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Polymers and Thermodynamics

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Classic thermodynamic equilibrium considerations, supported by simple molecular models, may lead to useful predictions about phase relationships in partially miscible systems that contain polymers. How quantitative the prediction is depends on the amount of experimental information, as well as, on the complexity of the system. The solubility parameter and group contribution approaches present the *first level* and allow a qualitative judgement whether a system is miscible or not. On this level, the entropy of mixing is not considered though it is higly important.

A *second*, higher level of prediction is supplied by the Flory-Huggins-Staverman equation which permits estimations of the temperature and chain length dependence on the location of miscibility gaps. On this level the concentration ranges of partial miscibility are not well covered.

Taking account of the ever present disparity in size and shape between molecules and repeat units improves the situation considerably and represents a *third* level of prediction. On this level the influence of pressure can reasonably accurately be dealt with.

If predictions of a high precision are required, the present-day theory fails, even in the simple case of a linear, apolar homopolymer solution. Extensive measurements then remain needed to determine the many empirical and theoretical parameters. Predictions on such a high level have a more than academic value, since they may supply better mathematical frameworks to be applied in less demanding calculations.

INTRODUCTION

Though the contrary is often thought, equilibrium thermodynamics is an indispensable tool for the understanding and, thereby, the control of important steps in polymer production and processing. Polymerisations frequently take place in solution, and demixing is not a rare phenomenon, not even if the monomer serves as the solvent. Such liquid-liquid phase separations are to be avoided since they disturb the production process by the segregation of highly viscous phases, i. e. impeding transfer of the heat of polymerisation. Examples can be found in the bulk polymerisation of ethylene, either at pressures of around 2000 bar, or in solution under milder conditions. The cause of the relatively small resistance to demixing shown by polymer solutions is to be found in the long-chain structure of macromolecules. Therefore, this sensitivity reveals itself still more emphatically when polymers are blended.

Knowledge of the dependence of ΔG, the Gibbs free energy of mixing, on molecular parameters and macroscopic variables, is essential to understand phase relationships. With polymer mixtures the value of ΔG is not seldom the sum of a number of terms, each larger than ΔG itself. Since liquid-liquid phase relations are sensitively determined by the composition dependence of ΔG, every single contribution must be scrutinized. The situation is further complicated by the elevated pressures and considerable shear rates applied in the processing of blends.

Theoretical models, as well as experimental techniques, have been and are still being developed. The simplest model, that of Flory, Huggins, and Staverman permits a qualitative ordering of part of the observed phenomena only. More advanced theories exist but still have to rely on empirical adaptation. We shall first discuss homopolymer solutions from the standpoint of the three levels of increasing accuracy of prediction mentioned in the summary, and then proceed with discussions of more complicated mixtures, like those containing copolymers.

Polymers consist of long-chain molecules in which the covalently bonded basic repeat unit (monomer) occurs many times. When the chemical structure of all repeat units is identical we have homopolymers, when two or three different monomers occur one speaks of co- or terpolymers. The number of monomer groups (or segments) in the chains is usually very large and differs between the various chains in the polymer, no matter how careful their synthesis may have been. Virtually all synthetic polymers have a chain length distribution.

Polymers have a negligible vapour pressure but this does not mean we would have to deal with condensed phases only. Many polymerisation processes take place in solution, at elevated temperatures and/or pressures and vapour phases appear frequently. Monomers are often relatively volatile and may cause sizeable vapour pressures that have to be accounted for. Removal of traces of monomer from a polymer is a related problem. Polymer solutions thus play an important role in both polymer research and engineering. Much effort has been devoted to partial miscibility, a frequently occurring phenomenon in polymer solutions and mixtures. Very complex phase relations appear in systems containing co- or terpolymers. The paint and lacquer industry is faced with problems related herewith (i. e. stability of solutions) and largely uses the first level approximations mentioned in the summary. Higher levels are at present practically unattainable because of the complexity of the systems.

The term 'level of prediction' might need some explanation. Prediction means calculation of data not (yet) known from the known data on a system. Obviously, to be able to calculate liquid-liquid phase relations (phase diagrams) on the basis of a minimum of experimental information would be the ultimate aim. Success along such lines is not merely a matter of developing a suitable expression for ΔG although it certainly is of primary importance to know

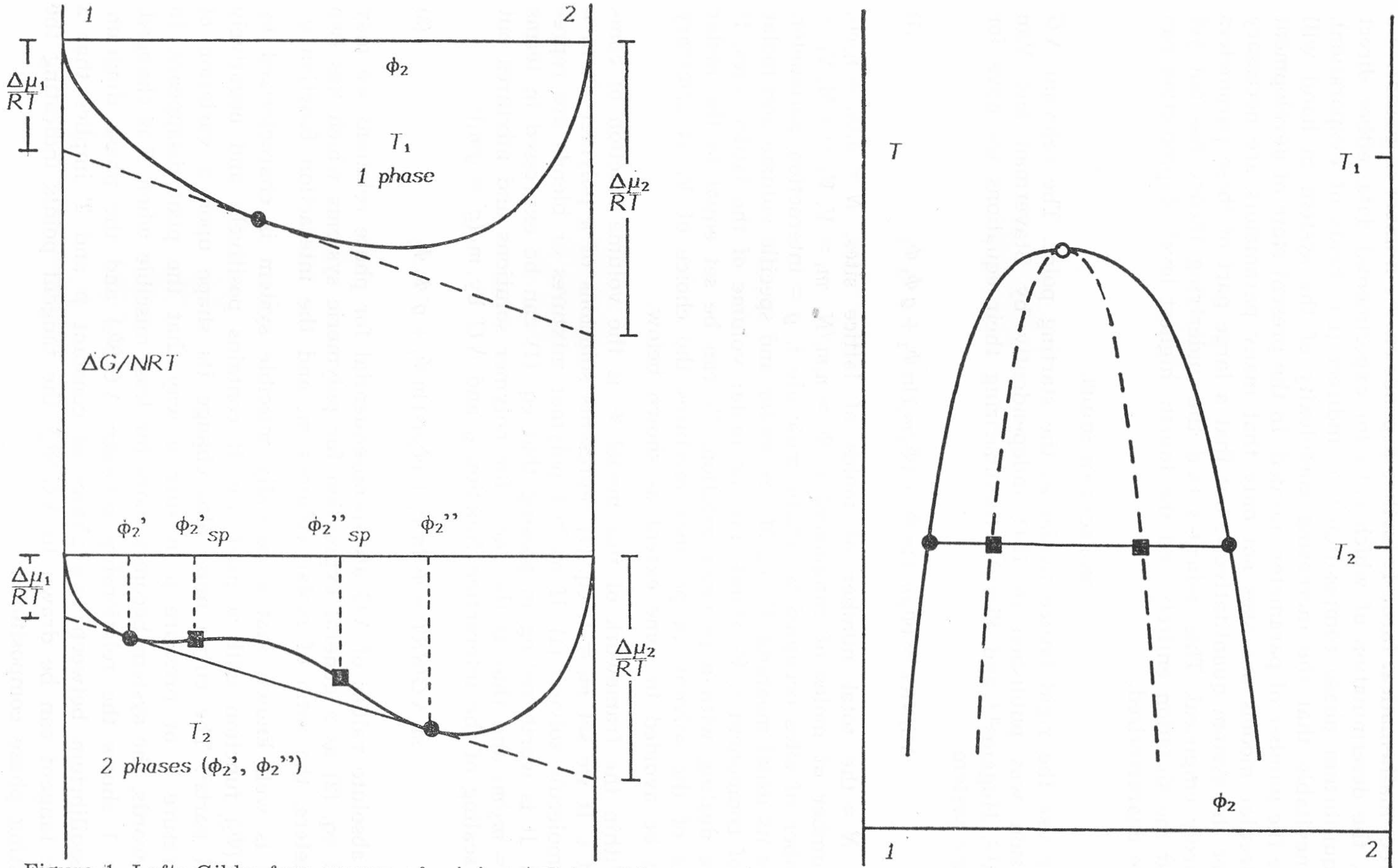


Figure 1. Left: Gibbs free energy of mixing ΔG in a binary system as a function of Φ_2, the volume fraction of the second component, showing the influence of temperature. Right: Phase diagram with binodal (———), spinodal (– – –), critical point (○) and tie line (●———●).

its correct mathematical form. It further depends on the number of parameters in ΔG, the determination of which calls for experimental data, either direct (i. e. equilibrium phase compositions) or indirect (i. e. heats of evaporation). It is inevitable that the increasing complexity of the system in hand will enlarge the number of parameters needed. In the present state of development of molecular models one sees not only that many parameters are necessary to cover the system quantitatively, but that a large part of these parameters are purely empirical. This indicates that the underlying theory has not yet grasped the situation entirely and the fourth, highest level of prediction can thus be characterized.

MOLECULAR MODEL

We use the rigid lattice model as the starting point. The relevant ΔG expression was published in 1941 independently by Staverman and Van Santen[1,2], Huggins[3,4] and Flory[5,6]. Summarizing their equations we have for a binary system

$$\Delta G/NRT = (\Phi_1/m_1) \ln \Phi_1 + (\Phi_2/m_2) \ln \Phi_2 + g\, \Phi_1 \Phi_2 \tag{1}$$

where $N =$ the total number of moles of lattice sites, $N = n_1m_1 + n_2m_2$, $n_i =$ number of moles of component i, $\Phi_i = n_im_i/N$, $m_i = V_i/V_L = v_iM_i/V_L =$ = number of sites occupied by chain molecule i, $g =$ interaction parameter, RT has its usual meaning, V_i, v_i, M_i are molar and specific volume and molar mass of component i, V_L stands for the molar volume of the lattice sites. If we are dealing with a polymer solution, V_L can be set equal to the molar volume of the solvent, in polymer mixtures the choice of V_L is arbitrary or can be avoided to some extent as shown below.

Within the framework of this model Φ_i is the volume fraction of component i. If we set $m_1 = 1$, eq. (1) represents solutions of a polymer (2) in a small-molecule solvent (1). If $m_1 > 1$ polymer mixtures or blends are represented. It is worth noting in passing that eq. (1) can be expressed in terms of $m = m_2/m_1$ and thus is the same for polymer solutions and mixtures but for a scaling of the interaction function g and ΔG by m_1 $(g' = gm_1)$:

$$m_1 \Delta G/NRT = \Phi_1 \ln \Phi_1 + (\Phi_2/m) \ln \Phi_2 + g' \Phi_1 \Phi_2 \tag{2}$$

Since absolute values of ΔG are inconsequential for phase relations we may regard eq. (2) as a general expression for polymeric systems which has two parameters, the ratio of molar volumes m, and the interaction function g'.

It is well known that a partially miscible system is characterized by a $\Delta G(\Phi_2)$ function with a plait, i. e. it contains positively and negatively curved parts[7]. The curve must also change its shape upon a variation of temperature T or pressure p in such a way that the plait disappears. In other words, the system becomes more (or less) miscible when T is changed. Figure 1 shows the relationship between $\Delta G(\Phi_2)$ and the phase diagram. The equilibrium between two phases at constant p and T implies that a double tangent can be drawn to $\Delta G(\Phi_2)$, the tangent points indicating the coexisting phase compositions.

The equilibrium condition of equality of chemical potentials is seen in the intercepts of the double tangent at $\Phi_2 = 0$ and $\Phi_2 = 1$, representing $\Delta \mu_1/RT$ and $\Delta \mu_2/RT$, respectively (μ = chemical potential). From eq. (2) we derive[1–7]

$$\Delta \mu_1/RT = \ln \Phi_1 + (1 - 1/m)\, \Phi_2 + \Phi_2^2\, (g' + \Phi_1\, \partial g'/\partial \Phi_1) \tag{3}$$

$$m^{-1}\, \Delta \mu_2/RT = m^{-1} \ln \Phi_2 + (1/m - 1)\, \Phi_1 + \Phi_1^2\, (g' + \Phi_2\, \partial g'/\partial \Phi_2) \tag{4}$$

Further, we see that the two points of inflexion in $\Delta G\,(\Phi_2)$ are determined by the spinodal condition[8,9]:

$$[\partial^2\, (\Delta G/NRT)/\partial \Phi_2^2]_{p,T} = 0 \tag{5}$$

or, with eq. (2),

$$1/\Phi_1 + 1/m\, \Phi_2 + \partial^2\, (g'\, \Phi_1\, \Phi_2)/\partial \Phi_2^2 = 0 \tag{5a}$$

The critical or consolute state is reached when, by a change in T or p, points of inflexion and tangent points have come to coincide. The critical state is characterized by[8,9]

$$[\partial^3\, (\Delta G/NRT)/\partial \Phi_2^3]_{p,T} = 0 \tag{6}$$

or

$$1/\Phi_1^2 - 1/m\, \Phi_2^2 + \partial^3\, (g'\, \Phi_1\, \Phi_2)/\partial \Phi_2^3 = 0 \tag{6a}$$

In eqs. (3)—(6a) we have assumed the interaction function g' to depend on the composition Φ_2 of the mixture. This already represents the third level of description and prediction, to be discussed below. The Flory-Huggins-Staverman (FHS) equation with g' independent of concentration is representative for the second level and we investigate its implications first.

In the usual notation[5,6,10] the symbol χ is used for the term $(g' + \Phi_1 \partial g'/\partial \Phi_1)$ in eq. (3). If g' does not depend on Φ_2 we see in eqs. (3) and (4) that the coefficients of the last terms are identical and equal to χ. If g' depends on Φ_2, the two coefficients are not identical and confusion may arise when the symbol χ is used for both[11]. Thus, in this paper we indicate concentration independence when we use χ. In the FHS case we have

$$\Delta \mu_1/RT = \ln \Phi_1 + (1 - 1/m)\, \Phi_2 + \chi\, \Phi_2^2 \tag{7}$$

$$m^{-1}\, \Delta \mu_2/RT = m^{-1} \ln \Phi_2 + (1/m - 1)\, \Phi_1 + \chi\, \Phi_1^2 \tag{8}$$

Spinodal:

$$1/\Phi_1 + 1/m\, \Phi_2 - 2\, \chi = 0 \tag{9}$$

Critical Point:

$$1/\Phi_1^2 - 1/m\, \Phi_2^2 = 0, \quad \text{or} \quad \Phi_{2C} = 1/(1 + m^{1/2}) \tag{10}$$

Since a spinodal passes through the critical point we can derive the critical value of χ by introducing eq. (10) into eq. (9). The result is

$$\chi_C = (1 + m^{-1/2})^2/2 \tag{11}$$

Binodals are loci of compositions of coexisting phases in the $T\,(\Phi_2)$ phase diagram. They can be calculated with eqs. (7) and (8) and the conditions for equilibrium between phases (1) and (2):

In order to calculate phase diagrams with eqs. (7)—(12) we must specify the temperature dependence of χ. Experiment often points to a simple linear dependence on T^{-1} being adequate[12]

$$\chi = \chi_s + \chi_h/T \tag{13}$$

where χ_s and χ_h are the entropic and enthalpic contributions to χ. To calculate examples we can choose arbitrary, albeit physically reasonable values, we set $\chi_s = 0$ and $\chi_h = 200\ K$. Figure 2 shows some examples so calculated and illustrates the effect a disparity in molecular size has on location and shape of the miscibility gap. Whether we have a polymer solution or a polymer mixture, the shape of the gap is determined only by m. However, the separation temperature differs and is determined by m_1. We note that, at constant m_2, miscibility decreases with increasing m_1. The division in the first two combinatorial (entropic) terms in eq. (1) by large numbers m_1 and m_2, representative for polymers, makes the system less stable than a comparable small-molecule mixture with $m_1 = 1$ and $m_2 = 1$. The asymmetry of the miscibility gap and its tendency to shift towards the axis of the smaller component was already understood by Van der Waals[9].

The interaction parameter g (or χ) is the key for predicting whether a system will be partially miscible. In the next section we shall discuss the Shultz-Flory method which provides a practical way of determining χ· Once its T dependence is known, we can calculate concentration and molar mass ranges of limited miscibility in binary systems with the FHS equation. We should remember that the Shultz-Flory method calls for some experimental effort, and also that it only deals with simple systems, binary homopolymer solutions. In industrial practice, the systems of interest are usually more complex and they vary frequently so that the collection of experimental data cannot normally be considered.

In such cases there is at present virtually no alternative to the theory of the solubility parameter[13] or the recent group contribution approach[13a]. The former can be seen as a method to calculate χ_h from literature data, like the heat of vaporization of the pure components. One has

$$\chi = \chi_s + V_L\,(\delta_1 - \delta_2)^2/RT \tag{14}$$

where

$$\delta_i = (\Delta\, E_i/V_i)^{1/2} \tag{15}$$

and $\Delta\, E_i$ = the energy of vaporisation of component i to a gas at zero pressure, V_i = its molar volume. The theory postulates that only a small difference between the solubility parameters δ_1 and δ_2 can be permitted for a binary mixture to remain miscible. In the application of the method χ_s is usually set equal to zero or to some arbitrary value.

APPLICATION OF FHS EQUATION

Literature mentions demixing experiments of solutions ($m_1 = 1$) of anionically prepared polymers, characterized by an extremely narrow chain length distribution. Such solutions can, to a good approximation, be considered as binary mixtures that should obey the equations discussed so far.

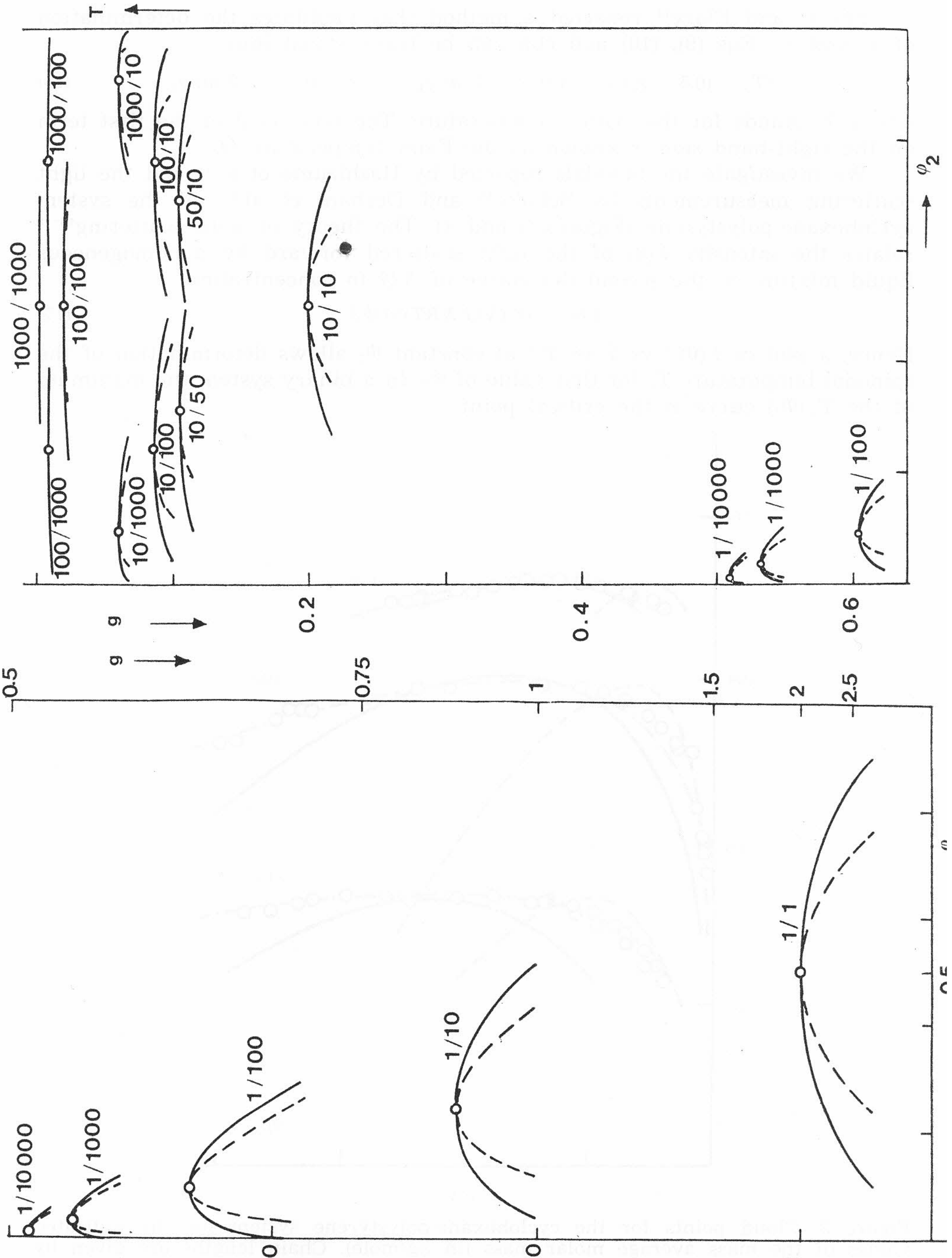


Figure 2. Miscibility gaps calculated by eqs. (7)—(12) for various indicated m_1/m_2 combinations. Binodals: ———, spinodals: — — —, critical points: o. $\chi(T)$ function as specified in text.

Shultz and Flory[14] reported a method that facilitates the determination of χ_s and χ_h. Eqs (9), (10) and (13) can be transformed into

$$1/T_c = (0.5 - \chi_s)/\chi_h + (m^{-1/2} + 2/m)/\chi_h = 1/\Theta + (m^{-1/2} + 2/m)/\chi_h \qquad (16)$$

where T_c stands for the critical temperature. The reciprocal of the first term on the right-hand side is known as the Flory temperature Θ.

We investigate the binodals reported by Hashizume et al.[15] and the light scattering measurements by Scholte[16] and Derham et al.[17] on the system cyclohexane/polystyrene (Figures 3 and 4). The theory of light scattering[16–19] relates the intensity $I(0)$ of the light scattered forward by a homogeneous liquid mixture to the second derivative of ΔG to concentration:

$$I(0) \propto \partial^2 (\Delta G/NRT)/\partial \Phi_2^2 \qquad (17)$$

Hence, a plot of $I(0)^{-1}$ vs T or T^{-1} at constant Φ_2 allows determination of the spinodal temperature T_s for that value of Φ_2. In a binary system the maximum of the $T_s(\Phi_2)$ curve is the critical point.

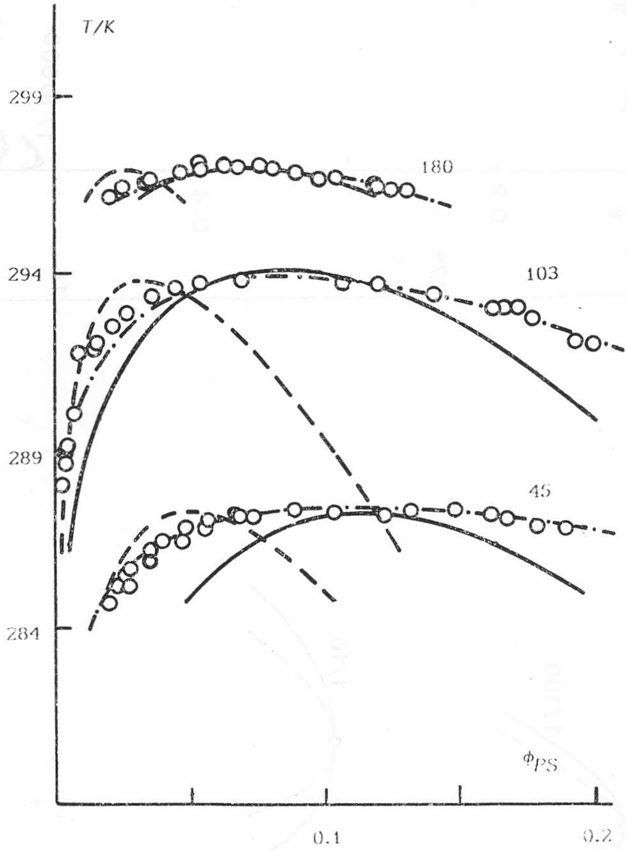


Figure 3. Cloud points for the cyclohexane/polystyrene system for the indicated values of the mass average molar mass (in kg/mole). Chain lengths are given by $M/100$. Curves calculated on the basis of the Shultz-Flory analysis (— — —), the third (———) and fourth level (—·—·—) approximations[20,21]. Data by Hashizume et al.[15].

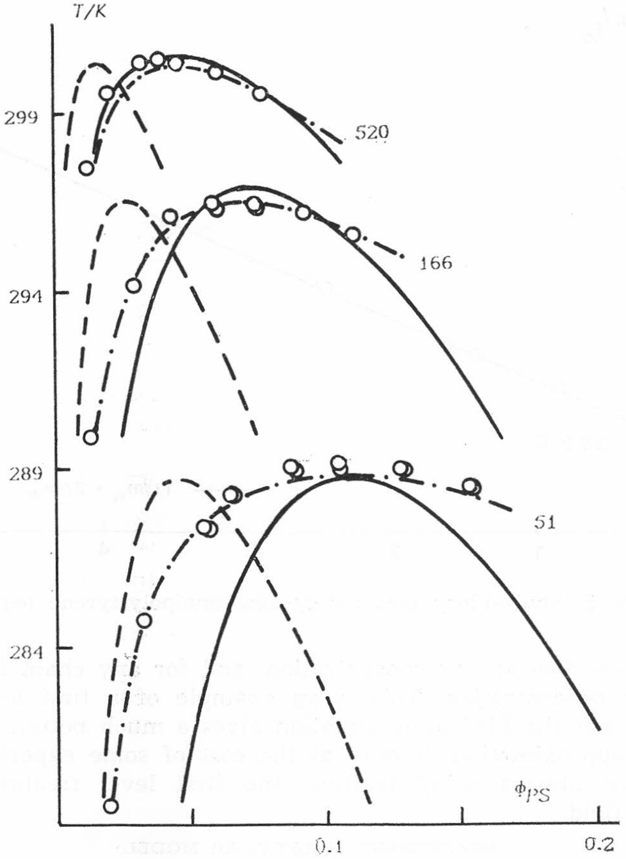
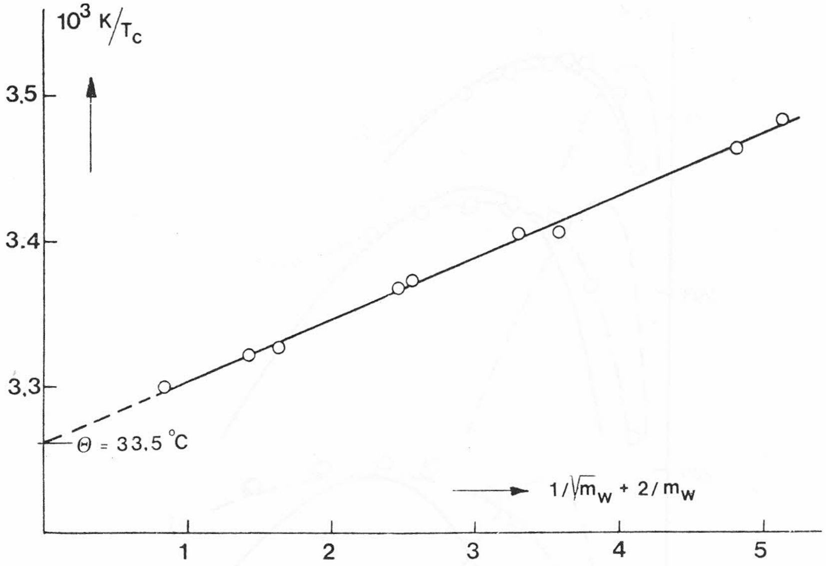


Figure 4. Spinodal points for the cyclohexane/polystyrene system for the indicated values of the mass average molar mass (in kg/mol). Curves calculated on the basis of the Shultz-Flory analysis (— — —), the third (————) and fourth level (—·—·—) approximations[20,21]. Data by Scholte[16] and Derham et al.[17]

Figure 5 shows the Shultz-Flory plot for cyclohexane/polystyrene which yields the values $\chi_s = -0.27$ and $\chi_h = 236$ K[20,21]. We are now able to calculate binodal and spinodal curves with eqs. (7), (8), (12) and (9) and compare them with the data (Figures 3 and 4). It is seen that the critical temperatures are obviously described well but the critical concentrations and coexisting phase compositions are not. Yet, a rough idea of the location and shape of miscibility gaps is obtained and we consider this result as an example of a second level prediction.

The predictive power of the solubility parameter theory is still inferior with the present system. Taking the δ values for cyclohexane and polystyrene from ref. [22] (8.2 and 9.1 $(\text{cal/cm}^3)^{1/2}$ at 25 °C) we note these values hardly to differ significantly and the system must therefore be expected to be miscible. In Figure 3 and 4 we see that the prediction is valid only for chain lengths



Figuée 5. Shulz-Flory plot for cyclohexane/polystyrene (eq. 16)).

smaller than ca 2000 at any concentration, and for any chain length only at high polymer concentration. This is an example of a first level prediction and we note that the FHS approximation gives a much better, more detailed second level approximation, if only at the cost of some experimental effort. The latter not always being feasible, the first level treatment keeps its place in the field.

REFINEMENT MOLECULAR MODEL

Staverman has already in 1937 pointed out that an essential improvement in the description of heats of mixing small molecule compounds can be obtained if the ever present disparity in size and shape between the molecules is taken into account[37]. As a consequence, the numbers of nearest-neighbour contacts will differ. These numbers determine the internal energy of a mixture and, hence, the heat of mixing. Staverman suggested to set the number of the nearest neighbours of a molecule proportional to its surface area, as a first approximation.

Aplication to polymer solutions and mixtures is straightforward and yields a concentration dependent interaction parameter g[20,21]:

$$g = g_0 + g_1/(1 - \gamma\, \Phi_2) \tag{18}$$

where $\gamma = 1 - \sigma_2/\sigma_1$, σ_i = surface area molecule or repeat unit i and g_1 may depend on T, for instance

$$g_1 = g_{10} + g_{11}/T \tag{19}$$

Spinodal and critical conditions are now given by

$$1/m_1\, \Phi_1 + 1/m_2\, \Phi_2 - 2\, g_0 - 2\, g_1\, (1 - \gamma)/(1 - \gamma\, \Phi_2)^3 = 0 \tag{20}$$

and

$$1/m_1 \Phi_1^2 - 1/m_2 \Phi_2^2 - 6\, g_1 \gamma\, (1-\gamma)/(1-\gamma\, \Phi_2)^4 = 0 \tag{21}$$

Elimination of g_1 from eqs. (20) and (21) yields[24]

$$J_s + J_c \Phi_2 = g_0 + J_c/\gamma \tag{22}$$

where $J_s = (1/m_1 \Phi_1 + 1/m_2 \Phi_2)/2$ and $J_c = (1/m_1 \Phi_1^2 - 1/m_2 \Phi_2^2)/6$. Eq. (22) represents a linear function between the left-hand side and J_c that allows determination of g_0 and γ from a series of experimental critical points. Eq. (20) then serves to calculate g_{10} and g_{11}. Application to the data on cyclohexane/polystyrene mentioned above leads to predicted binodals and spinodals that fit much better into the experimental concentration regions than the second level FHS equation did. This is not surprising since in this third level approach both critical temperatures and concentrations have been used in the determination of the parameters[20,21].

Still, the calculated binodals and spinodals cover a narrower concentration range than the experimental points. This shortcoming can be remedied with a further refinement of the model. Before proceeding, we draw attention to an interesting aspect of this third level treatment. The value found for γ (0.22) implies that σ_2/σ_1, the ratio of molecular surface areas, equals 0.78. The latter number is quite close to the value estimated with Bondi's essentially different procedure (0.87)[25].

The parameters g_0 and g_{10} cannot be dispensed with and have been thrown in to make the equations fit the data. Their molecular origin can be guessed if we follow a reasoning suggested long ago by Staverman[26]. This author pointed out that it does not suffice to consider only the internal energy of mixing on the basis of numbers of the nearest neighbours. The combinatorial entropy should also be calculated for numbers of contacts rather than numbers of molecules, as is the usual practice.

When we introduced the surface-area ratio σ_2/σ_1 we allowed the various species to differ in coordination number z_{ij}. The latter stands for the number of nearest neighbours j to molecule or segment i. If the two component molecules or repeat units differ in size but not much in shape we might assume $z_{11} \simeq z_{22}$. For a lattice on which all z_{ij} are identical the total number of arrangements is well known,[1-6,10] we denote this number by Ω_0. If $z_{11} \simeq z_{22} \neq \neq z_{12} \neq z_{21}$ we need to correct Ω_0 for over- and underestimations referring to z_{12} and z_{21}. Following a procedure suggested by Huggins[27] and Silberberg[28], we approximate the actual number of arrangements by

$$\Omega = \Omega_0\, (z_{12}/\bar{z})^{P_{12}}\, (z_{21}/\bar{z})^{P_{21}} \tag{23}$$

where $P_{12} \equiv P_{21}$ is the number of contact pairs between unlike species, and $\bar{z}$ is an average coordination number of contact pairs between unlike species, depending on the composition of the mixture, i. e.

$$\bar{z} \propto \sigma_1 \Phi_1 + \sigma_2 \Phi_2 \tag{24}$$

Using the regular solution approximation[29] for P_{12} one obtaines

$$g_0 = 2\, z_{22}\, (\ln Q)/Q;\ g_{10} = -z_{22} \ln\, (z_{12}\, z_{21}/z_{11}^2) \tag{25}$$

where $Q = 1 - \gamma\, \Phi_2$.

It is seen that eq. (25) thus supplies an after the fact explanation for the empirical parameters g_0 and g_{10}, though in a qualitative sense. It should be noted that Staverman has recently developed a rigorous treatment of contact statistics[30].

Fourth Level Predictions

In order to obtain a quantitative agreement between the calculated and measured binodals and spinodals we have to further improve the model. Two aspects that can be included in the rigid lattice model have not yet been considered, viz. the polymer coils being isolated at high dilution and the chains bending back on themselves.

The first aspect has been dealt with by Stockmayer et al.[31,32]. In polymer solutions there are (at least) two concentration regimes. At moderate and high concentration the system can be looked upon as a highly interwined assembly of chains and the segment distribution is essentially uniform. Owing to the connectivity of the segments within the chains they can no longer distribute evenly in the total volume when the polymer concentration drops below a given value determined by the chain length. Then we have isolated coils separated by regions of pure solvent.[10,33]

Stockmayer et al. have suggested to write the interaction function g as the sum of two terms, one for each concentration range:

$$g = g^* (T, m_2)\, P + g^c \tag{26}$$

where g^c, representing the concentrated regime, may be expressed by eq. (18). The term $g^* (T, m_2)$ expresses the differences relevant to the dilute regime as compared with the uniform segment density region. This term is attenuated by a probability factor P, the probability that a given volume element in the solution does not fall within any of the polymer coils. We can write

$$P = \exp\,(-\lambda_0\, m_2^{1/2}\, \Phi_2) \tag{27}$$

where λ_0 can be expressed in molecular parameters, obtainable from independent measurements[31,32].

This merely theoretical treatment of g^* later appeared not to lead to quantitative agreement with experiment[20,21,34,35] but the form of eqs. (26) and (27) appears to be correct or, at least, useful. A detailed analysis has revealed that the following empirical expression yields a satisfactory framework to accommodate the binodal and spinodal data at a low polymer concentration[20,21].

$$g^* = \{\beta_1 + \beta_2 (T - \Theta)\}\, (T - \Theta)\, (1 - 1/m_2)/m_2 \tag{28}$$

The analysis mentioned above also led to the conclusion that the parameter g_0 in g^c (eqs (18) and (26)) must depend on temperature and molar mass, the data leave no doubt about that. A suitable expression, again empirical, to deal with such effects reads

$$g_0 = \alpha_1 + \alpha_2/m_2 + (\alpha_3 + \alpha_4/m_2)\, (T - \Theta) \tag{29}$$

If eqs (26)—(29) are used in a simultaneous fit of binodal, critical point, spinodal and other light scattering data we obtain the descriptions shown in Figure 3 and 4. Now the binodal and spinodal points are covered in a satisfactory manner. It is seen that this, the fourth level of description, can at present only be achieved at the cost of a large number of empirical parameters. Recently, the same conclusion was reached by Einaga et al.[35]. It should be mentioned, however, that the trend expressed in eq. (29) was predicted by Staverman's calculation of the effect backbending of the chain on itself has on the combinatorial entropy of mixing, in particular in poor solvents[20,21,30,36]. It is only the same trend, though, there is an order of magnitude difference between Staverman's calculation and the effect derived from the experimental data[20,21]. We believe that the cause of the discrepancy must at least partly be sought in effects outside the scope of the rigid lattice model employed so far. It is a matter of the current study to investigate whether free volume might be held responsible.

Although the molecular origin of the many parameters can thus be indicated roughly, their number is still excessive and the procedure resembles curve fitting of a primitive kind. Yet it deserves the qualification fourth level because of its power of quantitative prediction. Examples are shown in Figures 6 and 7. Figure 6 shows osmotic pressures calculated on the basis of eqs (26)—(29) and their agreement with Krigbaum's experimental results[37]. In Figure 7 we show a ternary binodal measured by Hashizume et al.[15], and the curves calculated with the present fourth level approximation. The relevant ΔG expression is obtained from eq. (1) upon replacement of the second term on the righ-hand side by[38,39]

$$(\Phi_{21}/m_{21}) \ln \Phi_{21} + (\Phi_{22}/m_{22}) \ln \Phi_{22}$$

while $\Phi_2 = \Phi_{21} + \Phi_{22}$. We note a good agreement between experiment and prediction. The same result was obtained by Einaga et al.[35] which indicates that polymolecularity might not present an unsurmountable problem, once the binary systems have been adequately described.

CHAIN LENGTH DISTRIBUTION

Virtually all synthetic polymers possess molar mass distributions, wide or narrow. In the preceding section we have already indicated that the theory can deal with polymolecularity simply by writing as many combinatorial terms in ΔG as there are components in the polymeric constituents[38,39]:

$$\Delta G/NRT = \Sigma (\Phi_{1i}/m_{1i}) \ln \Phi_{1i} + \Sigma (\Phi_{2j}/m_{2j}) \ln \Phi_{2j} + g \Phi_1 \Phi_2 \tag{30}$$

where

$$\Phi_1 = \Sigma \Phi_{1i}, \; \Phi_2 = \Sigma \Phi_{2j} \text{ and } N = \Sigma n_{1i} m_{1i} + \Sigma n_{2j} m_{2j}.$$

The equilibrium conditions (12) now contain as many equalities as there are components in the system. Such sets of equations can be solved numerically[40,41]. Spinodal and critical conditions can be expressed in closed form[42-44]:

$$1/m_{1w} \Phi_1 + 1/m_{2w} \Phi_2 - 2 g_0 - 2 g_1 (1 - \gamma)/Q^3 = 0 \tag{31}$$

and

$$m_{1z}/m_{1w}^2 \Phi_2^2 - m_{2z}/m_{2w}^2 \Phi_2^2 - 6 g_1 \gamma (1 - \gamma)/Q^4 = 0 \tag{32}$$

where m_w and m_z are the mass- and z-average relative chain lengths.

We note that discussions of spinodals and critical points are similar to those for binary systems provided the single chain lengths m are replaced by m_w in the spinodal and by m_w^2/m_z in the critical condition. The shape of the, now quasi-binary, twodimensional phase diagram may become quite complex we refer to the literature for detailed analyses[11,20,21,40,41,43-46]. Distribution effects are not negligible as is often assumed, in particular, they cause the extreme (precipitation threshold[47]) of a cloudpoint curve (binodal in a binary system) generally not to be identifiable with a critical point[11,42-48]. Figure 8 gives two examples showing the magnitude of the effect the distribution may

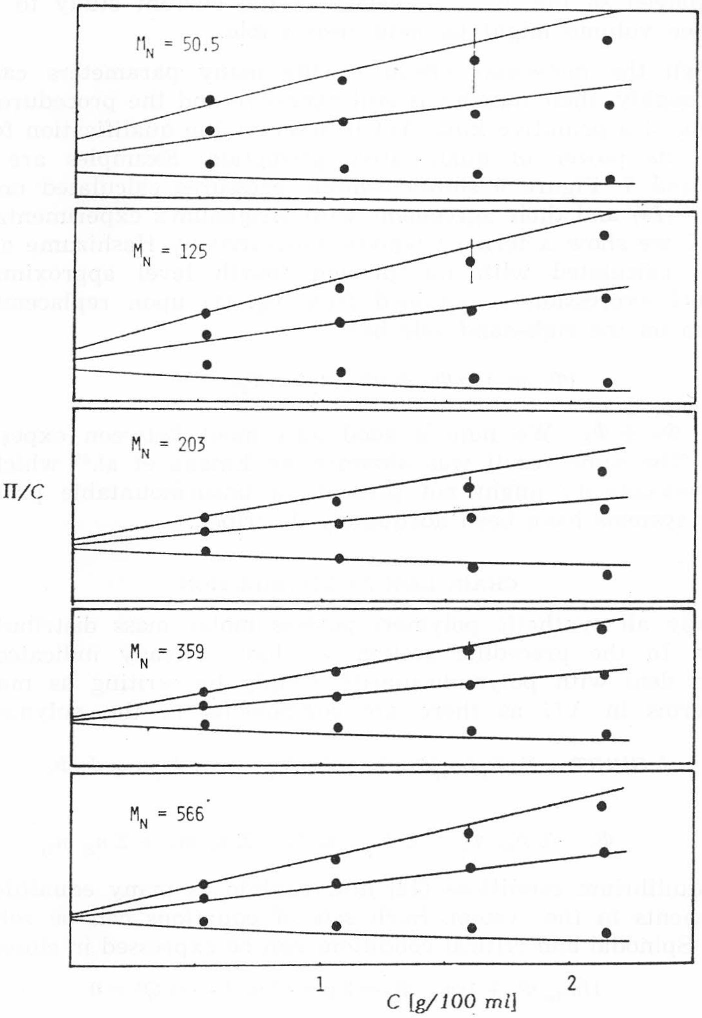


Figure 6. Reduced osmotic pressures (Π/C) for the cyclohexane/polystyrene system for the indicated values of the number average molar mass (in kg/mol) as a function of concentration C and temperature (top, middle and bottom curves for 50, 40 and 30 °C, resp.). Data by Krigbaum[37], fourth level prediction represented by curves[20,21].

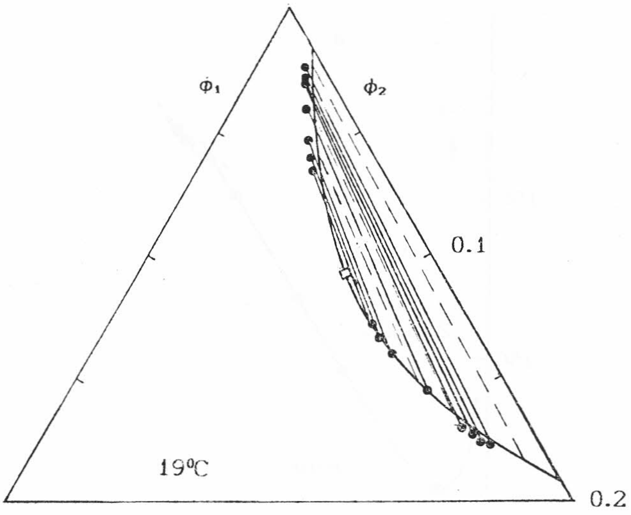


Figure 7. Ternary phase relations in the cyclohexane/polystyrene system. Molar masses of polymer constituents: 45 and 103 kg/mol. Data by Hashizume et al.[15]: (●———●). Curve represents fourth level prediction of binodal (———), tie lines (— — —) and critical point (□)[20,21].

have on the difference between critical and threshold temperatures and concentrations. Identification of threshold and critical concentrations and temperatures in quasi-binary systems is allowed in the first level of approximation only.

PRESSURE

The influence of pressure (expansion or contraction upon mixing) cannot be dealt with in rigid lattice considerations unless the g function is adapted in a semi-empirical way.[51] There are important polymerisation processes that are carried out at elevated and high pressures, such as the bulk polymerisation of ethylene at pressures of around two kilobars. The influence pressure has on thermodynamic properties reveals itself also under ambient conditions in the excess volume $\Delta V^{E}\,(=(\partial \Delta G/\partial p)_{T})$. With a rigid lattice, one has $\Delta V^{E} = 0$ and here is an obvious shortcoming of the fourth level approach discussed above.

The mean-field lattice-gas (MFLG) model provides a simple remedy for any level of approximation and permits dealing with the influence of pressure[51–55]. We represent a single component by a mixture of occupied (1) and vacant (2) sites on the lattice and write for ΔA, the Helmholtz free energy

$$\Delta A/NRT = \Psi_0 \ln \Psi_0 + (\Psi_1/m_1) \ln \Psi_1 + g\,\Psi_0 \Psi_1 \tag{33}$$

where $\psi_0\,(=1-\psi_1)$ and ψ_1 represent the site fractions of vacant and occupied sites, related to density ρ_1 and molar mass M_1 of the substance described, and to the molar volume v_0 of the lattice unit:

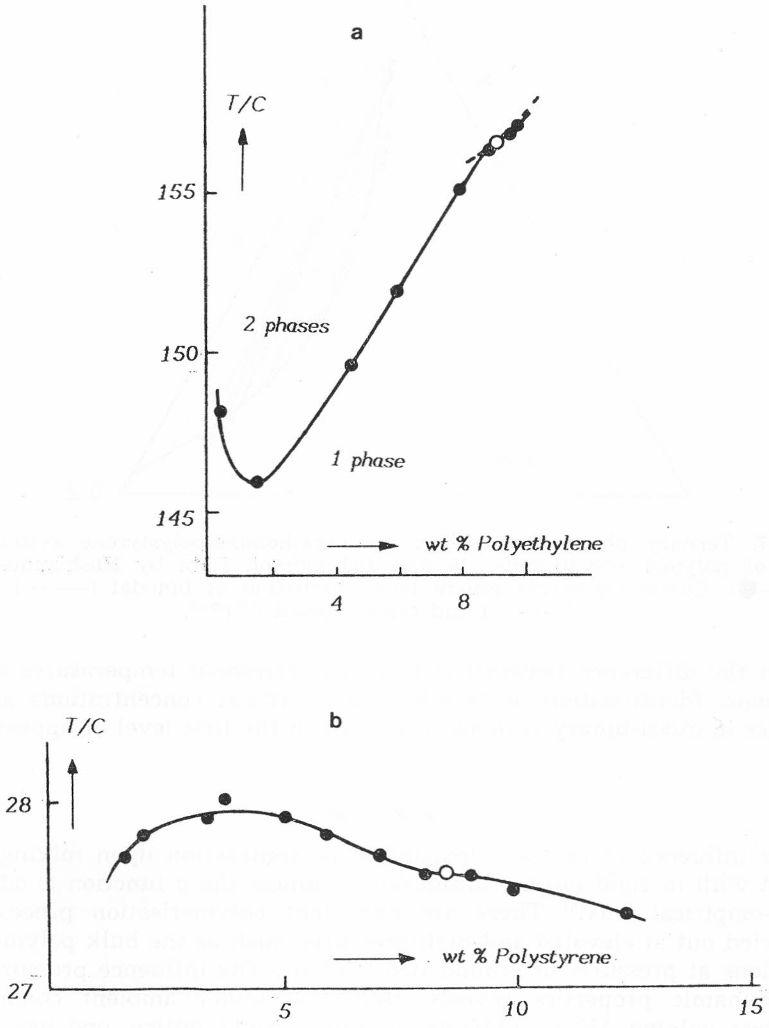


Figure 8. Cloudpoint curves in quasi-binary systems (cloud point temperature vs mass fraction of polymer). Critical point: o.

a) Polyethylene ($M_w/M_n = 27$; $M_z/M_w = 7$), solvent: n-hexane. Dashed curve indicates the location of the spinodal.

b) Polystyrene ($M_w/M_n = 1.07$; $M_z/M_w = 1.4$), solvent: cyclohexane.

where $m_1 =$ the number of lattice sites occupied by one molecule 1. With small molecules one usually finds that introduction of a value slightly deviating from unity improves the description. If eq. (33) is used to describe a polymer, m_1 is a measure of its molar mass, similar to the examples in the preceding sections.

The interaction function in the MFLG model has the same form as eq. (18):

$$g = g_0 + g_1/(1 - \gamma \Psi_1) \tag{35}$$

with $\gamma = 1 - \sigma_1/\sigma_0$. The expressions for spinodal and critical point in this pseudo-binary representation of a single component have the same form as those for a binary third level FHS mixture (eqs (20) and (21)):

$$1/\Psi_0 + 1/m_1 \Psi_1 - 2\, g_0 - 2\, g_1 (1-\gamma)/Q^3 = 0 \tag{36}$$

$$1/\Psi_0^2 - 1/m_1 \Psi_1^2 - 6\, g_1 \gamma (1-\gamma)/Q^4 = 0 \tag{37}$$

where

$$Q = 1 - \gamma \Psi_1.$$

The equation of state, derived with $p = -(\partial \Delta A/\partial \gamma)_{T, n1}$, reads

$$-pv_0/RT = \ln \Psi_0 + (1 - 1/m_1)\Psi_1 + \Psi_1^2 \{g_0 + g_1 (1-\gamma)/Q^2\} \tag{38}$$

and the total volume V is given by

$$V = Nv_0 = (n_0 + n_1 m_1)\, v_0 \tag{39}$$

where n_0 and n_1 are the amounts of vacant and occupied sites in moles.

This procedure has been shown to supply adequate descriptions and predictions of the influence of pressure on thermodynamic properties of pure compounds, with small as well as large molecules, polar and nonpolar[52-56].

Where a single component system is treated as a binary mixture of vacant and occupied sites, a system containing tho types of molecules will call for a ternary representation. The pseudo-ternary site fractions are related to the binary volume fractions by

$$\Phi_1 = \Psi_1/(1-\Psi_0);\ \Phi_2 = \Psi_2/(1-\Psi_0) \tag{40}$$

We refer to the literature[52-56] for details on equations and procedure for binary systems and only present below some results obtained with the model.

n-ALKANE/POLYETHYLENE

In the ΔA expression relevant to *n*-alkane/polyethylene we have an interaction term for the repeat units within the alkane and within the polyethylene. We assume the similarity between these repeat units to allow setting the interaction terms equal to each other. As a consequence, the interchange energy between the units in alkane and polyethylene can be set equal to zero, which implies that phase diagrams for binary *n*-alkane/polyethylene systems should be predictable with the parameters for the single constituents[52,54].

Various authors have published cloudpoint curves for this system using different *n*-alkanes[57-59]. Such systems exhibit the so called lower critical demixing, they separate into two phases upon an increase of T. The authors performed the experiments in closed tubes and the pressure varied along the cloudpoint curve since it was that of the vapour in equilibrium with the liquid mixture.

We neglect this small change of pressure and calculate spinodals, making use of the fact that spinodal and cloudpoint curves have a common tangent at the critical point (see e. g. ref. 11). Since the mass-average molar masses have been specified by various authors, we can calculate spinodals with the MFLG model and compare their location with the experimental cloudpoints. It is seen in Figure 9 that the predictions agree rather well with the observed two-phase regions.

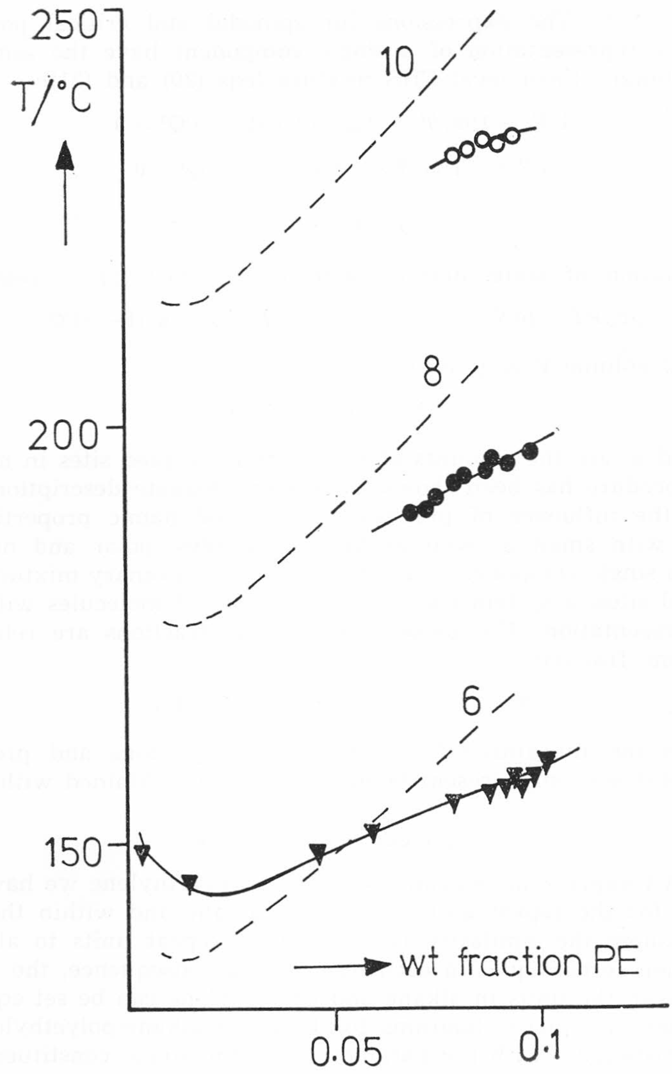


Figure 9. Comparison of experimental cloudpoint curves for linear polyethylene ($M_w = 177$ kg/mol) in *n*-hexane (▽), *n*-heptane (●) and *n*-octane (○), with spinodals (———) predicted with the mean-field lattice-gas model for constant pressure (in bars).

As a further test of the MFLG model we compare the dependence of cloudpoint curves in *n*-heptane on mass average molar mass of the polyethylene. In Figure 10 we see that the calculated spinodals predict the location of the miscibility gap quite well and do not deviate more than a few degrees C. The pressure dependence of cloudpoints also appears to be predictable in the correct order of magnitude (Figure 11).

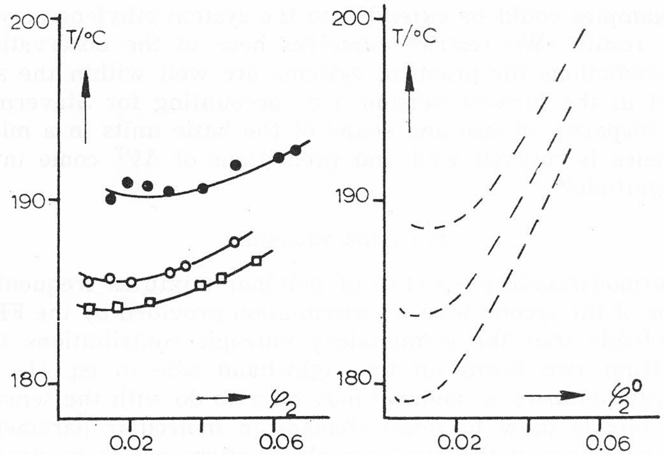


Figure 10. Comparison of experimental cloudpoint curves for linear polyethylene in *n*-heptane[59] for $M_w = 49$ (●), 83 (○) and 136 (□) kg/mol, with spinodals (———) predicted with the mean-field lattice-gas model.

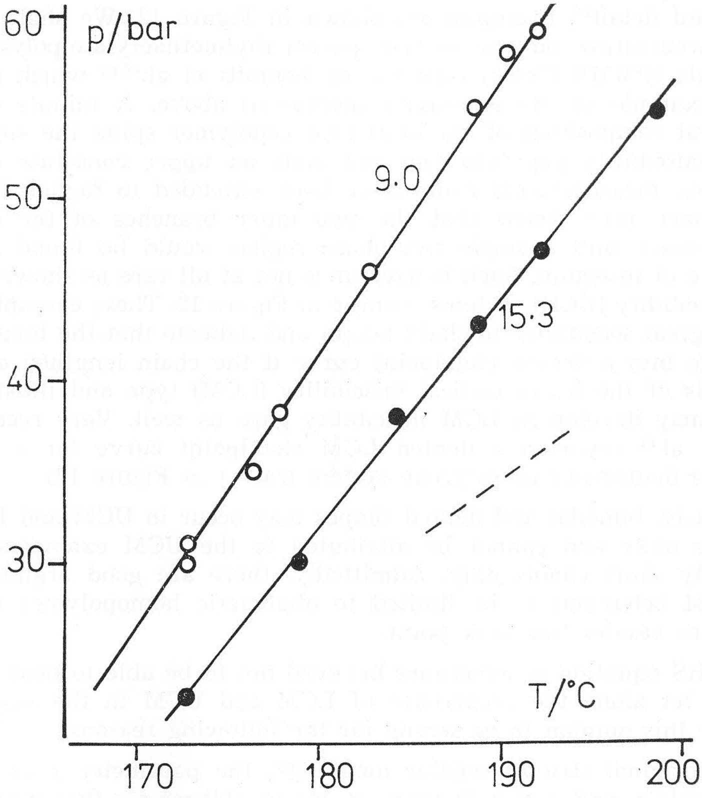


Figure 11. Pressure dependence of the cloud point of linear polyethylene in *n*-hexane for indicated polymer concentrations (in wt%). Pressure dependence predicted by the mean-field lattice-gas model in that concentration range: ———.

These examples could be extended to the system ethylene/polyethylene[52,60] with similar results. We restrict ourselves here to the observation that the third level predictions for practical systems are well within the scope of the MFLG model in the present version, i. e., accounting for Staverman's suggestions about disparity in size and shape of the basic units in a mixture. Pressure dependence is covered well and predictions of ΔV^E come into the right order of magnitude[56].

POLYMER MIXTURES

Bulk thermodynamic properties of polymer mixtures frequently fall outside the scope of the second level approximation provided by the FHS equation. It seems probable that the combinatory entropic contributions to ΔG being very small (first two terms on the right-hand side in eq. (1); division by relatively large numbers m_1 and m_2) may have to do with the sensitivity phase diagrams of blends show to small changes in molecular parameters. Improvements are necessary if the available observations are to be dealt with. Yet, the third level does not yet seem to be achievable with polymer mixtures in the present state of theoretical development.

Liquid-liquid phase diagrams in polymer mixtures show a wide variety in shape and detail[61], examples are shown in Figure 12. We shall develop a model, concentrating on the system polymethylmethacrylate/polystyrene-co--acrylonitrile (PMMA/PSAN) reported by Schmitt et al.[62,63] which is an illuminating example of the sensitivity mentioned above. A minute change in the chemical composition of the statistical copolymer splits the single lower consolute miscibility gap into two and adds an upper consolute cloudpoint curve. If the measurements could have been extended to higher T it would probably have been found that the two inner branches of the cloudpoint curves intersect, and a single two-phase region would be found above the temperature of insection. Such behaviour is not at all rare as shown by upper critical miscibility (UCH) systems *b* and *c* in Figure 12. These examples further point to a great sensitivity to chain length and indicate that the bimodal shape may change into a dented cloudpoint curve if the chain length(s) are varied. System *d* is of the lower critical miscibility (LCM) type and illustrates that shoulders may develop in LCM miscibility gaps as well. Very recently, Shibayama et al.[64] reported a dented LCM cloudpoint curve for a polyvinylmethylether/deutereous polystyrene system (case *f* in Figure 12).

Obviously, bimodal and dented shapes may occur in UCM and LCM polymer blends alike and cannot be attributed to the UCM examples referring to relatively short chains only. Admittedly, there are good arguments indicating UCM behaviour to be limited to oligomeric homopolymer mixtures[65], but they are besides this very point.

The FHS equation is sometimes believed not to be able to deal with LCM behaviour, let alone the occurrence of LCM and UCM in the same system. We believe this opinion to be wrong for the following reasons.

In its original strictly regular meaning[29], the parameter χ in eq. (13) is purely enthalpic, and $\chi_s = 0$. Defining χ_h by eq. (14) we see that it can only be positive. Consequently, only UCM can fall within this scope because it goes with $\partial\chi/\partial T < 0$. However, the strictly regular approximation defines χ_h as

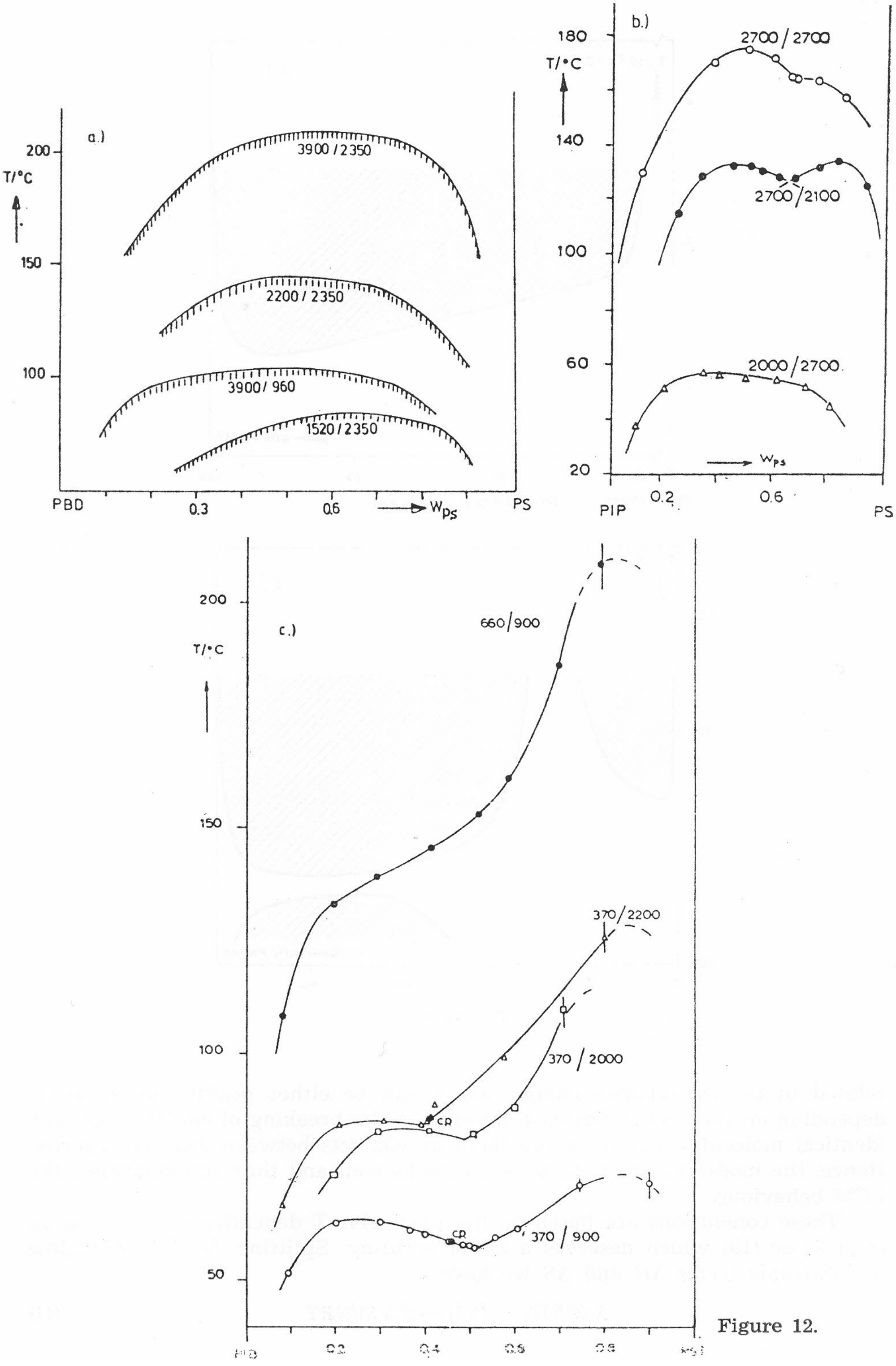
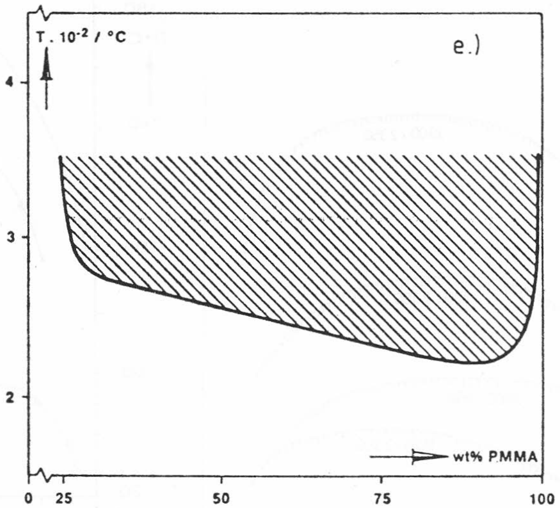

a.)
T/°C
200
150
100
3900 / 2350
2200 / 2350
3900 / 960
1520 / 2350
PBD
0.3
0.6
W_PS
PS
b.)
T/°C
180
140
100
60
20
2700 / 2700
2700 / 2100
2000 / 2700
W_PS
0.2
0.6
PIP
PS
c.)
T/°C
200
150
100
50
660 / 900
370 / 2200
370 / 2000
370 / 900
CR
CR
PB
0.2
0.4
0.6
0.8
PS

Figure 12.



PMMA/PSAN SAN: 72.4 % St.: 27.6 % AN

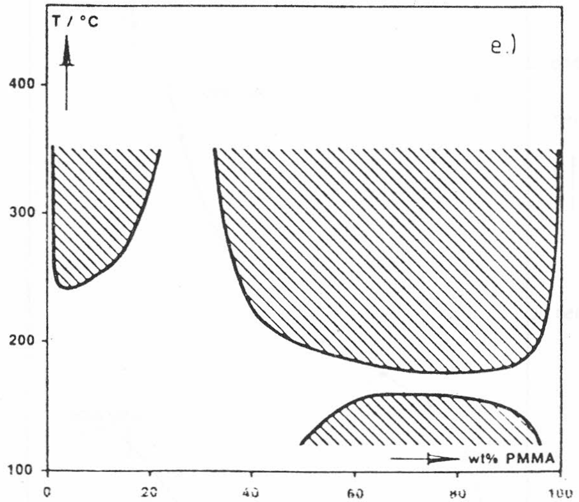


Figure 12.

related to the interchange energy which can be either positive or negative, depending on the energy changes involved in the breaking of contacts between identical molecules and replacing them by contacts between different species. Hence, the model allows χ_h to be negative as well and thus accommodates the LCM behaviour.

These conclusions are based on the particular T dependence expressed by eq. (13) or (19) which deserves a closer scrutiny. Splitting ΔG into enthalpic and entropic terms ΔH and ΔS we have

$$\Delta G/NRT = (\Delta H - T\Delta S)/NRT \tag{41}$$

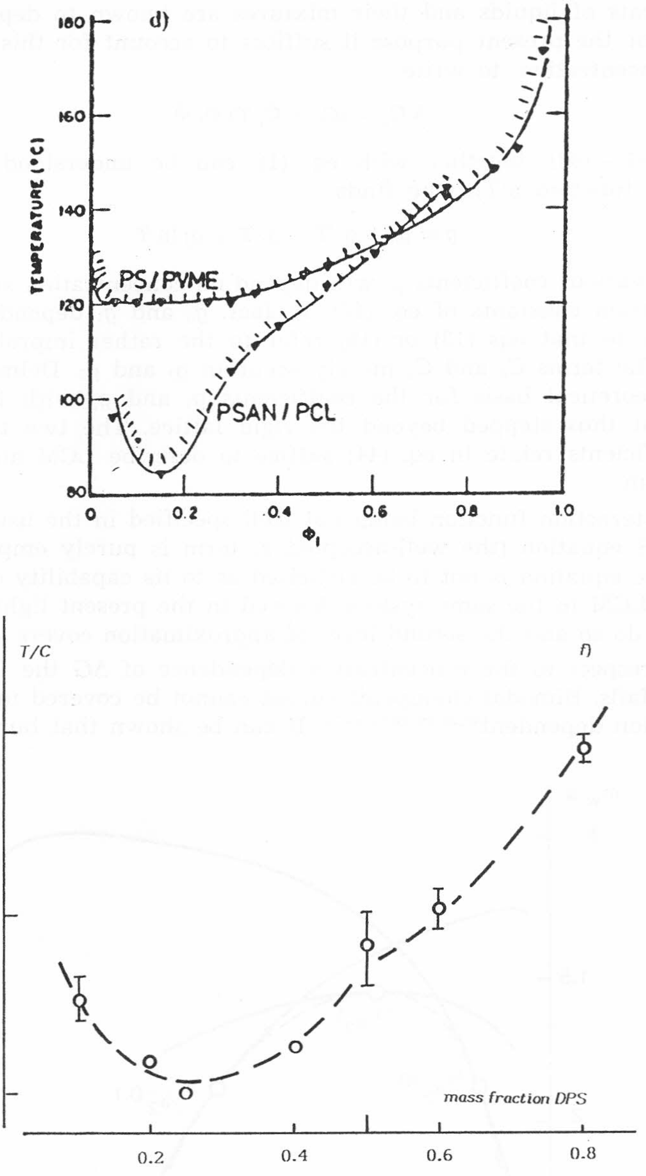


Figure 12. Various shapes of miscibility gaps in polymer mixture. a) Polybutadiene/polystyrene; b) Polyisoprene/polystyrene; c) Polyisobutylene/polystyrene; d) Polyvinylmethylether/polystyrene; e) Polymethylmethacrylate/polyacrylonitrile-co-styrene at 27.6% AN (top) and 28.7% AN (bottom); f) Polyvinylmethylether/deuterous polystyrene[64]. Mass average molar masses indicated, further particulars in ref. 61.

Also, ΔH and ΔS are related by means of ΔC_p, the specific heat 'of mixing' at constant p by

$$\Delta H = \int \Delta C_p \, dT; \; \Delta S = \int (\Delta C_p / T) \, dT \tag{42}$$

Specific heats of liquids and their mixtures are known to depend on temperature[66]. For the present purpose it suffices to account for this influence, and that of concentration, to write

$$\Delta C_p = (C_0 + C_1 T)\, \Phi_1 \Phi_2 \tag{43}$$

Eqs. (41)—(43), together with eq. (1), can be understood to define the interaction function $g(T)$. One finds

$$g = g_0 + g_1/T + g_2 T + g_3 \ln T \tag{44}$$

where the various coefficients g_i will depend on concentration and also contain the integration constants of eq. (42). In fact, g_0 and g_1 depend on these constants only so that eqs (13) or (19) refer to the rather improbable condition $\Delta C_p = 0$. The terms C_0 and C_1 merely occur in g_2 and g_3. Delmas et al.[67] supplied a theoretical basis for the coefficients g_1 and g_2 with Prigogine's cell model[68] but thus stepped beyond the rigid lattice. The two terms to which these coefficients relate in eq. (44) suffice to describe LCM and UCM in the same system.

The interaction function being not well specified in the usual applications of the FHS equation (the well-accepted χ_s term is purely empirical) we now see that the equation is not to be criticised as to its capability of dealing with UCM and LCM in the same system. Viewed in the present light it is perfectly capable to do so and the second level of approximation covers such behaviour.

With respect to the concentration dependence of ΔG the FHS expression definitely fails. Bimodal cloudpoint curves cannot be covered unless g is made concentration dependent[40,41,43–46,61,69,70]. It can be shown that bimodal or dented

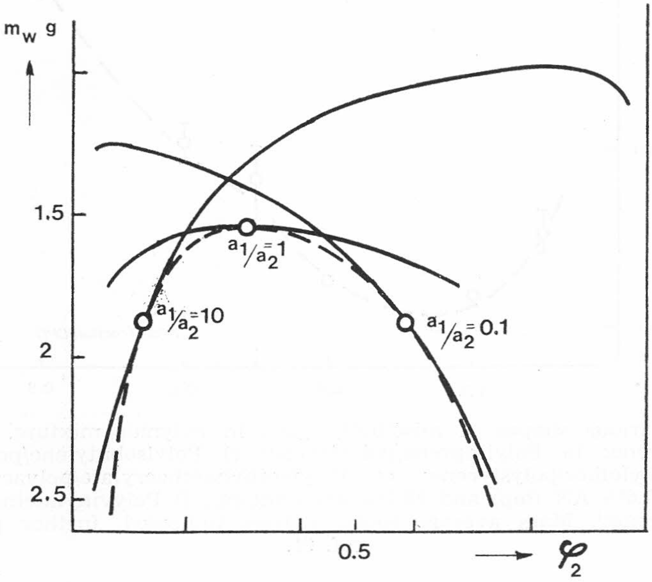


Figure 13. Cloudpoint curves (———), spinodal (– – –) and critical points (○) for polymer mixtures calculated by the multicomponent versions of eqs (7)—(12). The ratio m_z/m_w for polymer k is indicated by a_k; $m_{w2} = 5\, m_{w1}$.

cloudpoint curves in binary systems are accompanied by a bimodal spinodal curve[70], and the FHS framework does not have that possibility. This is seen in eq. (9) which is quadratic in Φ_2. Hence, at a given T (or χ), there can only be two spinodal values of Φ_2. Polymolecularity does not change that conclusion since the spinodal equation only replaces m_i for m_{iw}. Figure 13. illustrates this point and shows that miscibility gaps of the usual shape may be expected, whatever the width of the chain length distribution.

ENTROPY CORRECTIONS

From a molecular point of view a number of reasons can be advanced for g to depend on concentration. We have already seen that disparity in size and shape of the basis units in the system introduces a Φ_2 dependence expressed in eq. (18). However, with reasonable values for g_1 this equation does not produce bimodal spinodals[71]. For alternative reasons behind $g(\Phi_2)$ we rather explore the entropy of mixing and its combinatorial and non-combinatorial (free volume) aspects.

1) Contact Statistics

A rigorous way of dealing with the entropic aspects of different contact numbers was given recently by Staverman[30]. Here we use a more primitive approach and slightly refine the analysis leading to eq. (25). The latter did not distinguish the change in the nearest neighbour contact numbers of say species 1 when the composition of the mixture changes from pure 1 to pure 2. In a rough approximation the number of nearest neighbours might be expressed as

$$2\,P_{11} + P_{12} = n_1\, m_1\, (z_{11}\, \Phi_1 + z_{21}\, \Phi_2) \tag{45}$$

$$2\,P_{22} + P_{21} = n_2\, m_2\, (z_{22}\, \Phi_2 + z_{21}\, \Phi_1) \tag{46}$$

which equations express that, at $\Phi_i \rightarrow 1$, unit i has z_{ii} neighbours and z_{ij} at $\Phi_j \rightarrow 1$.

In the spirit of Staverman's suggestion (see eq. (18)) we might assume z_{ij} to be proportional to σ_i/σ_j. Proceeding in the usual manner (regular solution approach) and following the reasoning used in eq. (23), one obtains the following expression for the interaction function g[72]:

$$g = Q_1\, Q_2\, \{g_1 - z_{22}\, (\ln z - 2 \ln Q^*)\}/Q^* \tag{47}$$

where $z = z_{12}\, z_{21}/z_{11}^2$, $Q_1 = \phi_1 + s_{12}\, \phi_2$, $Q_2 = \phi_2 + s_{21}\, \phi_1$, $s_{ij} = z_{ij}/z_{ii}$, $Q^* = \phi_1\, Q_1 + z\, \phi_2\, Q_2$. For $s_{12} = s_{21} = 1$, Q^* reduces to Q.

Equations for chemical potentials, spinodal and critical point now become quite complex. Here we only give an example of the shape a spinodal curve may assume within the framework of this version of a contact statistical approach. Sets of parameters can be found that lead to the appearance of two spinodal curves, one of the UCM and the other of the LCM type (Figure 14). This is an interesting finding suggesting that the combinatory entropy might play a not negligible role in the occurrence of LCM and UCM in the same system. These aspects are subject of the current study[72].

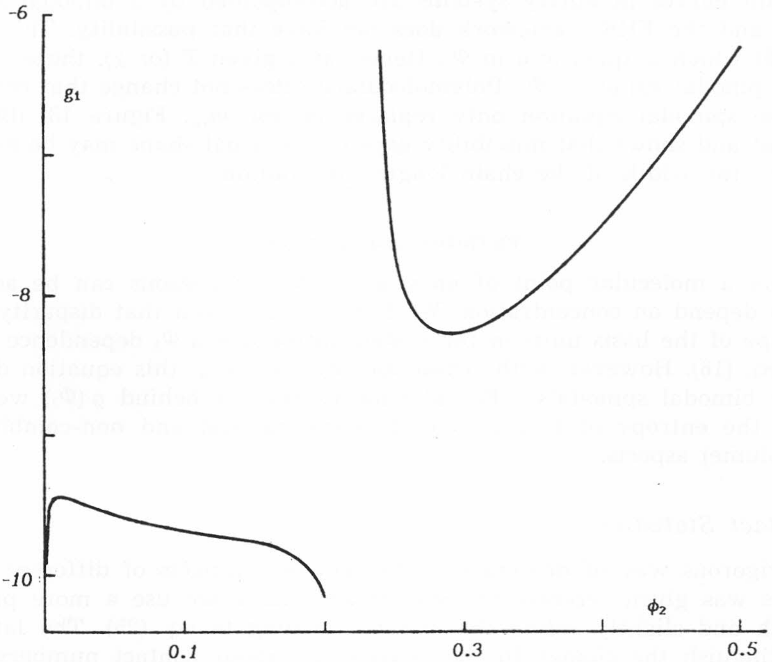


Figure 14. Spinodal calculated by eqs. (1) and (47) for $m_1 = 1500$, $m_2 = 3000$, $\sigma_1/\sigma_2 = 2$, $z_{22} = 6$, $z = 0.8$.

2) *Chain Flexibility*

Huggins has suggested amending the combinatory entropy of mixing by making allowance for the influence of the immediate surroundings of a repeat unit on its 'average randomness of orientation' with respect to the preceding unit in the chain.[73-75] We have shown elsewhere[71,76] that an application of this principle to polymer blends can produce bimodal spinodals, provided the interacting surface areas are included in the description. Examples *b* and *c* in Figure 12 may be seen as possibly representative since a change in randomness of orientation may be translated into the influence a stiffer chain (PS) has on the flexibility of the molecules in the rubbery constituent, and visa versa.

3) *Nonuniform Segment Density*

Another entropic reason might be provided by the situation mentioned in one of the preceding sections, the dilute solution effect. In polymer mixtures we might expect such an effect on both sides of the concentration axis. Extending Stockmayer et al.'s approach[31,32] for polymer solutions to mixtures we might write

$$g = g_1^{\mathrm{d}} P_1 + g_2^{\mathrm{d}} P_2 + g^{\mathrm{c}} (1 - P_1 - P_2) \tag{48}$$

where g_1^{d} and g_2^{d} refer to dilute solutions of polymers 1 and 2, dissolved in an excess 2 and 1, respectively, and g^{c} to the concentration range of uniform segment density. The damping factors P_i are defined in an analogous way as in eq. (27). It has been shown that eq. (48) produces bimodal spinodals for reasonable values of the parameters[69]. Hence, coil sizes and their dependence on temperature, molar mass and concentration may be expected to represent important parameters. Figure 15 demonstrates the various contributions to ΔG and shows that ΔG itself may be relatively small compared to the terms it consists of.

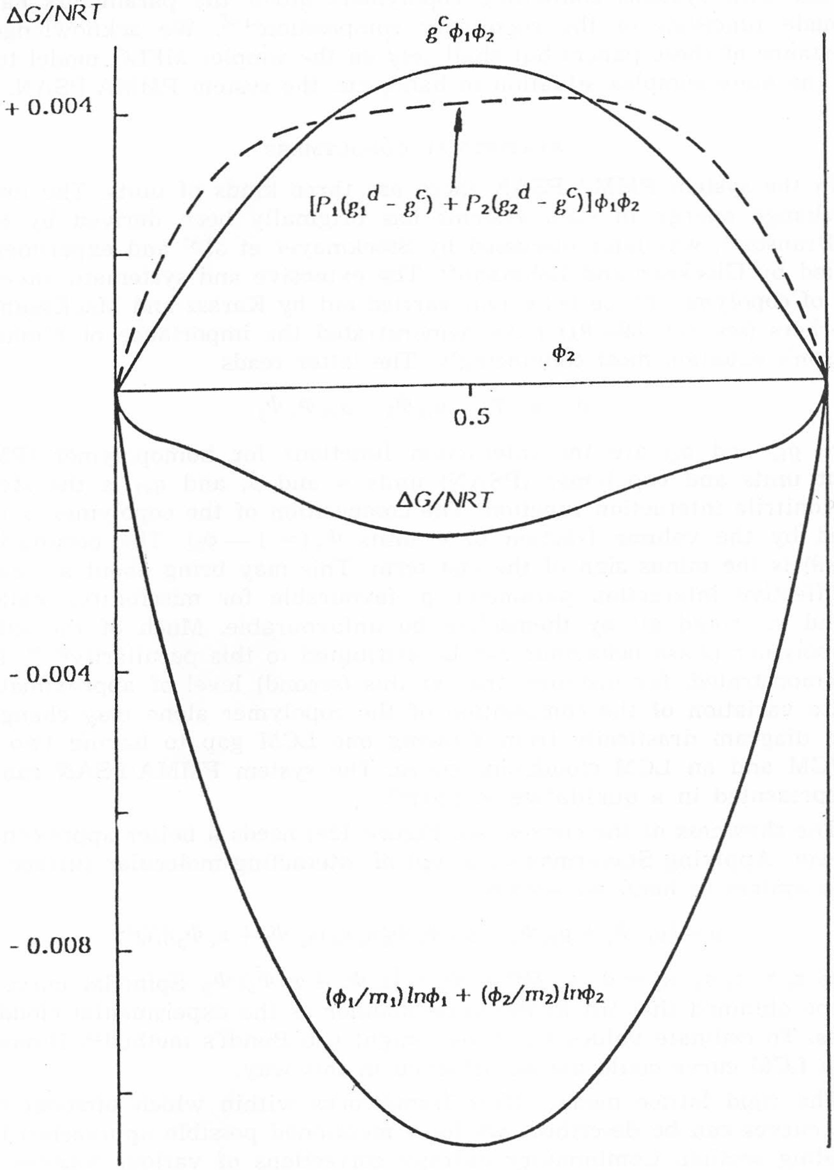


Figure 15. Free enthalpy of mixing ΔG calculated by eqs. (1), (27) and (48) for $m_1 = m_2 = 64$, $g_1{}^d = 0.05$, $g_2{}^d = 0.0535$, $\varepsilon_1 = 0$, $\varepsilon_2 = 0.1$, $\lambda_{01} = \lambda_{01} = 0.258$, $g^c = 0.0185$.

4) *Free Volume*

Noncombinatorial ('equation of state') contributions to ΔG have been advanced by several authors[65,77–83]. The cited references give ample examples to the relevance of the introduction of free volume parameters. Olabisi has shown that Flory's equation of state theory can produce a bimodal spinodal of the LCM type.[82] Walsh et al. have demonstrated that Flory's theory can be used with systems containing copolymers albeit the parameters have to be made functions of the copolymer composition[84,85]. We acknowledge the importance of these papers but shall rely on the simpler MFLG model to deal with the more complex situation in hand, viz. the system PMMA/PSAN.

STATISTICAL COPOLYMERS

In the system PMMA/PSAN there are three kinds of units. The internal interchange energy in such systems has originally been derived by Simha and Branson[86], was later discussed by Stockmayer et al.[87] and experimentally verified by Glöckner and Lohmann[88]. The extensive and systematic investigations of copolymer phase behaviour carried out by Karasz and MacKnight and coworkers (see ref. 89—91) have demonstrated the importance of Simha and Branson's equation most convincingly. The latter reads

$$g = g_{1\alpha}\, \Phi_\alpha + g_{1\beta}\, \Phi_\beta - g_{\alpha\beta}\, \Phi_\alpha\, \Phi_\beta \qquad (49)$$

where $g_{1\alpha}$ and $g_{1\beta}$ are the interaction functions for homopolymer (PMMA) repeat units and copolymer (PSAN) units α and β, and $g_{\alpha\beta}$ is the styrene--acrylonitrile interaction function. The composition of the copolymer is represented by the volume fraction of α units $\Phi_\alpha\, (= 1 - \phi_\beta)$. The peculiarity of eq. (49) is the minus sign of the last term. This may bring about a value for the effective interaction parameter g, favourable for miscibility, while $g_{1\alpha}$, $g_{1\beta}$ and $g_{\alpha\beta}$ could all by themselves be unfavourable. Much of the subtlety of copolymer phase behaviour can be attributed to this peculiarity[90–92]. It can be demonstrated, for instance, that at this (second) level of approximation a minute variation of the composition of the copolymer alone may change the phase diagram drastically from showing one LCM gap to having two gaps, an UCM and an LCM cloudpoint curve. The system PMMA/PSAN can thus be represented in a qualitative manner[93].

The skewness of the curves (see Figure 12e) needs a better approximation, however. Applying Staverman's concept of interacting molecular surface areas to the system in hand we obtain

$$g = [g_{1\alpha}\, \Phi_\alpha + g_{1\beta}\, \Phi_\beta - g_{\alpha\beta}\, \Phi_\alpha\, \Phi_\beta\, s_\alpha\, s_\beta/(s_\alpha\, \Phi_\beta + s_\alpha\, \Phi_\beta)]/Q^{**} \qquad (50)$$

where $s_\alpha = \sigma_\alpha/\sigma_1$, $s_\beta = \sigma_\beta/\sigma_1$, $Q^{**} = \Phi_1 + (s_\alpha\, \Phi_\alpha + s_\beta\, \Phi_\beta)\, \Phi_2$. Spinodal curves can thus be obtained that tilt in the same manner as the experimental cloudpoint curves. To estimate values for σ_i one might use Bondi's method[25]. Bimodality of the LCM curve could not be achieved in this way.

The rigid lattice model offers frameworks within which bimodal cloudpoint curves can be described; we have mentioned possible approaches in the preceding section. Combinatory entropy corrections of various sources could be introduced and possibly help to produce bimodality. However, it is then not immediately obvious that a small variation in Φ_α would let the bimodality vanish and for the moment we turn to other molecular aspects. Whatever the reason, a very peculiar concentration dependence of g is to be formulated for the observed phenomena to be covered. Though polymolecularity cannot be dismissed altogether, complex shapes of miscibility gaps are more likely to be caused by special forms of $g\,(\Phi_2)$[70].

Free volume offers a feature that causes g to depend so strongly on concentration that two extrema in spinodals may occur easily. In the MFLG approach the system PMMA/PSAN can be represented by the following expressions[93]:

$$\Delta\, A/NRT = (\psi_1/m_1) \ln \psi_1 + (\psi_2/m_2) \ln \psi_2 + \Gamma \tag{51}$$

where

$$\Gamma = \psi_0 \ln \psi_0 + (g_{01}\, \psi_0\, \psi_1 + g_{02}\, \psi_0\, \psi_2 + g_{12}\, \psi_1\, \psi_2)/Q^{***} \tag{52}$$

$$Q^{***} = \psi_0 + s_1\, \psi_1 + \delta_2\, \psi_2;\; s_1 = \sigma_1/\sigma_0;\; \delta_2 = s_{\alpha o}\, \Phi_\alpha + s_{\beta o}\, \Phi_\beta;$$

$$s_{\alpha o} = \sigma_\alpha/\sigma_0;\; s_{\beta o} = \sigma_\beta/\sigma_0;$$

$$g_{02} = g_{o\alpha}\, \Phi_\alpha + g_{o\beta}\, \Phi_\beta - g_{\alpha\beta}\, s_{\alpha o}\, s_{\beta o}\, \Phi_\alpha\, \Phi_\beta/\delta_2;$$

$$g_{12} = s_1 (g_{1\alpha}\, \Phi_\alpha + g_{1\beta}\, \Phi_\beta - g_{\alpha\beta}\, s_{\alpha o}\, s_{\beta o}\, \Phi_\alpha\, \Phi_\beta/\delta_2)$$

We shall not consider the values chosen for the many parameters to be very significant but merely observe that a set of values can easily be found that produces three spinodal curves, two LCM and one UCM spinodal (Figure 16). A slight change of the copolymer composition Φ_α, while all the other parameters are kept constant, then causes one of the LCM, as well as the UCM spinodal, to vanish, in qualitative agreement with the data (Figure 12e).

The calculated LCM spinodals are much narrower than the measured miscibility gaps if all s are set equal to unity. Though spinodal curves must be narrower than their cloudpoint curves, the difference here seems to be too large. However, it needs a value for $s_{\alpha o}$ only a little less than 1 to markedly broaden the LCM spinodal range.

It should be mentioned that the application of pressure to a polymer mixture has been demonstrated experimentally to cause cloudpoint curves to become bimodal[94]. This phenomenon might be related to the subtleties mentioned above and is being investigated theoretically at the moment[72].

BLOCK COPOLYMERS

Phase diagrams on polymer blends containing block copolymers have been extensively studied by Riess et al.[95] with the emphasis on the compatibilizing effect copolymer admixtures have in polymer mixtures. Here we turn to the simpler case of mixtures of a block copolymer with either of its homopolymers. Roe and Zin have studied the systems polystyrene-co-butadiene/polystyrene and polystyrene-co-butadiene/polybutadiene quantitatively and reported the interesting feature that addition of polystyrene to the block increases the temperature of mesophase formation while polybutadiene produces the opposite effect[96] (see Figure 17.).

Free volume models of polymers invariably have the interesting, though unrealistic, feature that they include a critical state and coexistence between

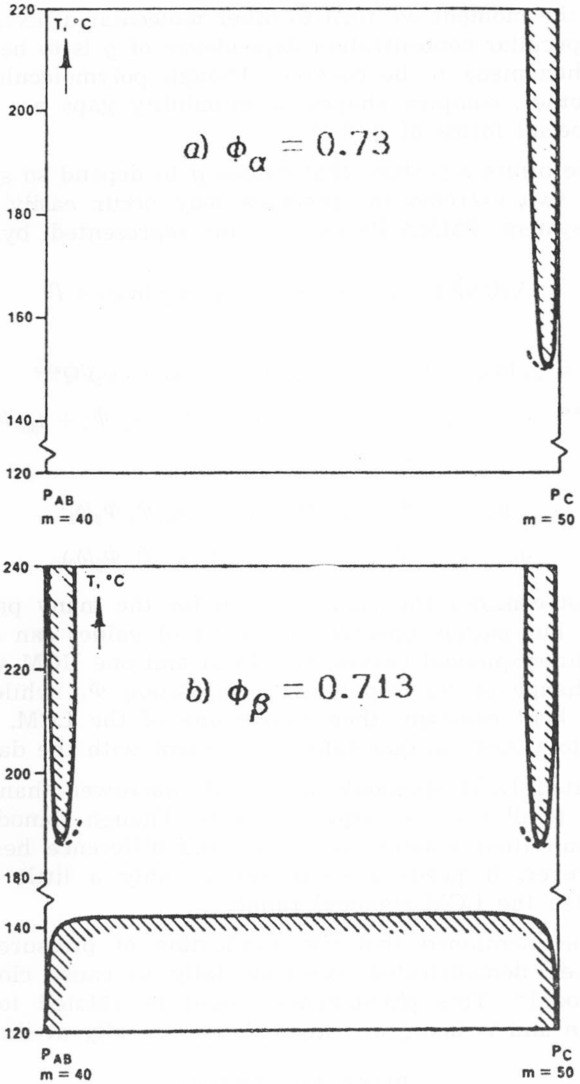


Figure 16. Spinodal curves for polymethylmethacrylate/polyacrylonitrile-co-styrene, calculated by the mean-field lattice-gas model (eqs. (51) and (52)) for a) $\Phi_\alpha = 0.27$, b) $\Phi_\alpha = 0.287$, otherwise all parameters identical. Drawn curves: $s_1 = s_{o\alpha} = s_{o\beta} = 1$; dashed curves: $s_1 = s_{o\beta} = 1$, $s_{o\alpha} = 0.9$.

phases differing in density. In the MFLG model, for instance, a single homopolymer shows such a critical state the condition for which is similar to that in a rigid- lattice FHS polymer solution (see eq. (10)):

$$\psi_{1c} = 1/(1 + m_1^{-1/2}) \tag{53}$$

which implies improbable densities as far as polymers are concerned. Also, large numbers arise for 'critical' pressures and temperatures. Remarkably

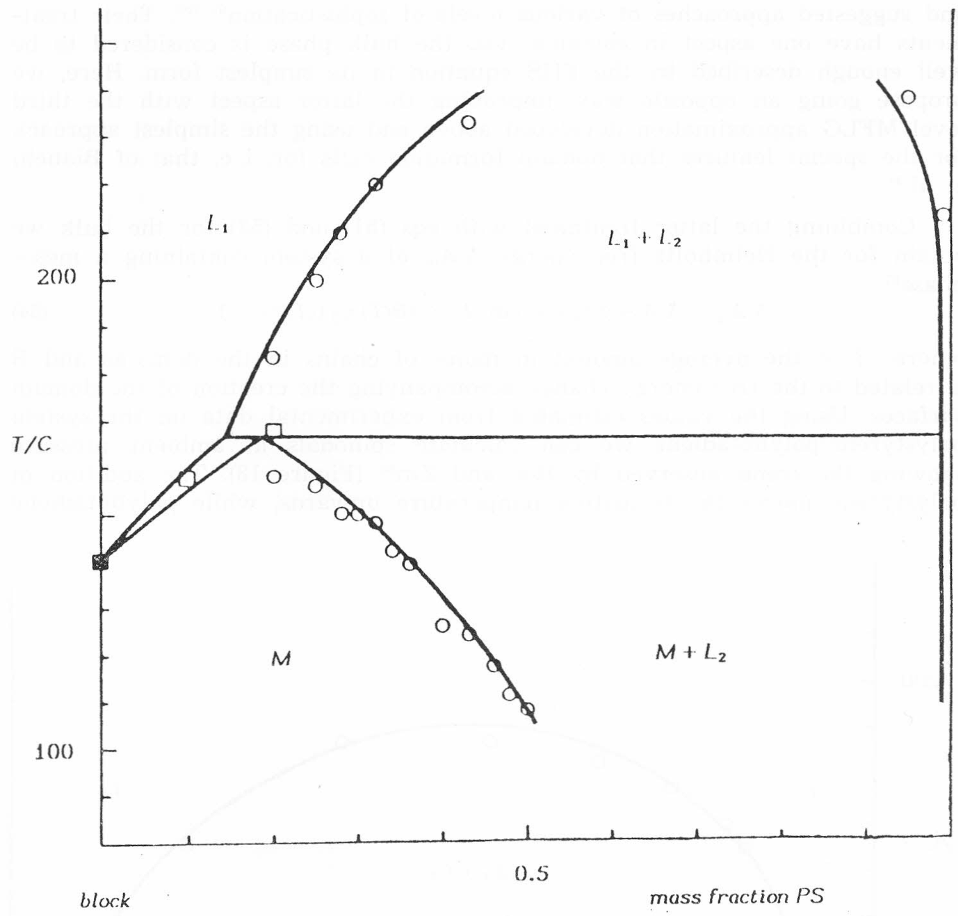


Figure 16.

enough, however, the MFLG model includes a quite different situation if the polymer is a copolymer in which the two types of repeat units differ in the nearest neighbour contact numbers ($\sigma_\alpha/\sigma_o < 1$; $\sigma_\beta/\sigma_o > 1$). Then, reasonable vacancy concentrations are calculated for the 'critical' state ($\Psi_{0c} \simeq 0.1$) and T_c comes down to an acceptable value (450 K)[97]. The model, in its present form not distinguishing between statistical and block copolymers, thus predicts separation into two disordered phases of slighly different density. We are not aware of any experimental indication as far as statistical copolymers are concerned, but it is known that block copolymers often shown transitions from a homogeneous melt into mesophases containing microdomains rich in one of the blocks[95,96]. Such transitions may be expected to go with small differences in density.

In such cases eqs (51) and (52) must be amended for the limited dimensions of the domains, as well as for the restrictions in conformation undergone by the block copolymer chains. Several authors have addressed the problem and suggested approaches of various levels of sophistication[98-102]. Their treatments have one aspect in common, viz. the bulk phase is considered to be well enough described by the FHS equation in its simplest form. Here, we propose going an opposite way, improving the latter aspect with the third level MFLG approximation developed above and using the simplest approach for the special features that domain formation calls for, i. e. that of Bianchi et al.[98].

Combining the latter treatment with eqs (51) and (52) for the bulk we obtain for the Helmholtz free energy ΔA_m of a system containing a mesophase[97]

$$\Delta A_m = \Delta A + 2\,(\psi_2/m_2)\ln\langle I\rangle + (B/T)\,\psi_2\,(\langle I\rangle^{-1/3} - 1) \tag{54}$$

where $\langle I\rangle$ = the average amount in moles of chains in the domains and B is related to the free energy change accompanying the creation of the domain surfaces. Using the values estimated from experimental data on the system polystyrene/polybutadiene we can calculate spinodals at ambient pressure showing the trend observed by Roe and Zin[96] (Figure 18). The addition of polystyrene moves the transition temperature upwards, while polybutadiene

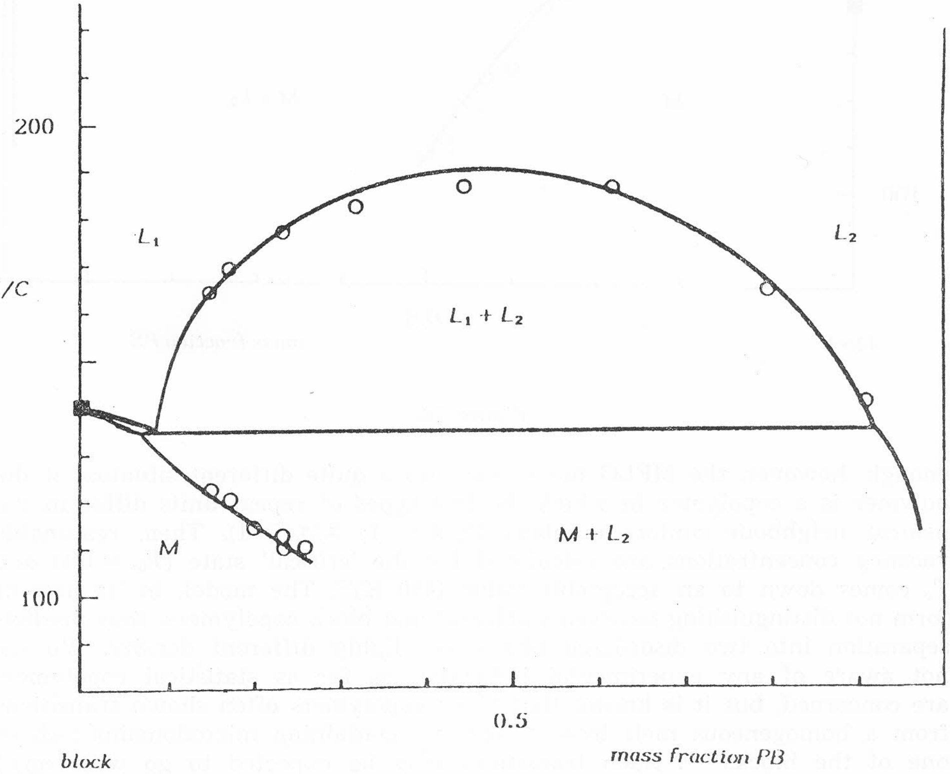


Figure 17. Phase relations in mixtures of a styrene-butadiene block copolymer with polystyrene(PS) (top) and with polybutadiene (PB) (bottom). L_1 and L_2 refer to homogeneous liquid phases, M to a microphase-separated state. Data by Roe and Zin[96].

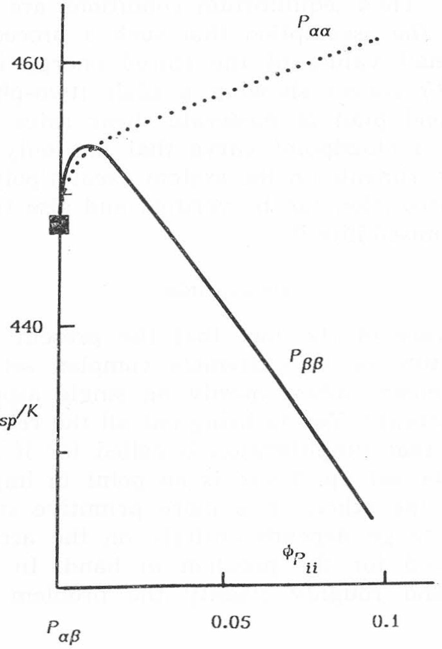


Figure 18. Mean-field lattice-gas description of a copolymer $P_{\alpha\beta}$ showing two phases differing slightly in density (■). Stability of the homogeneous liquid phase is affected by addition of homopolymer $P_{\alpha\alpha}$ $(\sigma_\alpha/\sigma_o \langle 1; \ldots.)$ or $P_{\beta\beta}$ $(\sigma_\beta/\sigma_o\rangle$ 1; ———); $\Phi_{\mathrm{P_{ii}}}$ = volume fraction of homopolymer P_{ii}.

has the opposite effect, except for an initial increase, not found in the experiment.

We do not claim this treatment to be unique, it is based solely on an interplay between contact numbers, packing (free volume), restricted conformations and free energy contributions for the domain surface area. Other approaches are conceivable, one might think of the different flexibility of the polystyrene and polybutadiene chains and use Huggins' orientational entropy terms. Alternatively, or in addition, local deviations from the overall concentrations of the three types of repeat units might affect the energy of mixing, as was very recently suggested by Balazs et al.[91]. Also, the entropy of mixing might need further adjustment, particularly with the extremely non-random sequence distribution encountered in block copolymers[72].

SHEAR

Polymer blends are produced in processes involving considerable shear rates. It is, therefore, very important to know the effect shearing forces have on the thermodynamic stability of a polymer mixture. This is an aspect of the topic that has so far not received the attention it deserves but has neither been altogether neglected. We refer to studies by a number of authors[103–109] and specifically draw attention to Wolf's treatment of flowing polymer solutions[109]. This author combined an expression for the energy stored by the solution in stationary flow with the FHS equation representing zero shear behaviour. Then, equilibrium conditions are applied to the stationary system under the assumption that such a procedure is permitted in view of the very small values of the stored energy involved. The model indicates that $\Delta G(\Phi_2)$ curves showing a plait (two-phase system at rest) easily develop a second plait at moderate shear rates. Hence, shear would induce bimodality in a cloudpoint curve that has only one extreme if the system is at rest. Experiments on the system decalin/polystyrene have shown that this surprising prediction can be verified and also that shear may either increase or decrease miscibility[110].

DISCUSSION

We are fully aware of the fact that the present paper offers only a highly simplified picture of an extremely complex set of problems. Much more advanced treatments, albeit mostly on single aspects, exist and have demonstrated their viability. Yet, to bring out all the relevant aspects in their interrelation we feel that simplification is called for if a balanced approach to all features is to be set up. There is no point in improving a single one of them and leaving the others in a more primitive stage of development. How far one wishes to go depends entirely on the accuracy of description and prediction required for the problem in hand. In that sense it might help to arbitrarily and roughly classify the problem into four levels of approximation:

1st Level: Solubility parameter theory predicts whether the system is miscible or not. No answers as to molar mass or concentration dependence.

2nd Level: The Flory-Huggins-Staverman model can deal with temperature and molar mass, but has concentrations wrong, excess volumes equal to zero, and thus predicts pressure to have no influence on thermodynamic properties.

3rd Level: FHS model extended by contact statistics and equation of state terms (MFLG) gives a better prediction of phase concentrations and makes the influence of pressure manageable.

4th Level: Extended FHS model amended for nonuniform segment density and chain back-bending gives quantitative descriptions and predictions.

Passing from the first to higher levels the number of parameters increases and, consequently, the amount of experimental information required to establish their values. With polymer mixtures in particular the total ΔG is small over the whole composition range and yet composed of a number of contributions having either sign and magnitudes not seldom exceeding that of ΔG itself. Yet, liquid-liquid phase relationships are governed by minute details in $\Delta G(\Phi_2)$ so that every single contribution has to be studied in depth to reach the maximum accuracy of description. In view of the resulting small values of ΔG we cannot expect theory to provide more than a useful mathematical framework that will always have to be 'calibrated' against actual measurements at any level of approximation. It should be remembered that the availability of such a framework effectively reduces the amount of experimental work needed.

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SAŽETAK

Polimeri i termodinamika

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Klasična termodinamička razmatranja ravnoteže, potvrđena na modelima jednostavnih molekula, mogu da dovedu do korisnih predviđanja u pogledu odnosa faaz u delimično mešljivim sistemima koji sadrže polimere. U kojoj su meri ta predviđanja kvantitativna zavisi kako od količine eksperimentalnih informacija tako i od kompleksnosti sistema. Pristupi tome problemu razmatranjem parametara rastvorljivosti i doprinosa grupa predstavljaju prvi nivo i dozvoljavaju da se kvantitativno proceni da li je sistem mešljiv ili ne. Na tome nivou ne razmatra se entropija mešanja mada je veoma značajna.

Drugi, viši nivo predviđanja postiže se primenom Flory-Huggins-Stavermanove jednačine, koja omogućava da se proceni kako temperatura i duljina lanca polimera utiču na lokaciju oblasti nemešljivosti. Na tom nivou intervali koncentracija pri kojima je sistem delimično mešljiv nisu dobro obuhvaćeni.

Ako se uzmu u obzir uvek prisutne nejednakosti u veličini i obliku molekula i monomernih jedinki znatno se poboljšava moć predviđanja. Na tome trećem nivou predviđenja može se dosta tačno tretirati uticaj pritiska.

Ako se zahtevaju veoma precizna predviđanja, postojeće teorije ne zadovoljavaju, čak ni za jednostavan slučaj rastvora linearnog apolarnog homopolimera. U tome slučaju neophodno je izvršiti velik broj merenja da bi se odredili mnogi empirijski i teorijski parametri. Predviđanja na tako visokom nivou nemaju samo akademski značaj, budući da ona mogu da pruže bolji matematički aparat koji bi se mogao primenjivati za grublja izračunavanja.