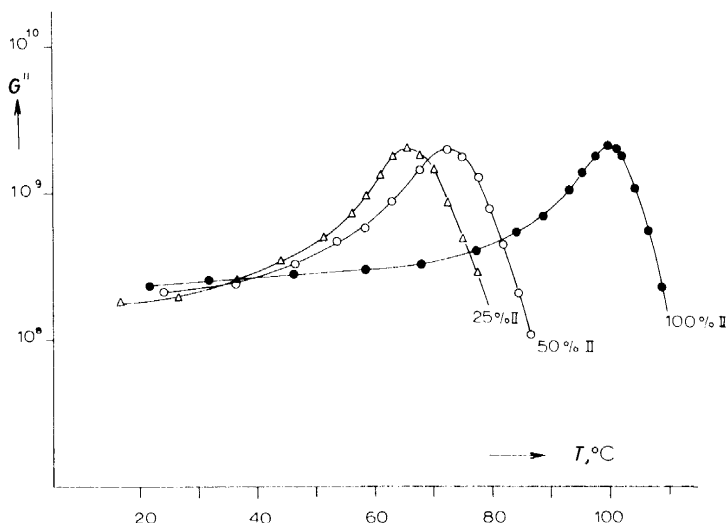

Figure 15. Loss modulus in shear (G'', dyn cm^{-2}) at a frequency of 0.2 Hz as a function of temperature for mixtures of narrow distribution polystyrenes (per cent by weight of constituent II indicated). $M_{n,\mathrm{I}} = 2 \times 10^3$; $M_{n,\mathrm{II}} = 1.25 \times 10^6$.

measurements. Two anionic polystyrene samples from Pressure Chemical Co. were used with weight average molecular weights of 2×10^3 and 1.5×10^6. The polystyrene mixtures were prepared by evaporation of the solvent from homogeneous solutions in ethyl methyl ketone under stirring, and drying for several days under vacuum at 40 °C. The glass temperature was defined as the temperature at which the mechanical loss modulus at a frequency of 0.2 Hz shows a maximum. The pure 2×10^3 sample was measured with the Perkin-Elmer Thermomechanical System[47]. The mixtures and the constituents gave only one peak which points to complete miscibility in the temperature and concentration ranges covered (*Figure 15*). In addition, T_g shows the usual linear dependence on $1/M_n$ (*Figure 16*). All this points to

chain-length compatibility. The secondary peak reported by Buchdahl and Nielsen may have been due either to incomplete mixing (non-equilibrium state) or to end groups that are of a chemical nature different from those in the Pressure Chemical anionic polystyrene.
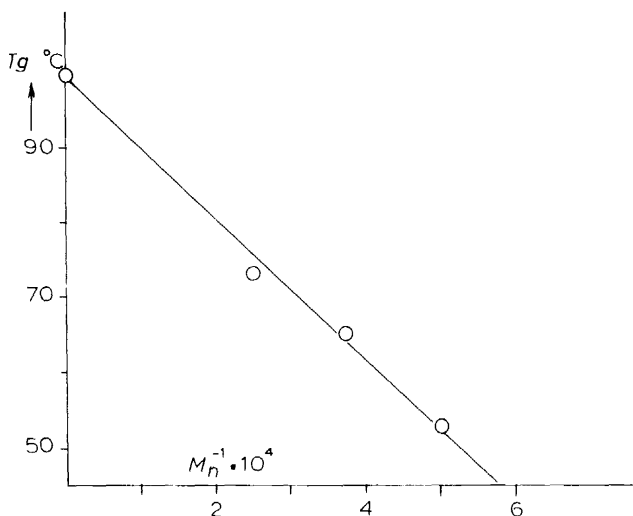

Figure 16. Glass temperature T_g as a function of $1/M_n$ for the systems in *Figure 15* and constituent I.

EXPERIMENTAL METHODS

Various methods exist for determining the compatibility of polymers. We refer to literature for a complete survey[2-7] and only discuss two procedures based upon thermodynamic principles. In our opinion light-scattering techniques supply the most reliable data whereas the better-known mutual solvent method may easily lead to incorrect conclusions.

I. Light scattering methods

In a homogeneous system the intensity of the scattered light is proportional to the second derivative of ΔG with respect to concentration and depends further on the scattering angle ϑ [40-51]:

$$1/I(\vartheta) \propto \partial^2 \Delta G/\partial\varphi_2^2 + f_\vartheta(\vartheta) \tag{16}$$

We have $f_\vartheta(0) = 0$, so that

$$1/I(0) \propto \frac{\partial^2 \Delta G}{\partial\varphi_2^2} = f(T, \varphi_2) \tag{17}$$

The stability limit of the system is defined by equation (1), hence, at the spinodal, $1/I(0) = 0$.

At a given concentration φ_2 the scattered intensity can be measured as a function of the scattering angle. Extrapolation to zero angle yields $I(0)$. In

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this way $I(0)$ values can be determined for different temperatures and be plotted, e.g. as $I(0)^{-1}$ against T^{-1}. By extrapolation to $I(0)^{-1} = 0$ one finds the spinodal temperature for that φ_2 value (*Figure 17*).
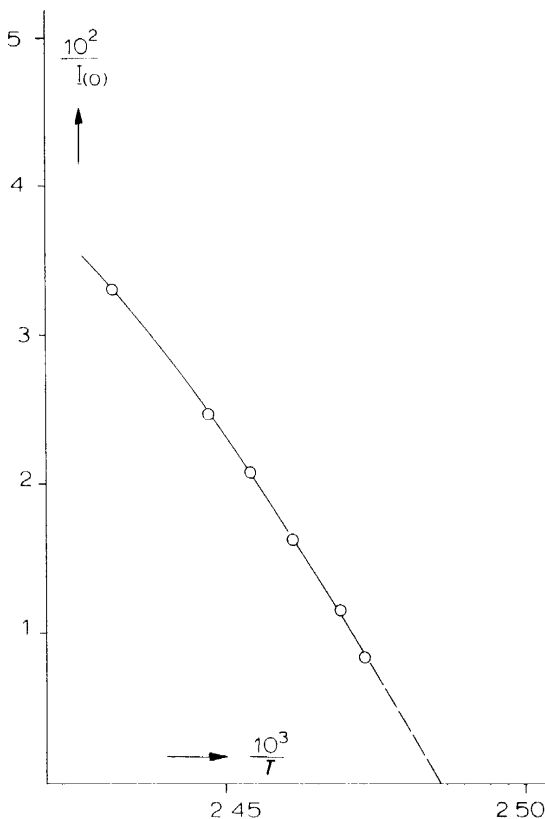

Figure 17. Scattered light intensity at zero scattering angle as a function of temperature. System: n-octadecane–polystyrene ($M = 4 \times 10^3$, concentration: 40 per cent by wt).

The proportionality constant in equation (17) contains the dependence of the refractive index of the mixture on its composition. The extrapolation method has the advantage that such data do not need to be known, but it is subject to the limitation that the system must have a miscibility gap. Miscible systems can be dealt with, but call for knowledge of the parameters in the proportionality constant in equation (17)[48].

There are two ways of applying the extrapolation method. One is to choose the measuring temperatures in such a way that the miscibility gap is approached as closely as possible without being entered into[48-51]. The second, more recent method by Gordon *et al.*[39,52] is devised so as to allow entering the miscibility gap deliberately in order to approach the spinodal more closely. Entering the two-phase region happens very quickly by means of a temperature pulse (pulse induced critical scattering) and the system is brought

back to a temperature above the cloud point before it can separate into two phases. In the mean time, however, the intensity of the light scattered at a fixed angle has been recorded. Applications of the method have proven that spinodal temperatures determined in this way are in excellent agreement with other thermodynamic information[35, 39].

Figure 17 shows an example of the light-scattering method, applied to the system polystyrene–n-octadecane under conditions where it is homogeneous. The solutions were prepared in a dust-free special light-scattering cell. The polystyrene concentrations were too high for filtration of the solution to be feasible. The solutions were homogenized at 150 °C by successive
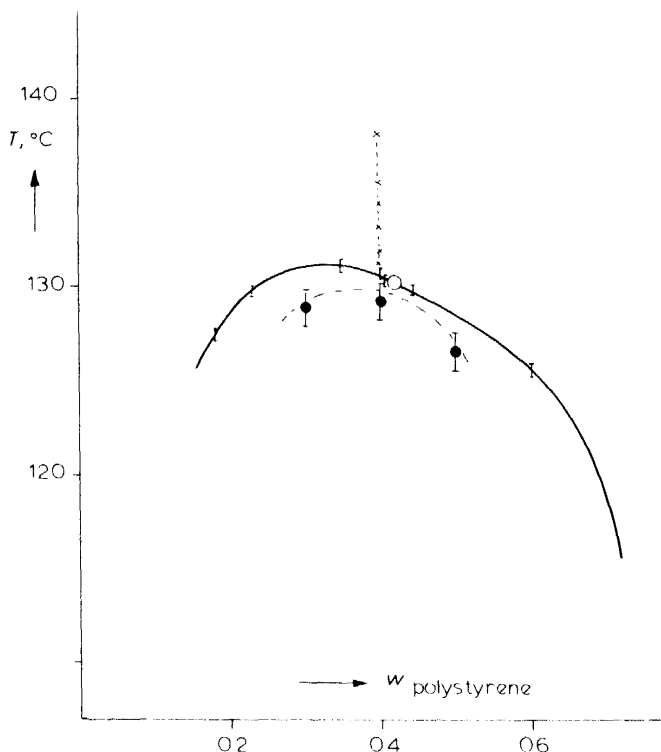

Figure 18. Cloud-point (———), spinodal (———) and critical point (O) in the system of *Figure 17.* Estimated experimental errors are indicated. Crosses denote measuring temperatures in light-scattering (*Figure 17*). *w* = weight fraction.

shaking and vibrating of the cell until no heterogeneity could be observed by eye (2 hours). Vibration was then continued up to a total dissolving time of about 16 hours. The accuracy of the measuring temperature is estimated to 0.3 °C, but the extrapolation adds to the uncertainty in the spinodal temperature (0.5 °C). The cloud-point curve and the critical point were determined by means of phase-volume-ratio measurements, and are consistent with the location of the spinodal (*Figure 18*).

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II. The mutual solvent method

The phase behaviour of a mixture obtained upon mixing solutions of polymer 1 and of polymer 2 in the same solvent is often used as a criterion for the compatibility of the solvent-free polymer 1–polymer 2 system. The reliability of the method rests entirely on the validity of the assumption that the miscibility gap in the two-polymer system extends far enough into the solvent–polymer 1–polymer 2 composition triangle to be discernible in relatively dilute solutions of the mixed polymer. The method is based on calculated ternary phase diagrams reported by Tompa[26,61] and Scott[62] which indicate that incompatibility may indeed reveal itself down to fairly low concentrations. This behaviour is shown schematically in *Figure 19b*. In such situations the
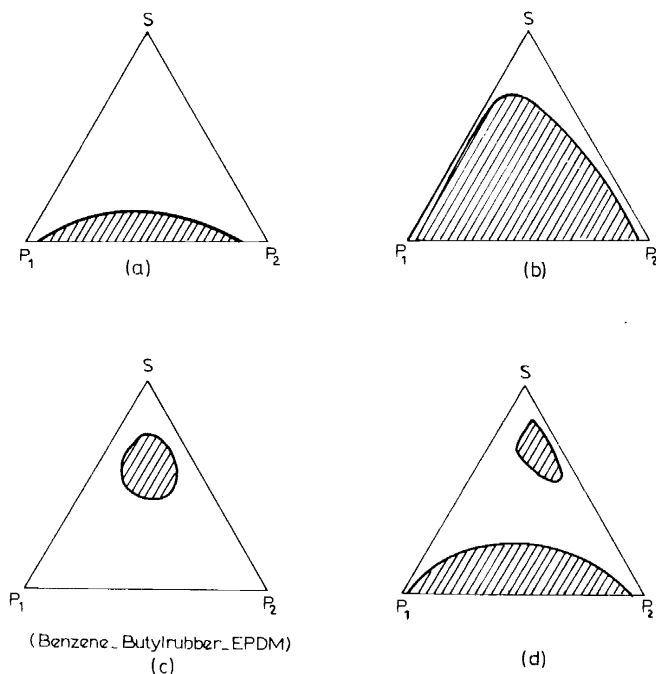

Figure 19. Possible liquid–liquid phase behaviour of quasi-ternary solvent (S)–polymer 1 (P_1)–polymer 2 (P_2) systems. Hatched areas denote two-phase regions. Schematical.

mutual solvent method will give the right answer; however, in *Figure 19a* it will lead to an incorrect conclusion. The only difference between the two cases is the nature of the solvent. In both situations the solvent is completely miscible with each of the polymers.

Another source of erroneous conclusions is a phase behaviour like that depicted in *Figure 19c*. Here we would conclude that the two polymers are incompatible, whereas they are completely miscible, The systems benzene–butyl–rubber–EPDM rubber and diphenyl ether–atactic polypropylene–

linear polyethylene present examples of such closed miscibility gaps (*Figure 20a*). Liquid–liquid phase relations may be even more complicated as is shown schematically in *Figure 19d*. As far as the solvent-rich part of the diagram is concerned we have an experimental example in the system diphenyl ether–isotactic polypropylene–linear polyethylene (*Figure 20b*).
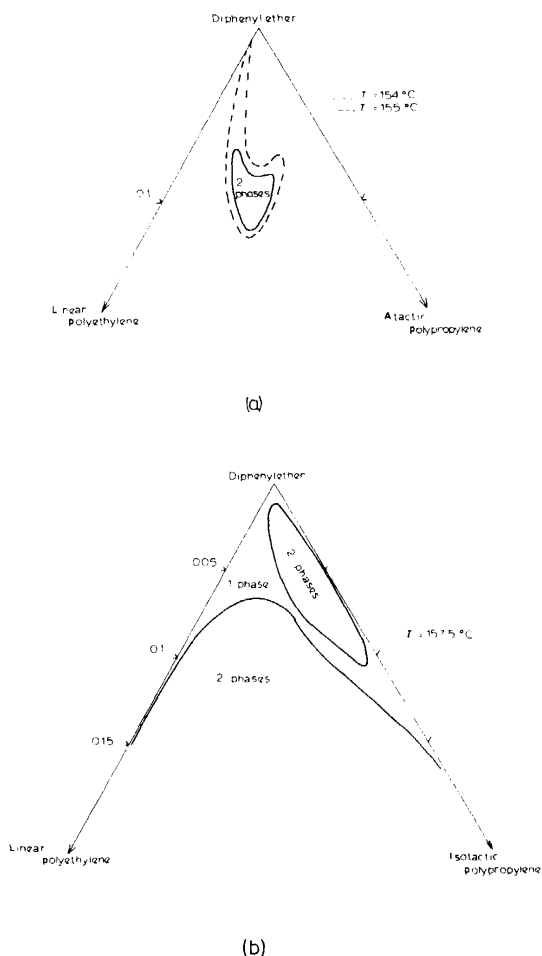

(a)

(b)

Figure 20. Closed miscibility gaps in the system diphenyl ether–polyethylene–polypropylene[32,41].

The data upon which *Figure 20b* is based do not extend beyond about 15 wt % of mixed polymer. The question as to the compatibility of molten polyethylene/polypropylene blends remains open, and *Figure 19d* may well be inappropriate for that system. In this connection recent observations by Kryszewski *et al.*[63] might be mentioned. These workers studied the inter-diffusion of molten polyethylene and polypropylene and measured *inter alia* infrared absorption bands characteristic for polyethylene and polypropylene

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at various distances from the interface between molten films of the two polymers. Kryszewski *et al.* conclude that there must at least be partial miscibility in molten blends of polyethylene and polypropylene.

This is a significant new development dealing with solvent-free mixtures. In the present context it offers additional support to our opinion that the mutual solvent method does not permit reliable conclusions about the state of the solvent-free polymer mixture and should therefore be regarded with reserve. An adequate increase of the mixed-polymer concentration is impracticable because of the steep rise of the viscosity with concentration.

CONCLUSIONS

In the present paper we have tried to show that polymer compatibility is a very complicated and subtle phenomenon that cannot be dealt with by the mere statement that in most polymer mixtures the free enthalpy of mixing is positive. Summarizing some of the parameters that are determinative for the miscibility of two polymers, we have:

1. ΔH, the heat of mixing, the most important parameter. A small positive value already suffices to cause demixing. Formally it can be treated by introduction of the Van Laar type parameter g in the lattice theory, and by the interaction parameter X_{12} in Flory's equation of state treatment.

2. At a given level of ΔH, phase relations are markedly influenced primarily by the average chain lengths and to a lesser extent by the chain length distributions of the two polymers.

3. The combinatorial entropy terms in the free enthalpy of mixing may be outweighed by correction terms that may be of entropic (non-combinatorial) and/or enthalpic nature. Their effect is a distortion of the miscibility gap which may even shift towards the composition region of the phase diagram representing mixtures rich in the constituent with the longer chain lengths.

4. Small changes in the difference between the thermal expansion coefficients or the thermal pressure coefficients of the two polymers have a marked influence on the location of the miscibility gap.

Provided g is made an appropriate function of concentration the lattice expression for ΔG can deal quantitatively even with the most unusual shapes of miscibility gaps. This is a descriptive rather than predictive quality, but the lattice treatment is indeed very powerful in this respect.

The equation of state theory is superior in that it can predict the order of magnitude of the effect which the average chain lengths and the thermal expansion and pressure coefficients have on the location of the two-phase region. It also predicts lower critical solution phenomena. In a quantitative respect, however, it still has to prove its usefulness. The remarkable shift mentioned under (3), for instance, seems to be beyond its range so far.

Two parameters of considerable importance have been left out of consideration here. Dealing with subtle effects we must expect chain branching in homopolymers and sequence length distribution in copolymers to have an influence on phase relations that may at least be similar to that exercised by the four parameters dealt with in this paper. The reason for leaving them out of consideration is the present apparent lack of theoretical relations needed in model calculations.

Partial miscibility in a homopolymer on account of large differences in chain length theoretically does not seem to be impossible. In linear polyethylene and anionic polystyrene no experimental indication has been found for chain-length incompatibility.

Two thermodynamic methods for establishing compatibility have been analysed. The familiar mutual-solvent method proves to be unreliable because miscibility of the mixed-polymer solution does not necessarily imply miscibility of the solvent-free polymer mixture and vice versa. Light-scattering measurements on polymer mixtures supply unambiguous thermodynamic information. They are limited to one-phase systems although the success of the Pulse Induced Critical Scattering method of Gordon *et al.* has shown that the metastable part of the two-phase region can be entered into.

The extreme sensitivity to chain length might be employed to bring the many incompatible polymer pairs within reach of the light-scattering methods.

APPENDIX

Calculation of phase relations in mixtures of two polymers

(a) Polymer 1 (monodisperse)–polymer 2 (polydisperse):
The program MEXPREC calculates concentration and molecular weight distribution of polymer 2 in both phases and the g-value at which the separation takes place, starting from known values of

S_0 = molecular weight polymer 1,
$w(M)$ = molecular weight distribution of polymer 2 (exponential or a set of delta functions),
φ_2 = volume fraction of polymer 2,
r = V'/V'', ratio of the volumes of the phases concentrated ($''$) and dilute ($'$) in polymer 2.

For a concentration dependent interaction parameter g

$$g = g_0 + g_1\varphi_2 + g_2\varphi_2^2 \tag{A1}$$

the concentration dependence (g_1 and g_2) should also be known.

With an estimated starting value for the distribution coefficient $\sigma \left[= (1/m_i) \ln \varphi_i''/\varphi_i' \right]$ the weight of polymer 2 in the concentrated phase, w_2'', is calculated from

$$w_2'' = \int_0^\infty \frac{w(M)}{1 + r\,e^{-\sigma M}}\,dM \tag{A2}$$

by means of an accurate integration subroutine. In addition to equation (A2) the following integrals are calculated

$$N'' = \int_0^\infty \frac{M^{-1}\,w(M)}{1 + r\,e^{-\sigma M}}\,dM \tag{A3a}$$

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$$N' = N - N'' \qquad \text{(A3b)}$$

$$Z'' = \int_0^\infty \frac{M\, w(M)}{1 + r\, e^{-\sigma M}}\, dM \qquad \text{(A4a)}$$

$$Z' = Z - Z'' \qquad \text{(A4b)}$$

$$(Z + 1)'' = \int_0^\infty \frac{M^2\, w(M)}{1 + r\, e^{-\sigma M}}\, dM \qquad \text{(A5a)}$$

$$(Z + 1)' = (Z + 1) - (Z + 1)'' \qquad \text{(A5b)}$$

where N, Z, $Z + 1$ are the relevant moments of the initial distribution $w(M)$ and of the distributions of the fractions in the two phases.

From this m_n', m_n'', m_w', m_w'', m_z' and m_z'' are easy to calculate. The concentrations of polymer 2 in the phases are then

$$\varphi_2'' = (r + 1)\, w_2''\varphi_2 \qquad \text{(A6a)}$$

and

$$\varphi_2' = [\varphi_2(r + 1) - \varphi_2'']/r \qquad \text{(A6b)}$$

From $\Delta\mu_1'' = \Delta\mu_1'$ and $\Delta\mu_{2i}'' = \Delta_{2i}'$. g_0 and σ_{calc} are calculated according to

$$g_0 - g_1 = \left[\sigma - \frac{1}{S_0}\ln\frac{1 - \varphi_2''}{1 - \varphi_2'} - 3(\varphi_2''^2 - \varphi_2'^2)(g_1 - g_2) - 4(\varphi_2''^3 - \varphi_2'^3)g_2\right]\Bigg/$$
$$[2(\varphi_2'' - \varphi_2')] \qquad \text{(A7)}$$

$$\sigma_{\text{calc}} = \varphi_2''(S_0^{-1} - m_n''^{-1}) - \varphi_2'(S_0^{-1} - m_n'^{-1}) + 3(g_2 - g_1)(\varphi_2''^2 - \varphi_2'^2)$$
$$+ 3(g_1 - 2g_2)(\varphi_2''^3 - \varphi_2'^3) - g_0 - g_1)[\varphi_2''^2 - \varphi_2'^2 - 2(\varphi_2'' - \varphi_2')]$$
$$\text{(A8)}$$

With an adequate extrapolation subroutine σ_{start} is changed and the calculation repeated until

$$|\sigma_{\text{calc}} - \sigma_{\text{start}}| < \varepsilon \cdot \sigma_{\text{calc}}$$

Starting with a reasonable σ this is possible in less than 10 iteration steps. Normally an accuracy of $\varepsilon = 10^{-4}$ suffices.

(b) Two polydisperse polymers.

Instead of S_0 in MEXPREC the molecular weight distribution of polymer 1, $X(M)$, must be given. The distribution coefficient of polymer 1 is

$$\alpha \left[= (1/m_{1i}) \cdot \ln\frac{\varphi_{1i}''}{\varphi_{1i}'} \right]$$

The program MENGPOL starts with estimated values of σ and α. In the equations mentioned below the concentrated ('') and dilute phase (') are the phases concentrated and dilute in polymer 2 respectively.

The weight of polymer 2 in the concentrated phase is calculated with

equation (A2) and similarly the weight of polymer 1 in this phase is

$$w_1'' = \int_0^\infty \frac{X(M)\,dM}{1 + r\,e^{-\alpha M}} \tag{A9}$$

With the same integration subroutine as in MEXPREC the average molecular weights of both polymers and the concentrations in the two phases are calculated with equations (A3)–(A6). The weight of polymer 1 in the concentrated phase has to be

$$w_1''{}_{calc} = \frac{1 - \varphi_2''}{(r + 1)(1 - \varphi_2)}$$

By comparing this value with equation (A9) it is possible to change α_{start} with an extrapolation subroutine in such a way that, after some iterations, $w_1'' = w_1''{}_{calc}$ within 10^{-4} per cent. From the equality of the chemical potential of all species of a polymer in both phases,

$$\Delta\mu_{1i}'' = \Delta\mu_{1i}' \text{ and } \Delta\mu_{2i}'' = \Delta\mu_{2i}'$$

it is possible to calculate g_0 and σ_{calc} with

$$g_0 - g_1 = [\sigma - \alpha - 3(g_1 - g_2)(\varphi_2''{}^2 - \varphi_2'{}^2) - 4g_2(\varphi_2''{}^3 - \varphi_2'{}^3)]/$$
$$[2(\varphi_2'' - \varphi_2')] \tag{A11}$$

$$\sigma_{calc} = \frac{\varphi_2''}{m_{n_2}''} - \frac{\varphi_2'}{m_{n_2}'} + \frac{\varphi_1''}{m_{n_1}''} - \frac{\varphi_1'}{m_{n_1}''} - 3(g_1 - g_2)(\varphi_2''{}^2 - \varphi_2'{}^2)$$
$$+ 3(g_1 - 2g_2)(\varphi_2''{}^3 - \varphi_2'{}^3) - (g_0 - g_1)[\varphi_2''{}^2 - \varphi_2'{}^2 - 2(\varphi_2'' - \varphi_2')] \tag{A12}$$

By comparing σ_{calc} with σ_{start} a new starting σ value, σ_2 is calculated with the extrapolation subroutine. With σ_2 and the α value from the iteration on equation (A10) as α_{start}, a new iteration is performed. With properly chosen values for σ_{start} and α_{start} one can get $\sigma_{calc} = \sigma_{start}$ within 10^{-4} per cent in less than 10 iteration steps.

Because it is sometimes difficult to know a proper value for r it is possible to perform both MEXPREC and MENGPOL procedures for a given g_0 values have to be carried out. For $\varphi_2 > \varphi_{2c}$, r goes to zero and if $\varphi_2 < \varphi_{2c}$, r separation temperature is possible if the temperature dependence of the interaction function is known.

In both systems the phase compositions are not cloud points but coexisting phases. To obtain a cloud point several separation calculations for different r values have to be carried out. For $\varphi_2 > \varphi_{2c}$ r goes to zero and if $\varphi_2 < \varphi_{2c}$ r goes to infinity in the cloud point (φ_{2c} is the critical concentration).

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Note added in proof:

Dr L. P. McMaster kindly drew the authors' attention to hitherto unpublished calculations by Dr O. Olabisi and himself which show that a shift of the miscibility gap to the 'wrong' side of the phase diagram may be obtained by an appropriate choice of the interaction energy parameter X_{12}. Such shifts are brought about by rather large negative values of X_{12}. It may therefore be that the criticism we expressed on pages 20 and 27 has been a little too severe.